

TABLE I
SYSTEM: $\text{Pb}(\text{NO}_3)_2\text{-NH}_4\text{NO}_3\text{-H}_2\text{O}$ AT 25°

Original complex Wt., % $\text{Pb}(\text{NO}_3)_2$	Wt., % NH_4NO_3	Saturated solution Wt., % $\text{Pb}(\text{NO}_3)_2$	Wt., % NH_4NO_3	Moles per mole H_2O	Solid phase
...	...	37.17 ²	0.00	0.0322	$\text{Pb}(\text{NO}_3)_2$
48.03	9.72	33.99	12.35	.0344	$\text{Pb}(\text{NO}_3)_2$
59.64	10.04	34.02	16.28	.0372	$\text{Pb}(\text{NO}_3)_2$
38.39	26.74	33.65	28.75	.0487	$\text{Pb}(\text{NO}_3)_2$
41.87	31.90	32.61	36.92	.0581	$\text{Pb}(\text{NO}_3)_2$
35.91	41.39	30.79	44.58	.0680	$\text{Pb}(\text{NO}_3)_2$
39.06	42.03	29.63	48.47	.0735	$\text{Pb}(\text{NO}_3)_2$
32.36	54.54	29.44	49.00	.0743	$\left\{ \begin{array}{l} \text{Pb}(\text{NO}_3)_2 \\ + \text{NH}_4\text{NO}_3 \\ \text{NH}_4\text{NO}_3 \\ \text{NH}_4\text{NO}_3 \end{array} \right.$
27.84	55.22				
15.37	62.65	18.04	56.15		
...	...	0.00	68.17		

of saturated solution and original complex pass through the compositions of the two simple salts with average deviation of 1.1%.

From the molar ratio of lead nitrate to water, shown in column 5, it is apparent that addition of ammonium nitrate increases the solubility of the salt markedly. A plot of the change in solubility, as thus defined, is shown in Fig. 2, in which are shown also curves for potassium nitrate and sodium nitrate calculated from the work of Glassstone and Saunders.

Summary

The solubilities in the system $\text{Pb}(\text{NO}_3)_2\text{-NH}_4\text{-NO}_3\text{-H}_2\text{O}$ at 25° have been determined. The solubility of lead nitrate is increased by ammonium nitrate, but to a smaller degree than by potassium nitrate. No double salts have been found as solid phases.

NEW YORK, N. Y.

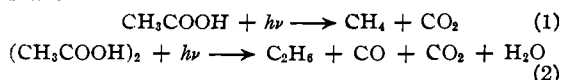
RECEIVED JULY 1, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Studies in the Mechanism of Decomposition. I. The Vapor Phase Photolysis of Acetic Acid

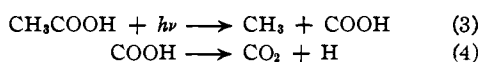
BY MILTON BURTON

In order to explain certain observations on the pyrolysis of acetic acid, Hurd¹ suggested the formation of ketene as an intermediate reaction product. F. O. Rice^{2a} showed that such formation might be considered a logical consequence of a free radical chain mechanism. However, Franck and Rabinowitsch,³ in discussing the photolysis of organic molecules by the intermediary of free radicals and atoms, pointed out that certain polyatomic molecules might decompose directly into stable molecules and that the work of L. Farkas and Wansbrough-Jones⁴ indicated that acetic acid is an example of such a compound. That conclusion was based primarily upon an analysis of the ultimate products of the decomposition, which showed such a clear correspondence of yields among the products that the two reactions following appeared to be the only tenable ones in the gaseous state



Although they reported a yield of approximately 1% by volume of hydrogen, Farkas and Wansbrough-Jones favored the idea that that substance, as well as traces of acetylene found, might be a product of some subsequent reaction of the resultant molecules.

This appears to be a clear-cut case in which to test whether decomposition takes place by rupture into free radicals or by rearrangement of a stable constellation of groups into stable constellations of ultimate molecules. The mirror methods developed by Paneth⁵ and by F. O. Rice and his co-workers⁶ and used by Pearson⁷ in the study of the photochemical decomposition of aldehydes and ketones are well suited to the test. In a previous communication⁸ the writer described a procedure for the detection of hydrogen atoms in the presence of free radicals and indicated evidence for the reactions



(1) Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, p. 334.

(2) Rice and Rice, "The Aliphatic Free Radicals," Johns Hopkins University Press, Baltimore, 1935, (a) p. 135, (b) p. 14, (c) p. 187.

(3) Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(4) L. Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **13**, 124 (1932).

(5) Paneth and co-workers, *Ber.*, **62**, 1335 (1929); *Z. physik. Chem.*, **37**, 155 (1930); *Nature*, **125**, 564 (1930); *Ber.*, **64**, 2702 (1931); **64**, 2708 (1931); *et seq.*

(6) Ref. 2 reviews this work thoroughly.

(7) Pearson, *J. Chem. Soc.*, 1718 (1934); Pearson and Purcell, *ibid.*, 1151 (1935).

(8) Burton, *THIS JOURNAL*, **58**, 692 (1936).

to account for at least part of the photolysis of acetic acid.

In this report, evidence will be presented which will show that the photolysis of acetic acid can be explained entirely by a free radical mechanism but that the above indicated mechanism is incorrect.

Experimental

Light Sources.—In the work reported in the previous communication and referred to briefly in Part I following, a quartz Hanovia mercury vapor lamp operating in series with a rheostat on a 110-volt storage battery line was used. At that time no special precautions were employed to maintain constancy of current, which was held at about 4-5 amperes.

