

Mechanism of the Photolysis of Propionaldehyde

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TABLE VI. Ionic dimensions in A units, calculated for silver picrate solutions in alcohol-xylene.

D	a	r_c	r_a
3.2	6.1	3.2	2.9
2.7	5.9	4.2	1.7
2.6	5.7	4.6	1.1

Figs. 2 and 3 should have an upward concavity, as has indeed been observed experimentally on several solutions of silver picrate. The explanation is also in keeping with the observed decrease of t_c with decreasing dielectric constant (Fig. 7), because formation of aggregates is favored in solvents of low D values. These computations are not, however, shown here, as they need further verification before publication would be justifiable.

One could attempt to use values of K and t_c to compute ionic radii. The theory of Bjerrum,³ developed later by Kirkwood,¹⁰ establishes a relation between K and the distance of nearest ionic approach. When the latter is known, the figures

¹⁰ J. A. Kirkwood, J. Chem. Phys. 2, 767 (1934).

of t_c in conjunction with Stokes' equation can be used to compute ionic radii. A few figures are shown in Table VI, using Bjerrum's equations. They refer to silver picrate in alcohol-xylene and include the closest distance of approach a and the ionic radii r_c and r_a in A units.

An interesting conclusion is that the dimensions are several angstroms. Thus the ions appear to be of molecular size. While the trend for r_c is in keeping with the formation of aggregates, r_a shows an unaccountable decrease with a decrease of dielectric constant. The figures substantiate only partly the explanation suggested above, based on large positive ions, and indicate that the transference numbers may have to be revised.

In any case the data obtained seem to be of interest and warrant a continuation of the research.

The author wishes to thank several of his colleagues in the Research Department of The Detroit Edison Company both for discussion and assistance, in particular Howard A. Boltz for having built the necessary electrical measuring apparatus.

Mechanism of the Photolysis of Propionaldehyde

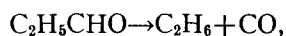
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(Received September 28, 1942)

The photolysis of propionaldehyde at $\lambda\lambda 2537$, ~ 2900 , and $\sim 3200\text{\AA}$ has been studied by the Paneth mirror method. The alkyl radicals produced are exclusively ethyl; no atomic hydrogen can be detected by the guard mirror method in amounts exceeding 2 percent of the total number of mirror-active particles present. The yield of C_2H_5 radicals has been determined and compared with the yields of CO , H_2 , and C_2H_6 . The results are most readily interpreted in terms of competing primary decomposition processes producing free radicals in one reaction and ultimate molecules in another. Whereas the former reaction increases in importance at shorter wave-lengths, the latter becomes less significant. On the other hand, an explanation for the results can be given on the basis of a mechanism involving only the production of free radicals in the primary process at all wave-lengths. The role played by excited propionaldehyde molecules (of life which may be $> 10^{-8}$ sec.) and by freshly formed (energy-rich) C_2H_5 and HCO radicals on their first collision is also considered. The mechanism of energy transfer within the propionaldehyde molecule is discussed and it is shown that the products of the primary decomposition are probably determined by geometric considerations and by the relative heights of the dissociation levels involved in the normal state.

IT is not possible to write a single over-all equation for the photolysis of propionaldehyde. Although the principal equation is



it has been generally recognized since the work of Leighton and Blacet¹ that such other sub-

¹ P. A. Leighton and F. E. Blacet, J. Am. Chem. Soc. 54, 3165 (1932).

stances as hydrogen, butane, and polymer are produced in the process. It was such products that created the suspicion that free radicals were involved and that prompted the repeated efforts² to detect them.

Recent work by May, Taylor, and Burton³ employing the Paneth mirror method has successfully shown that free radicals are produced in the photolysis of well-purified propionaldehyde. Although the same authors were able to demonstrate by the guard mirror method⁴ that the production of free hydrogen atoms at 2537A was certainly less than 2 percent of the total free-radical production (and perhaps non-existent), they were not able to decide conclusively the nature of the radicals; i.e., whether they were methyl, ethyl, or a mixture of the two. The research reported herein was intended initially to clear up this portion of the problem. In the course of the work data were obtained which are here used to indicate the probable nature of the primary process. It will be shown also that the investigation throws some light on the mechanism of energy transfer within the molecule, as well as on possible secondary processes.