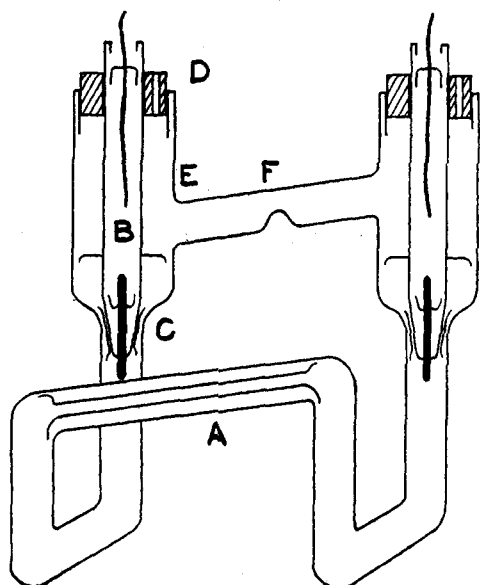


Fig. 1.—Capillary mercury arc.

In all later work the quartz capillary mercury arc shown in Fig. 1 was employed. It is a modification of the lamp described by Forbes and Heidt.⁹ The capillary tube A has a slight slope and is 4 cm. long and about 2 mm. in internal diameter. The entire lamp is of quartz except for the tubes B, which are of Pyrex glass. The bottoms of those tubes have tungsten wires sealed in as shown and are ground to fit into the quartz tubes at C. The openings at C may be regulated by withdrawing the tubes B slightly. The tubes are thereafter held in fixed position by the rubber stoppers D, which are grooved to permit ready access of air into the reservoirs E. The tube F serves to permit flow of mercury from one reservoir to the other as described by Forbes and Heidt. (In the writer's experience with this lamp no such flow of mercury was observed even on three-hour periods of operation. The mercury levels were never that far displaced.) Contact is made by inserting nickel or iron wires in the mercury in the tubes B. The wires are so connected that the upper end of the capillary is negative. The lamp as described was used in a

(9) Forbes and Heidt, *THIS JOURNAL*, **58**, 4349 (1931).

110-volt battery circuit containing a rheostat so adjusted as to permit a current of 4.0 amperes. In starting the lamp the mercury column in A was broken by heating with a sharp flame. During operation a rapid stream of water was flowed over the capillary tube from an ordinary wing-top which had been cut down so that its edge would rest evenly on the full length of the tube. The lamp was supported in a glass funnel in such a way as to drain off the water. It was not necessary to keep the legs of the lamp immersed, for water was flowing down them constantly during operation. The filling of the tube was conducted simply by boiling out the air while holding the tube at a convenient angle to promote entrance of mercury. From time to time, between runs, the outer surface of the capillary was cleaned with hydrochloric acid.

Chemicals.—The acetic acid used was the analyzed product of General Chemical Co., of A. C. S. grade. It was subjected to four recrystallizations and decantations before introduction into the apparatus. Only about 25% of the original sample was used. The acetone was the A. C. S. grade of Eimer and Amend further purified by the method of Shipsey and Werner¹⁰ to a constant boiling point of 56.0° uncorrected. The sodium bromide and sodium chloride were Eimer and Amend T. P. grades and were merely dried to constant weight at 130° before use.

Apparatus and Technique.—The methods used were very similar to those already described by Pearson.⁷ The apparatus is indicated in Fig. 2. The purified liquid was introduced into reservoir A, frozen (or cooled) in carbon dioxide-toluene mixture, evacuated, and then allowed to warm to room temperatures (above the melting points both of acetone and of acetic acid). This process of cooling, evacuation and warming was repeated once in reservoir A. Then, by suitable manipulation of the stopcocks and application of the freezing mixture, the liquid could be distilled to either of the reservoirs B or C where it was subjected to further repeated cooling, evacuation and warming as already described for at least three additional successive times. In this way entrapped gases were eliminated.

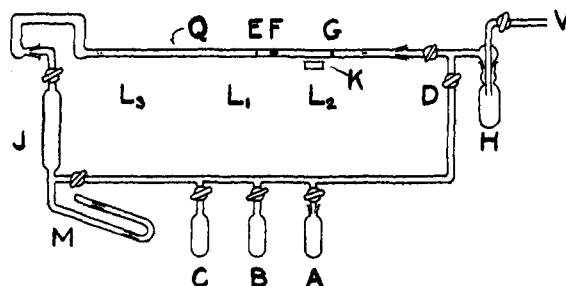


Fig. 2.—Reaction system.

Regular stopcock grease was used in all stopcocks and joints. The length of the constricted portion of the tubing, including the quartz reaction tube Q and allowing for the ground glass joints to which it was sealed, was fixed at 88 cm. The tube Q had an average internal diameter of almost exactly 5 mm. The tube J contained silver turnings intended to trap out mercury vapors. The mercury manometer M had a slope ratio of 25:1 and permitted

(10) Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

TABLE I
SERIES OF EXPERIMENTS WITH LEAD GUARD MIRROR

Expt.	22	23	24 ^a	25
Substance	Acetone	Acetic acid	Acetone	Acetic acid
Pres. at M, mm.	2.2-2.4	2.1-2.25	2.0	2.2
Mirror E (Pb)	Heavy	Very light	From expt. 23	Light
Distance of E from L ₁ , cm.	7	2.6	2.8	5.2
Guard mirror F (Pb) 1.5-2 cm. long	Heavy	Heavy	From expt. 23	Heavy
Mirror G (Sb)	Very light	From expt. 22	Very light	From expt. 24
Distance of G from L ₁ , cm	19.2	18.5	18.7	19
Time of run, minutes	85	75	78	180
Effect on E	Partly removed	Only trace left	Gone in 22 min.	Still present
Effect on F	None	Attacked near E in 65 min.	None
Effect on G	None	Gone	None	Gone

^a Expt. 24 followed sixteen hours after expt. 23.

readings accurate to 0.01 mm. The apparatus was connected to a carbon dioxide-toluene trap and a mercury vapor pump system at V. During a run, the path of the vapors was from one of the reservoirs A, B or C through J and the reaction tube Q to the receiver H, which was cooled in a carbon dioxide-toluene mixture. After the reservoir was exhausted the liquid was then distilled back from the receiver H through the now opened stopcock D to the reservoir. It was found that the small amount of product impurity formed during the photolyses did not sensibly affect the results in subsequent runs. The irradiated zones were at either L₁, L₂ or L₃, as will be indicated below. K represents a light filter (cooled with flowing water during runs) containing a suitable solution between crystal quartz plates 1 cm. apart. A copper cylinder around the reaction tube served as a screen which was used while the arc and the flow of gas were adjusted. It was slipped aside at zero time, exposing the irradiated zone but shielding the mirror or mirrors. When the filter was not used, the reaction tube itself was cooled with running water. Under no circumstances did the temperature of the reaction tube rise above that of the room.

Part I. Detection of Atomic Hydrogen in the Presence of Methyl.—In these early experiments, the results of which have already been reported,⁸ the apparatus was not quite the same as shown in Fig. 2. The reaction tube system was sealed to the rest of the apparatus and not affixed with ground glass connections. In other respects it was substantially the same as in the latter experiments.

In this part the depression between F and G contained a small pellet of lead; that after G contained one of antimony. A transparent lead test mirror of the weight desired was deposited at E (after suitable preparation of the surface²) and a heavy lead guard mirror was deposited at F. A very light antimony mirror was then deposited at G. Such mirrors were deposited only when desired. On some occasions, as is evident from Table I, a mirror might be used for more than one experiment.

In Table I there are indicated the results of a typical series of experiments on the vapors of acetone and of acetic acid. During the experiments of this part, the reaction tube was illuminated at L₁, approximately 40 cm. from its beginning, by the unfiltered Hanovia arc located about 0.7 cm. from the tube. The arc was not always located at the same distance from the beginning of the tube in this series. It is for that reason that the distances of the mirrors from the irradiated zone vary from experiment to experiment.

The efficacy of the heavy lead mirror as a guard to prevent the passage of methyl radicals is indicated with acetone as a known case⁷ in expt. 22. It will be shown below that under similar conditions of operation irradiated acetone will yield more than ten times as many mirror-active particles as acetic acid. Lead mirrors may be shifted, but not removed, by hydrogen atoms, while antimony mirrors are attacked both by free methyl radicals and hydrogen atoms.¹¹ Consequently, it can be concluded from this experiment that, if acetic acid produces only free methyl radicals and no hydrogen atoms, it could be passed through the reaction tube under these same conditions for at least eight hundred and fifty minutes without any visible effect on the antimony mirror. However, expt. 23 showed that acetic acid vapor removed that mirror under similar conditions of operation in seventy-five minutes. A fresh lead mirror was simultaneously attacked in that experiment. The fact that the guard mirror used in expt. 23 was still effective at the end of the run was shown in expt. 24 with acetone, which again failed to remove a fresh antimony mirror. The fact that the antimony mirror used in expt. 24 was

(11) Pearson, Robinson and Stoddard, *Proc. Roy. Soc. (London)*, **142**, 275 (1933).

sensitive to mirror-active particles was verified in expt. 25 with acetic acid vapor.

Similar experiments were performed from time to time and on the basis of these results it appeared clear that acetic acid was yielding particles capable of attacking lead mirrors and others which would attack antimony although they had no effect on lead. It was concluded and reported⁸ consequently that the photolysis of acetic acid yielded both methyl radicals and hydrogen atoms. However, the subsequent results of Part II showed that the effect on the lead mirror could not be quantitatively duplicated. A check-up of the results indicated that, although methyl radicals and hydrogen atoms had been observed simultaneously during the photolysis of acetic acid, they did not both originate in that compound. The hydrogen atoms came from the acetic acid; the methyl radicals came from the acetone which had been adsorbed in the system (perhaps in J) and swept along with the acetic acid. Whenever a series such as shown in Table I was run, there would be apparent formation of methyl radicals during the photolysis of acetic acid. It was only when particular precautions were taken to eliminate the last traces of acetone before the acetic acid runs that no lead mirror removal was observed with the latter.

The conclusions to be drawn from this part are: (1) hydrogen atoms can be detected by this process in the presence of methyl radicals. (2) Acetic acid vapor of itself does not interfere with the sensitivity of lead mirrors to free methyl radicals. (3) Hydrogen atoms apparently are produced during the photolysis of acetic acid vapor.

Part II. Comparisons of Rates of Mirror Disappearance.—The previous part is not conclusive as to the possibility of free methyl formation during the photolysis of acetic acid. It may well be, for example, that under the conditions of the experiments hydrogen atoms are more mirror-active than free methyl radicals, so much so that the latter would not be detected within the time required to establish the presence of the atoms.

This group of experiments was initiated when it was still believed that methyl radicals detected in such experiments as expt. 23 (Table I) were originating in the acetic acid. The purpose was to compare the rates of removal of standard lead and antimony mirrors by acetone and by acetic acid. The former yields only methyl radicals;⁷ the

product of the latter was in question.¹² The conditions of the test were kept constant for each of the mirrors. The pressure of the vapors was set at approximately 2.3 mm. at the manometer. Standard mirrors were deposited as described by Pearson⁷ by comparison with a smoked-glass tube. To obtain some measure of accuracy by this method the results of a large number of runs were averaged. For convenience, the water filter was used with the arc light shown in Fig. 1 at L₂ 2.3 cm. from the reaction tube in the antimony tests; in the lead tests the light was placed 1 cm. from the tube at L₁ without a filter. In the first experiments neither the standard lead mirrors nor the standard antimony mirrors were ever satisfactorily removed in the photolysis of acetic acid in a reproducible manner. As already indicated, the erratic results were finally traced to the presence of residual acetone. Satisfactory results for lead and antimony mirrors with acetic acid were obtained only either after the acetone had been thoroughly removed from the system or before it had been introduced. The averaged results of this part are shown in Table II.