EXPERIMENTAL

The work involved in this investigation may be summarized as follows: (1) check of the half-life of radicals produced by the photolysis of propionaldehyde, (2) analytical determination of the radicals involved, (3) analytical determination of the free radical to carbon monoxide ratio, and (4) analytical determination of the more volatile gases produced in the photolysis, both in the presence and the absence of lead mirrors. Except for part (1) the effects of variation of wave-length and temperature were also examined in each case. In addition, and incidental to the main purposes of this work, an effort was made to detect production of free hydrogen atoms at the longest wave-lengths employed, namely, at about 3200A.

Light Sources

No effort was made to maintain real constancy of the light sources other than to fix their posi-

² T. G. Pearson and J. H. Purcell, *J. Chem. Soc.* 1151 (1935); W. West, *J. Am. Chem. Soc.* 57, 1931 (1935).

³ May, Taylor, and Burton, *J. Am. Chem. Soc.* 63, 249 (1941).

⁴ M. Burton, *J. Am. Chem. Soc.* 58, 1645 (1936).

tions accurately by stops. Unless otherwise indicated, the light intensities at the irradiated zone were probably constant within about 10 percent for any given wave-length.

2537A

The source was a low pressure spiral lamp of the type previously described.³ The Hanovia Chemical and Manufacturing Company, manufacturers of the lamp, state that 98 percent of the ultraviolet light is concentrated at 2537A, leaving a possible maximum of 2 percent at 1850A. The energy output was controlled by a constant current transformer, the primary of which was held constant by means of an Adjust-a-volt transformer.

2900A

The light source was a General Electric H-6 lamp in a quartz envelope. Spectrographs showed that when a chlorine-mercuric chloride filter⁵ was employed (as in this work) the range transmitted was 2800–2967A with a maximum at ~2900A corresponding to about 80 percent of the energy.

3200A

The light source was the H-6 lamp described above with a Pyrex filter in place of the chlorine-mercuric chloride one. Photographs of the transmitted mercury lines showed complete absorption by the Pyrex filter below 3000A with a broad maximum of transmitted light at ~3106–3291A. The longer wave-lengths transmitted are known to be without substantial effect in the photolysis of the aldehydes.

Temperature Control

For the 30° runs an electric fan manually controlled was used to keep the temperature constant to $\pm 1^\circ$.

For the 100° runs at 2537A, the spiral lamp was placed inside an asbestos shield just large enough to enclose the lamp and the irradiated zone. Heat from a micro gas burner was used to supplement the heat of the lamp and to maintain constancy of temperature. In the work at 2900 and 3200A, steam escaping through two nozzles

⁵ Cf. E. J. Bowen, *J. Chem. Soc.* 76 (1935).

onto the irradiated zone, delimited by asbestos shields, maintained the temperature at $100 \pm 1^\circ$.

Except for the irradiated zone the reaction tube in each case was at room temperature, usually $18\text{--}25^\circ$.

Chemicals

Propionaldehyde was purified, stored, and prepared for use according to the method described by May, Taylor, and Burton.³ The corrected boiling range of the fraction used was $48.1\text{--}48.3^\circ\text{C}$ which may be compared with the range $47.8\text{--}48.0^\circ\text{C}$ reported by them.

Mercuric bromide used in separating the diethyl mercury from the excess propionaldehyde was purified by reprecipitating Eimer and Amend C.P. mercuric bromide from absolute alcohol. After drying, the mercuric bromide was kept at 100°C under vacuum for several hours.

1. HALF-LIFE EXPERIMENTS

In this part we worked with apparatus like that already described³ and, following that method, obtained a value for the half-life (i.e., time required for half the radicals to disappear) of 4.0×10^{-3} sec. which, considering the uncertainty of the visual method for following (lead) mirror removal, is in good agreement with the value of 3.9×10^{-3} sec. previously given. The actual data obtained are not here reviewed. Since the earlier result is based on more data, we believe it to be more reliable.

2. DETERMINATION OF THE NATURE OF THE RADICAL PRODUCED

In this part we followed the technique employed by F. O. Rice and his co-workers.⁶ The high vacuum techniques already established were maintained throughout this work. Free radicals produced by streaming the propionaldehyde at an input pressure of 2.5 mm through the irradiated zone, were allowed to react with a mercury mirror. The resultant product was collected, together with unaffected propionaldehyde, in a reservoir cooled at liquid-air temperatures. The amount of mercury product collected in any one prolonged run was insufficient for analysis. Con-

sequently, after closing and opening the appropriate stopcocks, the propionaldehyde was separated from the mercury alkyl compound by raising the temperature of the reservoir to that of a chlorobenzene mush ($\sim -45^\circ$) and distilling the propionaldehyde back to the storage reservoir maintained at liquid-nitrogen temperature. Several runs using ~ 250 g of propionaldehyde were made in this way at any one condition of light and temperature (in the irradiated zone). The trap was then removed for recovery and analysis of the mercury alkyl.