TABLE II
COMPARISON OF TIMES OF REMOVAL OF MIRRORS BY
ACETIC ACID AND BY ACETONE

	Acetic acid	Acetone
Antimony	35.5 min.	137 sec.
Lead	≥120 min.	39 sec.

Under the conditions of the test it is clear that free methyl caused the disappearance of lead more quickly than that of antimony. If the mechanism of reactions 3, 4 were correct, it could be concluded that half the effect on the antimony mirror with acetic acid might be due to free methyl, *i. e.*, that such radicals by themselves would have caused the removal in about seventy minutes. It would then be expected that the photolyzed acetic acid would remove the lead mirrors in about twenty minutes. It consequently must be concluded either that no free methyl is formed during the photolysis of acetic acid or that its mirror-activity compared with that of hydrogen atoms is so slight that it is unobservable.

In check experiments to find what effect, if any, free methyl might have on the photolysis of acetic acid, a small amount of acetone was introduced deliberately into the acetic acid. The rate of

(12) See Rice, ref. 2, pp. 51-54, for the treatment of a parallel case in a mixture containing free methyl and free methylene.

lead mirror removal was then found to depend on the actual quantity of acetone in the acetic acid.

Part III. Effect of Distance of Mirror from the Irradiated Zone.—The evidence so far presented is not absolutely conclusive that no free methyl is formed during the photolysis of acetic acid. It is known that at room temperatures hydrogen atom has a much greater half-life than free methyl.^{2b} The shape of the curve showing variation of time of disappearance of the mirrors with distance from the irradiated zone might consequently be used to establish whether or not free methyl is formed during the photolysis of acetic acid.

In this group of experiments no filter was used. The arc of Fig. 1 was located at L_2 so that the edge of the irradiated zone near the mirrors was now 22.8 cm. from the beginning of the constricted portion of the system. The light itself was fixed 1 cm. from the reaction tube. The pressure of the vapors was set at approximately 2.3 mm. at the manometer corresponding to a streaming velocity for acetic acid vapor at the beginning of the constricted region of approximately 29.7×10^2 cm. per sec.

The results of all these experiments (not the averages) are shown graphically in Fig. 3. Pearson's values are plotted from his average figures⁷ for acetone entering at a pressure of 1.65 mm. and a streaming velocity of 12.3×10^2 cm. per sec. No explanation is offered at this time for the opposed concavity of the curves obtained by Pearson and by this writer. It should be pointed out that the difference may be related to the different pressures at which the work was conducted as well as to the fact that Pearson's work may have a higher accuracy in view of the greater number of his experiments. It is, however, clear that the general trends of the two curves are similar and quite different from the curve for acetic acid, which is almost a horizontal straight line. Evidently, the half-life of the active product from the photolysis of acetic acid is much greater than that from acetone and is probably hydrogen atom. Also, we are forced to assume either that free methyl is far less effective than hydrogen atom in causing removal of antimony mirrors or that it is entirely absent in the photolysis of acetic acid.

The first assumption is excluded by the findings of Paneth and Lautsch,¹³ who report that methyl and ethyl radicals adhere to a mirror on the first

collision. It will be shown below that the slight slope of the acetic acid line is reasonably traceable to the clean-up reactions involving hydrogen atom. Consequently, there is evidence that no free methyl is formed during the photolysis of acetic acid. The upper curve of Fig. 3 shows the ratios of times of disappearance of mirrors under the influence of acetic acid and acetone, respectively. It is calculated from the two curves below. It is this curve which is the basis for the previous statement that under similar conditions acetone yields more than ten times as many mirror-active particles as does acetic acid.

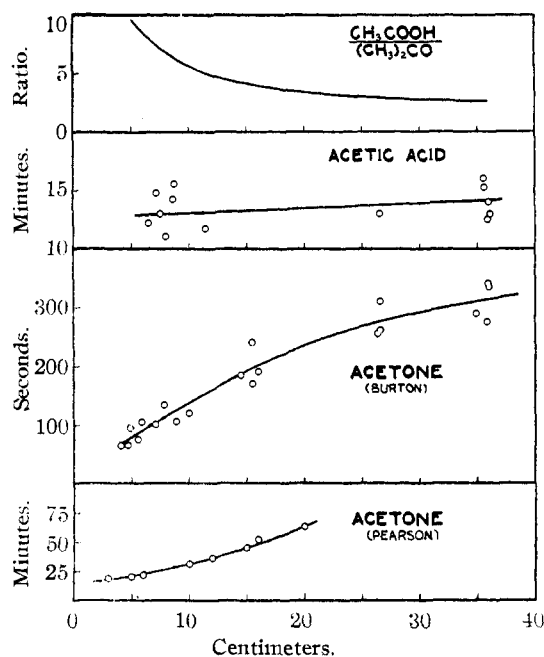


Fig. 3.—Effect of distance from irradiated zone on time of antimony mirror removal.

The formula, given by Paneth and Lautsch,¹⁴

$$t = \frac{X_2 - X_1}{V} - a \frac{(X_2^2 - X_1^2)}{2VP}$$

is used for an estimation of the time required for a particle to travel from the irradiated zone to any point under consideration. In that formula, X_1 and X_2 are, respectively, the distances of the edge of the irradiated zone and of the point from the beginning of the tube, V is the streaming velocity, a is the average pressure gradient, in this case 0.00261 cm. Hg per cm., and P is the pressure (*i. e.*, 0.23 cm.). The time required for a particle to travel 30 cm. from the irradiated zone comes out to be 0.58×10^{-2} sec. The average pressure between the irradiated zone and that

(13) Paneth and Lautsch, *Ber.*, **64**, 2702 (1931).

(14) Paneth and Lautsch, *ibid.*, **64**, 2708 (1931).

point readily may be calculated to be about 0.13 cm. If N be the number of collisions which a hydrogen atom would suffer¹⁶ in an atmosphere of acetic acid at 76 cm. pressure, then it is evident that the number of collisions suffered under the conditions of these experiments in these 30 cm. would be

$$N_{30} = N \frac{\text{Average press.} \times t}{76}$$

If $N = 10^{10}$, $N_{30} = 10^5$; on the other hand, if $N = 10^{11}$, $N_{30} = 10^6$.

If we now examine the acetic acid curve of Fig. 3, it may be seen that the extrapolated time of mirror disappearance at the irradiated zone is 12.1 minutes and that the estimated time at a distance of 30 cm. is 13.9 minutes. The difference of the reciprocals of the times is a measure of the fraction of hydrogen atoms which have disappeared in that 30 cm. That fraction is $1.8/13.9$ or approximately 0.13 and is equal to the probability of an individual hydrogen atom undergoing reaction in that 30 cm.

Since the rate of reactive collisions may be expressed¹⁶ by

$$k = Ae^{-E/RT}$$

where we may here take k as the total number of reactive collisions (in the unit of time chosen), A as the total number of collisions per hydrogen atom (in the same time), E as the energy of activation per mole, R as the gas constant and T as the absolute temperature, it is found that, substituting 0.13 for k and the appropriate values for A and T , at room temperature E is 8.1 kcal. if N is 10^{10} or 9.5 kcal. if N is 10^{11} . These figures are only approximate. There is the implicit assumption that the steric factor is 1. They also depend on the estimate of the decrease in the concentration of hydrogen atoms along the tube, which in turn depends upon data which are not extremely accurate. If we assume that the change in concentration may really be either a quarter or four times as great as the estimate, then the limiting values for E will be 7.3 and 10.3 kcal.

Part IV. Effect of Wave Length.—The absorption spectrum of acetic acid has been investigated by Ley and Arends.¹⁷ The continuum begins at about 2300 Å., reaches a maximum at 2040 Å., falls to a slight minimum at about 1925 Å. and rises thereafter to the limit of the study

(15) Cf. Bonhoeffer and Harteck, "Grundlagen der Photochemie," Verlag von Theodor Steinkopff, Dresden, 1933, p. 183.

(16) Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932.

(17) Ley and Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

at about 1850 Å. Inasmuch as Farkas and Wansbrough-Jones⁴ indicate evidence for decomposition into stable molecules and this paper on the other hand offers evidence for a free radical mechanism, it may be surmised that the shape of the absorption curve is related to a variation in the production of free radicals with wave length. The following tests were conducted to discover whether there is any threshold of free radical production other than the beginning of the continuum.

All traces of acetone were removed from the system. The arc of Fig. 1 was removed to a distance of 2.3 cm. from the reaction tube at L_2 . The filter vessel already described, containing either distilled water, 0.1 N sodium chloride or 0.125 N sodium bromide solutions, was inserted between them as indicated in Fig. 2. The data of Fromherz and Menschick¹⁸ show that in 1-cm. layers of these concentrations sodium chloride cuts off fairly sharply at 2000 Å., whereas the sodium bromide solution cuts off at about 2300 Å. Tests of the arc lamp with a Moll thermopile and galvanometer indicated a slightly higher photon intensity in the region 2300–2000 Å. than in the 2000–1849 Å. region. About 94% of the energy was above 2300 Å. Standard antimony mirrors were deposited 2.5 cm. from the irradiated zone and the acetic acid was passed through, as before described, at a pressure of approximately 2.3 mm. The results of these experiments are summarized in Table III.

TABLE III
EFFECT OF WAVE LENGTH ON TIME OF ANTIMONY MIRROR REMOVAL BY PHOTOLYZED ACETIC ACID

Filter	Range, Å.	Index of energy intensity	Average time of mirror removal, min.
Water	>1849	10	35.5
0.1 N NaCl	>2000	9.74	95
.125 N NaBr	>2300	9.4	>>133

No indication of mirror removal with the sodium bromide filter was ever obtained although after one such test the activity of the mirror was checked in a run with the water filter. Although one hundred and thirty-three minutes was the maximum time employed for such a test, it was not considered necessary to prolong it any further since no characteristic sharpening of the mirror, which always occurs long before complete removal, was ever observed.

The results show a somewhat higher yield of atomic hydrogen per photon below 2000 Å. than

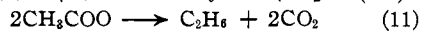
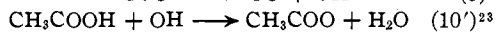
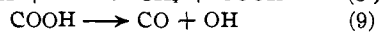
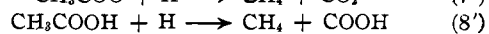
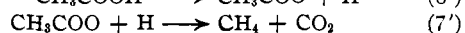
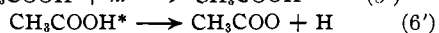
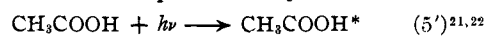
(18) Fromherz and Menschick, *ibid.*, **B3**, 1 (1929).

above that value. If that be true, it may possibly indicate that the absorption maximum at 2040 Å. is associated with decomposition into stable molecules. At any rate, the evidence is clear that there is decomposition into atomic hydrogen in the range 2300–2000 Å. and that the beginning of the continuum is probably also the threshold of free radical production. The tests with the sodium bromide filter establish that it is a true photo decomposition which is being observed and not a secondary effect due to the intense line 2537 (*e. g.*, photosensitization by excited mercury vapor).