Purification and Identification of Alkyl Mercury Compounds

The trap containing the salts was removed and attached to a cold finger as described by Rice and Rice.⁶ The trap was evacuated and heated to 100°C in a water bath. Cold water was passed through the cold finger and the alkyl mercuric bromide sublimed, condensing on the finger. The system was always closed during an actual sublimation, in this way insuring equilibrium and preventing fractionation. After the sublimation, the trap was removed and cleaned of excess mercuric bromide. The apparatus was reassembled and the alkyl mercuric bromide was resublimed back onto the bottom of the trap, by passing steam through the finger while the trap was kept at 0°C . This procedure was repeated ten times.

Identification of the alkyl mercuric bromide was made by analyses for carbon, hydrogen, and bromine using the micro technique of Niederl and Niederl⁷ with some modifications. The micro combustion tube used in the carbon-hydrogen analyses was of the usual design but contained ~ 3.5 cm of gold sponge⁸ near the exit end to remove any mercury vapor. Details of the analysis of the alkyl mercury compounds are given in Table I. The ratio H : C : Br is included because the possibility of a slight contamination by mercury must be considered. The ratio calculated in this manner is based on the carbon analyses, which are the most accurate. Evidence for ethyl radicals as the only radicals formed in any measurable amount seems conclusive.

⁶ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals* (Johns Hopkins Press, Baltimore, 1935).

⁷ Niederl and Niederl, *Organic Quantitative Micro Analyses* (John Wiley and Sons, New York, 1938).

⁸ M. Furter, *Mikrochemie* **10**, 66 (1931).

TABLE I. Details of analysis of alkyl mercury bromide samples.

Sample	Wave-length A	H	Percent C	Br	H	Ratio C : Br	Br
2i	2537	1.56	7.66	23.7	0.204	1	3.10
4a	2537	1.75	7.99	26.4	.219	1	3.29
5a	3200	1.77	7.76	25.0	.228	1	3.19
C ₂ H ₅ HgBr (theor.)		1.61	7.76	25.8	.208	1	3.32
CH ₃ HgBr (theor.)		1.02	4.06	27.1	.255	1	6.67

3. FREE RADICAL: CARBON MONOXIDE RATIO

The method of counting free radicals, developed by Feldman, Ricci, and Burton,⁹ was followed in this work. In brief the method is to deposit an excess of lead as a sensitive mirror, to pass the gas containing free radicals (e.g., partially photolyzed propionaldehyde) over the mirror and to collect the products, and to measure analytically the amount of lead transported. On the basis of the assumption that the lead was transported exclusively as lead tetraethyl, the amount of free ethyl reacting with the lead during the period of the photolysis could then be determined. It will be shown in the discussion that a satisfactory standard value to which the production of free radicals can be related is the yield of carbon monoxide in the experiment; the method for determining the latter is indicated in the next part. In Table III the yield of ethyl is expressed as a C₂H₅/CO ratio. The experiments listed are numbered in chronological order. All experiments actually completed are included in the table.

4. MORE VOLATILE PRODUCTS

When the gaseous products were to be analyzed, the high vacuum required during a run (of about five minutes) was maintained with a mercury piston. At the end of the run, when the flow of propionaldehyde vapor had been stopped and while the receiver was still maintained at ~77°K, pumping was continued until all the fixed gases produced had been transferred to a gas analysis system of the Saunders-Taylor type.¹⁰ In order to insure complete removal of

such gases from the propionaldehyde, pumping was interrupted several times while the solid in the receiver was repeatedly melted and refrozen. This process was continued until no further gas could be drawn off in this way.