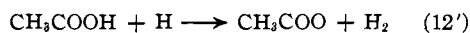
Discussion

The experimental results indicate that hydrogen atoms are formed in the photolysis of acetic acid but that methyl radicals are not. Reaction 3, suggested previously,⁸ therefore cannot be the primary step of the photolysis. Also, all primary steps which yield radicals, such as CH_3CO , which decompose readily¹⁹ into free methyl and another molecule, are eliminated. Consequently, although Terenin²⁰ reports the emission bands of hydroxyl during the photolysis of acetic acid, it cannot be formed in the primary decomposition. Finally, any mechanism suggested must account for the production of free hydrogen and free hydroxyl and must be the chemical equivalent of reactions 1 and 2 or otherwise agree with the analysis reported by Farkas and Wansbrough-Jones.⁴

Mechanism 1.—The mechanism summarized below meets the requirements just indicated.



Hydrogen atom should also disappear by the reaction



(19) Norrish, *Acta Physicochim. U. R. S. S.*, **3**, 171 (1935).

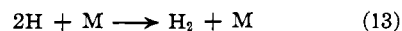
(20) Terenin, *ibid.*, **3**, 181 (1935).

(21) Reactions denoted by a single ' refer to single acetic acid molecules; reactions denoted by double " refer to double molecules. When the primes are not indicated in a reaction involving the acetic acid molecule, the reference is to both reactions.

(22) The activation of acetic acid is chosen as the correct primary step in order to show a presumable relationship to results obtained with formic acid, as discussed in a following report. However, in contradiction to the assumption of activation, the evidence in this report indicates immediate dissociation.

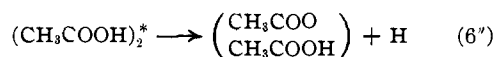
(23) The possibility of such reactions as $\text{CH}_3\text{COOH} + \text{OH} \longrightarrow \text{CH}_3\text{OH} + \text{COOH}$ and $\text{CH}_3\text{COOH} + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{CH}_2\text{COOH}$ is generally excluded at low temperatures. *Cf. ref. 2, p. 190–191.*

and to a very much smaller extent (of no quantitative significance) by

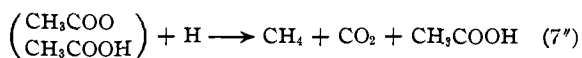


The suggested mechanism fits previously estimated activation energies. Rice^{2c} assigns a value of E for the reaction step 5,6 of 96 ± 8 kcal., well below the 123 kcal. corresponding to the beginning of the continuum at 2300 Å.²⁴ It is possible that Rice's value may be somewhat low and that the beginning of the continuum actually corresponds to the energy of activation. For the decomposition $\text{CH}_3\text{COO} \longrightarrow \text{CH}_3 + \text{CO}_2$ he assigns a value of 40–70 kcal. which would account for the fact that no free methyl is observed in this photolysis. On the other hand, he assigns a value of only 10–25 kcal. for reaction 9, which would indicate a fairly rapid reaction yielding hydroxyl and carbon monoxide.

If, in addition, we assume on the basis of the vapor pressure measurements of Holland,²⁵ as did Farkas and Wansbrough-Jones, that double molecules of acetic acid also enter into the decomposition reactions, the mechanism may be modified in the following respects



The hydrogen atom in this case will have somewhat less translational energy than in the single molecule case and the chances of recombination before the particles have left their mutual spheres of influence will be greater. The H will react then with the CH_3COO part of the molecule or the CH_3COOH part, with the probability that the former part, being nearer to the H atom, will enter into more frequent collisions. Thus, we have the reaction



which is equivalent to reaction 7'. On the other hand, if the H atom reacts with the CH_3COOH part of the molecule, we have reactions equivalent to 8' and 12' and all the accompanying and succeeding reactions. In order to explain the lower yield of carbon dioxide than might be expected on the basis of the evidence that there are only half as many single as double molecules present, Farkas and Wansbrough-Jones were forced to assume that the nature of the orientation in the molecule determined the direction of the reaction. While

(24) The continuum may perhaps begin at 2400 Å., corresponding to 117 kcal.

(25) Holland, *Z. Elektrochem.*, **18**, 234 (1912).

such a view might also apply in this case, it is interesting to note that no special assumptions have to be adopted in order to explain all the products formed.

Farkas and Wansbrough-Jones give the following analysis of the products (neglecting water): 41% CO₂, 23% CH₄, 17.5% CO, 17.5% C₂H₆ and 1% H₂. The small yield of H₂ compared with CO indicates that reaction 8 proceeds much faster than reaction 12. Reaction 7 must be presumed to occur as a primary reverse reaction before the product particles of reaction 6 have had an opportunity to depart from each other's fields of influence. In other words, reaction 7 must be expected to take place entirely within the irradiated zone in a time too small for the particles to move any perceptible distance in the streaming vapor. Consequently, it seems logical to conclude that the energy of activation determined in Part III corresponds to reaction 8; *i. e.*, the energy of activation of reaction 8 is 7.3–10.3 kcal. per mole. From the ratio of H₂ yield to CO yield it may be calculated that the energy of activation of reaction 12 is correspondingly 9.0–12.1 kcal. per mole if the steric factor be assumed to be unity. However, the energy emitted in the reaction 2H + M → H₂ + M is known to be about 102 kcal.²⁶ and the difference between that figure and the energy of activation of step 5,6 is certainly higher than the just calculated value for reaction 12. This seems improbable and it accordingly appears likely either that the calculated values for reactions 8 and 12 are too low and that the acetic acid curve of Fig. 3 should correspond more closely to a horizontal straight line than is indicated by the data or that the beginning of the continuum may be nearer 2500 Å. than supposed. The latter conclusion would be contradictory to the results of Part IV.

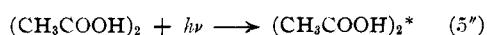
Mechanism 1 is not the chemical equivalent of reactions 1 and 2. This may readily be seen by reference to reactions 8 and 11 from which it is evident that the production of one ethane molecule is necessarily accompanied by the formation of one methane and two carbon dioxide molecules. There is no such requirement in reaction 2. On the other hand, the requirements of the analysis of the product are met. The total yield of carbon dioxide according to mechanism 1 is equal to twice that of ethane plus that of methane minus that of carbon monoxide or $2 \times 17.5 + 23 -$

17.5 = 40.5%, which is in good agreement with the analysis. The correspondence of yields of carbon monoxide and ethane is also required by this mechanism. Furthermore, the free radical mechanism explains the formation of hydrogen quite naturally. There is no need to make special assumptions. The traces of acetylene are not explained by this mechanism but they might well arise from some rarer reactions of atomic hydrogen.

The conclusions of Farkas and Wansbrough-Jones are founded on the assumptions of associated acetic acid molecules at extremely low pressures, not all of which are properly orientated. The mechanism suggested here does not involve such an assumption. Reference to the reactions indicates that the quantum yield of carbon dioxide will vary depending on the relative rates of the competing reactions 7 and 8. At higher wave lengths where reaction 7 would be favored, the quantum yield of carbon dioxide should be nearer 1; at lower wave lengths, because of the greater initial velocities of the product particles, reaction 8 would be favored and the quantum yield would be raised with 2 as the upper limit. Similarly, the observed yield of atomic hydrogen should be favored by lower wave lengths. The conclusion as to hydrogen is in agreement with the results of Table III. The conclusion as to carbon dioxide is in disagreement with the figure of approximately 1 for the quantum yield reported by Farkas and Wansbrough-Jones. Using their figures for the analysis of the products, it is apparent that the calculated quantum yield, using mechanism 1, is approximately 1.9. Either their single estimate of the quantum yield has even less accuracy than they indicate or mechanism 1 must be incorrect.

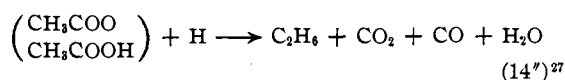
Mechanism 2.—There is, however, another free radical mechanism which may be valid. It is based entirely on the assumption that both single and double molecules are present, and is given below because its calculated quantum yield of carbon dioxide, assuming that each photon absorbed leads to reaction, is 1. Until there is more accurate information about the quantum yield of the photolysis of acetic acid, there is no basis for choice between mechanism 1 and this one.

For single molecules the principal reactions are 5', 6' and 7'. For double molecules the principal reaction is

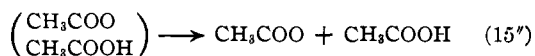


(26) Birge, *Proc. Nat. Acad. Sci.*, **14**, 12 (1928).

followed by 6'' and either 7'' or



The reactions just indicated are the exact stoichiometric equivalent of Farkas and Wansbrough-Jones' suggested mechanism. They are consequently in agreement with the analysis of the products and the reported quantum yield of one for carbon dioxide. Reactions 7'' and 14'' are the equivalent in effect of their so-called properly orientated double molecules. Reactions 5' and 5'' are the activation reactions, 6' and 6'' the decomposition reactions. In the latter are produced the hydrogen atoms reported herein. Not all of them, however, escape from the field of influence of the other product radical. At the longer wave lengths nearly all of them react with the residual body in reactions 7' and 7'' or 14''. No such hydrogen atoms can be detected by the mirror method. Only those that escape are detectable. Evidently, as the wave length decreases beyond the limit required to effect decomposition, the excess energy is divided up among the various degrees of freedom and some of it goes to give the radicals increased velocity relative to each other. For the double molecule, more excess energy is required to produce the same velocity of separation, so that it might be expected that somewhat more of the hydrogen atoms will escape the back reaction after 6' than after 6''. Once free of the residue, however, there is no distinction between them. When the residue is that of a double molecule, a simple decomposition may be expected to occur



The hydrogen atoms may then enter reactions 8', 12' and 13. On energetic grounds reaction 8' might be favored over reaction 12' since the C-C bond is weaker than the O-H bond.²⁸ The termolecular reaction 13, because of the relative scarcity of hydrogen atoms, may be considered so rare that it is non-occurring. The hydrogen atoms may also enter equivalent reactions with

(27) Reasoning *ad hoc*, the explanation of reaction 14'' is that the close proximity of the CH₃COO group with its free valence force loosens the C-O bond in the CH₃COOH and thus causes the H to act preferentially on that bond to form water with the —OH.

(28) The C-C bond has in general a strength of about 84 kcal. while that of the O-H bond in acetic acid has been estimated to be 96 ± 8 kcal. (see Rice, ref. 2c) and according to these results may have an even higher value. On the other hand, steric factors may retard 8' as compared with 12' (ref. 2, Chap. VI).

double acetic acid molecules. In effect they will be the same as those just given for 8' and 12'.