When the analysis of the first fraction, consisting of CO and H₂, had been completed, a second fraction was drawn off in a similar way at the temperature of *sec.* butyl chloride mush (~138°K).¹¹ No effort was made to draw off less-volatile products, such as butane, because of the difficulty of separation from the propionaldehyde.¹

Although, in general, the Saunders-Taylor technique was followed, slight modifications proved desirable. In the original technique the procedure is simply to burn the gas on a hot platinum wire, drawing the products through gold leaf (de-ozonizer), and then to absorb the water and CO₂ formed in magnesium perchlorate ("anhydrone") and freshly dried KOH, respectively. A difficulty with the technique involves the latter substance, which must not be too dry, for the rate of absorption of CO₂ will then become too slow. We found it necessary to use anhydrone for drying after the absorption of CO₂ in KOH even when supposedly dry KOH was used. The explanation is simply that this apparatus is capable of measuring microscopic amounts of water vapor and, when they are not carefully removed, they have a measurable effect considerably disturbing to the accuracy of the analysis. Having discovered this, we thereafter used only semi-dry KOH and dried the residual gas.

In the case of ethane, Saunders and Taylor found it necessary to apply a correction factor, since they consistently obtained analyses indicating C₂H_{6.6}. We have found that in this latter case the difficulty is at the *beginning* of the analysis. Traces of moisture present in the oxygen must be removed before it is measured and mixed with the sample prior to combustion. Under such circumstances "pure" ethane gives a value of *n* in C_nH_{2n+2} ranging from 1.91 to 2.10 (depending on the method of calculation), and no arbitrary correction need be applied.

In some analyses of the first fraction, a

⁹ Feldman, Ricci, and Burton, J. Chem. Phys. 10, 618 (1942).

¹⁰ K. W. Saunders and H. A. Taylor, J. Chem. Phys. 9, 616 (1941).

¹¹ Cf. D. S. Herr and W. A. Noyes, Jr., J. Am. Chem. Soc. 54, 3165 (1932).

TABLE II. Details of ethane analyses.

Expt.	Obs. vol. V_1	Calc. vol. ^a V_2	n in $C_{2n}H_{n+2}$	
			$\frac{CO_2}{V_1}$	$\frac{CO_2}{V_2}$
128	4.33	4.16	1.96	2.04
129	6.42	6.26	2.05	2.10
140	4.01	4.15	1.98	1.91
141	4.17	4.23	2.00	1.97

$$^a V_2 = \frac{2 \times \text{contraction} - CO_2}{3}$$

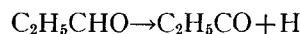
separate determination of H_2 and CO was made (e.g., in experiments 117, 112, and 118). However, after it was determined that the fraction contained only these two gases and that the determination of H_2 and CO by calculation from the contraction over anhydron was reliable, the absorption of CO_2 was omitted. Similarly, once it had been determined by analyses that the 138°K fraction contained only C_2H_6 , but few analyses on this fraction were conducted; usually, the volume was simply measured and taken to be ethane. The data on the basis of which it was concluded that the 138°K fraction was solely ethane are summarized in Table II.

The results obtained in the analyses in the various runs at wave-lengths of $\sim 3200A$, $\sim 2900A$, and $2537A$ at temperatures of 25° and 100° are summarized for experiments with lead mirrors in Table III and for experiments without mirrors in Table IV. Experiments are numbered in chronological sequence.

Tests for Atomic Hydrogen at 3200A

The guard mirror technique used by May, Taylor, and Burton³ was emulated by us in an effort to detect atomic hydrogen in experiments at 3200A. In each experiment a heavy lead mirror 4 cm wide was deposited at the edge of the irradiated zone. A faint, narrow standard antimony mirror was then deposited about 5 cm from the irradiated zone. The time of removal of the antimony mirror in the course of a usual experiment (photolysis of propionaldehyde streaming at an input pressure of 2.5 mm) was then noted. In three separate experiments it was found that a barely detectable fading of the antimony mirror, corresponding to no more than 10 percent removal, could be observed in 30 minutes. It had been previously established that at approximately the same free radical concentration (cf. Table

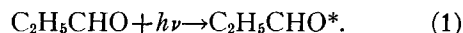
III) at 2537A similar antimony mirrors without the lead guard mirror were removed in duplicate experiments in less than two minutes. In other words, the free radicals present at 3200A were ~ 150 times as effective in removing antimony as was the fraction which leaked by the guard; the concentration of atomic hydrogen seems to be even less than the maximum 2 percent reported by May, Taylor, and Burton.³ The reaction



may therefore be neglected as a possible source of molecular hydrogen in these experiments.

DISCUSSION

Absorption of light by propionaldehyde involves only excitation of the carbonyl group.¹²

TABLE III. Summary of data with mirrors.^a

Expt.	λ , A	T	Time, min.	H_2 cm	CO cm	Pb μg	$\frac{C_2H_5}{CO}$	C_2H_6 cm
119	3200	30°	3	0.42	7.95	35	0.31	4.71
120			3	0.34	6.38	29	.33	4.11
128			3	0.53	8.90	39	.31	6.07
148 ^b			1.5	0.43	6.92	36	.36	5.15
149 ^b			1.5	0.42	7.31	40.1	.33	5.04
129		100°	3	0.62	9.25	37.5	.288	6.42
130	2900	30°	1.5	0.36	4.04	26.6	.454	2.25
131			1.5	0.43	4.43	30.2	.477	2.69
132			3	0.94	8.98	57.2	.438	5.20
150 ^b			1.5	0.36	4.80	34.0	.49	2.44
151 ^b			1.5	0.31	3.57	26.2	.51	2.03
133		100°	3	0.93	9.24	56.6	.42	5.99
134			3	0.90	9.10	53.5	.40	5.40
101	2537	30°	3	0.74	8.64	48	.38	
102			3	0.71	8.27	45	.37	
103			3	0.75	8.70	46	.36	
104			3	0.77	8.83			
105			3	0.68	8.42			
117			3	0.57	6.15			3.97
127			3	0.62	6.60			4.62
142			3	0.71	7.94	43	.373	5.42
143			3	0.60	7.43	40	.371	4.97
106		100°	3	1.00	11.10	44	.274	
107			3	0.94	10.46			
114			1.5	0.43	5.47	22.5	.284	
139			1.5	0.36	5.10	23.5	.318	3.41
140			1.5	0.47	5.89	29.5	.345	4.01

^a Lead mirrors in each run were placed at the edge of the irradiated zone. The gas pressures are recorded in cm of mercury and were measured at 23°C for a volume of 0.488 cc in the Saunders-Taylor apparatus.

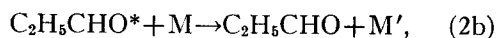
^b 1 cm illuminated zone.

¹² Cf. G. K. Rollefson and M. Burton, *Photochemistry and the Mechanism of Chemical Reactions* (Prentice-Hall, Inc., New York, 1939), p. 223.

Thereafter, the energy may be made ineffective by fluorescence



or by molecular deactivation

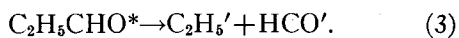


or it may be made effective as the result of an energy shift within the molecule leading either to rearrangement and an ultimate molecule decomposition or to rupture into free radicals.¹³

The possible primary decomposition processes involved in this case are all predissociation mechanisms of different types. The results that may be expected depend in part upon the stability (i.e., the "natural" life) of the excited state. In general, provided sufficient energy is available, a rupture into radicals seems favored by its simplicity. Whether the molecule decomposes by rupture or by rearrangement will depend on (a) the amount of energy, (b) the time available, i.e., the life of the excited molecule, and (c) the extent of rearrangement required for the ultimate-molecule mechanism. Such considerations have led to conclusions that decomposition of complex molecules into radicals is favored by short wave-lengths and that ultimate-molecule decomposition, if it involves a profound rearrangement of the component parts, occurs with higher probability in a distorted field; i.e., as an induced predissociation.¹³

The Free Radical Process

Analyses of the mercury alkyl product show that the only alkyl radicals produced are C_2H_5 . Furthermore, the guard-mirror experiments of May, Taylor, and Burton³ at 2537Å and our own experiments at 3200Å indicate the absence of H atoms in any significant quantity. Thus, the only free radical decomposition process we have to consider is



The prime marks (') after the radicals indicated that they are formed with excess energy depend-

TABLE IV. Summary of data without mirrors.

Expt.	$\lambda, \text{\AA}$	T	Time, min.	CO cm	H ₂ cm	C ₂ H ₆ cm
124	3200	30°	3	8.27	0.50	7.01
125			3	7.99	.52	7.11
144°			9	4.42	.29	3.61
145°			9	3.92	.28	3.09
126	2900	100°	3	8.82	.57	7.97
135			1.5	4.25	.50	3.10
136			1.5	4.50	.61	3.72
146°			9	6.41	.64	5.57
147°	2537	30°	9	6.49	.59	4.95
137			1.5	4.96	.66	4.00
138			1.5	4.75	.69	3.90
118			1.5	5.41	.45	3.65
121	100°	100°	1.5	6.01	.46	3.94
122			3	6.79	.54	4.70
123			3	6.92	.58	4.91
141			3	6.70	.52	4.17

* Incident light at half intensity.

ing on the wave-length.¹⁴ This energy is available, e.g., as activation energy, up to the first collision. Thereafter, the radicals reach thermal equilibrium very quickly.