As a result of the escape of the hydrogen atoms and their entrance into reactions 8 and 12, the radicals CH₃COO and COOH are liberated. The reaction CH₃COO → CH₃ + CO₂, as has been shown, would not be expected to occur. Reaction 9 would occur as already indicated and account for Terenin's observation of OH; the OH might also enter into reactions such as 10'. Reaction 11 would also follow. The relative scarcity of products other than CH₄, C₂H₆, CO, CO₂ and H₂ would indicate either that very little atomic hydrogen becomes available for reactions 8 and 12 or that reaction 12 is favored over 8 or that reaction 10 is favored over other possible reactions involving OH.²³ If mechanism 2 is correct, the first hypothesis must be near the truth (irrespective of the others); it is supported by the only available data for the quantum yield of carbon dioxide, *i. e.*, approximately 1.0. Were reaction 11 to occur to any great extent, the observed quantum yield might be nearer 2.0. (It may be said that the principal weakness of mechanism 2 lies in the necessity of this hypothesis. It seems unreasonable to believe that the great majority of the hydrogen atoms should not escape the influence of the other product particle even at very short wave lengths.)

It may now be seen that the suggested mechanism fits all the known data on this reaction including estimated energies of activation.

It has been shown that the energy of activation for the reaction involving the disappearance of hydrogen atom may be about 7.3–10.3 kcal. If the quantum yield of carbon dioxide be nearly 1.0, reaction 8 could not be an important factor in the production of CH₄. Therefore, reaction 12, which is known to produce 1% of H₂, would account for most of the disappearance of atomic hydrogen. The value of *E* of 7.3–10.3 kcal. would then apply to that reaction. It is probably much too low, as already indicated under mechanism 1. (The discrepancy here is even greater than for mechanism 1 and may be interpreted against the validity of mechanism 2.)

The principal advantage of the free radical mechanism here suggested over that indicated in reactions 1 and 2 is that it explains the formation of molecular hydrogen quite naturally as well as the formation of hydroxyl, which incidentally need be present in but very small concentration

to be detected by its emission spectrum.²⁹ The remarks as to traces of acetylene and variation of yield of atomic hydrogen and of quantum yield of carbon dioxide with wave length made in reference to mechanism 1 also apply to mechanism 2. However, the effect on quantum yield of carbon dioxide would not be so marked in this case as in mechanism 1. The increased production of atomic hydrogen at the lower wave lengths would be just as perceptible and in agreement with Table III.

Patat and Sachsse³⁰ and Rollefson³¹ have both indicated reasons why, in the event of competition between decompositions into stable molecules and into free radicals, the free radical yield should be favored by the lower wave lengths. Consequently, there appears to be no way with the data at hand to decide whether a decomposition into stable molecules is occurring.

Furthermore, the interpretation to be put on the data is questionable. Either of mechanisms 1 or 2 will fully explain all the reactions involved. Apart from the doubts expressed above as to mechanism 2, there is no fundamental reason why either one may not be correct. There is no *a priori* reason why we should expect a quantum yield of one molecule decomposed per photon absorbed in the case of a molecule as complicated as that of acetic acid.³² Norrish, Crone and Saltmarsh³³ have shown, for example, in the case of acetone that the low quantum yield in the continuum may be ascribable to an intramolecular stabilization because of the dissipation of energy within the large number of degrees of freedom before it becomes available for disruption of a bond. In that case they have also established the existence of decomposition in the discrete fluorescence region before the continuum. If the quantum yield of decomposed molecules were actually one, it would be expected that rupture takes place at the locus of absorption and that there would be no decomposition (*i. e.*, predissociation) before the continuum.

The results of Table III indicate that acetic

(29) Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935).

(30) Patat and Sachsse, *Z. physik. Chem.*, **B31**, 105 (1935).

(31) Rollefson, Paper presented before Physical Section, A. C. S. meeting, Kansas City, April, 1936.

(32) Franck, Sponer and Teller, *Z. physik. Chem.*, **18**, 88 (1932).

(33) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

acid suffers no photolysis (yielding atomic hydrogen) before the continuum. Farkas and Wansbrough-Jones' estimate of a quantum yield of carbon dioxide of 1.0 may be interpreted as evidence in favor of mechanism 2 and a conclusion that rupture takes place immediately and at the locus of absorption. A decisive choice between mechanisms 1 and 2, however, awaits a more certain determination of the quantum yield.

Conclusions.—The only well-founded conclusions are that at least part of the reaction takes place by a free radical mechanism such as here indicated and that no other mechanism is required to explain all the facts so far known.

Acknowledgment.—The author wishes to express his appreciation to Professor James Franck of Johns Hopkins University, who suggested this investigation, and to Professor H. Austin Taylor for his frequent advice and suggestions.

Summary

1. Details are given of a method for detecting hydrogen atoms in the presence of free methyl.
2. Hydrogen atoms but no free methyl radicals are formed during the photolysis of acetic acid.
3. A free radical mechanism is indicated which fits all the facts known about that photolysis.
4. Energies of activation have been computed for two reactions involving atomic hydrogen and acetic acid.
5. It is shown that according to the mechanism suggested the quantum yield of carbon dioxide should increase at shorter wave lengths, the lower and upper limits being 1 and 2, respectively. Farkas and Wansbrough-Jones report a quantum yield of approximately 1.0.
6. The production of atomic hydrogen is apparently slightly favored by decrease in wave length.
7. No production of atomic hydrogen is observed above 2300 Å. The results and other data available are in harmony with a conclusion that the acetic acid spectrum does not have a predissociation region and that in the continuum rupture takes place immediately at the locus of absorption.

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RECEIVED JULY 9, 1936