Radicals are produced at all wave-lengths—although not always to the same extent. The maximum yield of free radicals, in terms of the $\text{C}_2\text{H}_5/\text{CO}$ ratio, occurs at intermediate wave-lengths (cf. Fig. 1), but this does not necessarily mean that the ratio of free radical to ultimate molecule processes reaches a maximum at such intermediate wave-lengths, nor even, indeed, that the wave-length 2900Å has any special significance, for more thorough coverage of wave-lengths might relocate the maximum.

Proposed Mechanism

The data are not such as to warrant a completely detailed consideration of the possible mechanism at all wave-lengths. However, certain aspects are sufficiently striking to merit special attention. The results at 2537Å are susceptible to the simplest interpretation. Here a possible satisfactory mechanism can be contrived from reaction 3 followed or accompanied by the reac-

¹³ M. Burton and G. K. Rollefson, J. Chem. Phys. 6, 416 (1938).

¹⁴ The amount of excess energy is estimated on the basis of the value assumed for the strength of the $\text{C}_2\text{H}_5\text{CHO}$ bond. If we assume ~75 kcal. [cf. M. Burton, J. Chem. Phys. 7, 1072 (1939)], the excess energies are: at 2537Å, 37 kcal.; at 2900Å, 22 kcal.; at 3200Å, 15 kcal.

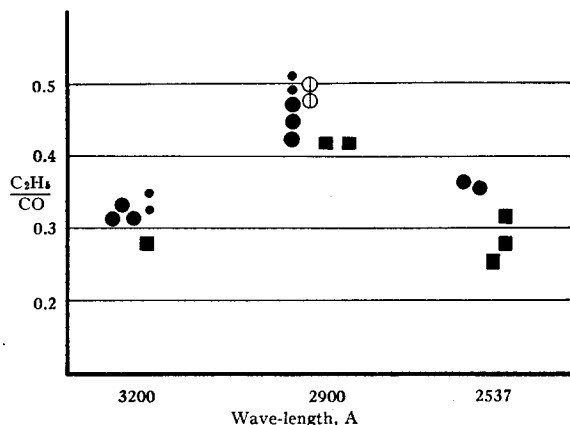
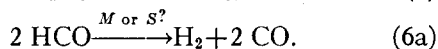
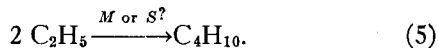
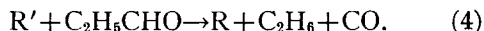
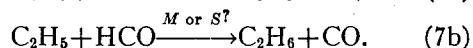
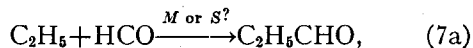


FIG. 1. C_2H_6/CO ratio as a function of wave-length. \circ Without mirror, $30^\circ C$, full intensity; \oplus Without mirror, $30^\circ C$, half intensity; \bullet With mirror, $30^\circ C$, full intensity; \bullet With mirror, $30^\circ C$, narrow illuminated zone; \odot With mirror, $30^\circ C$, half intensity; \square Without mirror, $100^\circ C$, full intensity; \blacksquare With mirror, $100^\circ C$, full intensity.

tions shown.



Reactions 6a and 6b are intended to represent over-all reactions rather than precise mechanisms. It is possible that formaldehyde is formed by reaction 6b and that a portion of it then decomposes to give the over-all effect 6a. Our data cannot distinguish such reaction steps. There are also other possible reactions which require only casual mention, e.g.,



If reactions 7a and 7b occur at all, their rates will be affected by the absence or presence of a mirror since the latter would remove the C_2H_5 radicals required. In turn, the participation of HCO radicals in reactions 6a and 6b would be affected. At 2537 Å, as can be seen from Figs. 2 and 3, the C_2H_6/H_2 ratios remain constant,¹⁵

¹⁵ It should be noted that data involving H_2 are more uncertain than others because of the greater relative experimental error involved in the determination of the small volumes of hydrogen.

within experimental error, in the absence or the presence of a mirror. It is for this reason that we eliminate reactions 7a and 7b from further detailed consideration.

Reaction 4 is an induced predissociation reaction of a type suggested by Taylor and Burton¹⁶ in the case of the nitric oxide-catalyzed pyrolysis of acetaldehyde; it is characterized by the fact that an odd-electron molecule furnishes the required intense distorted field. Evidence that reactions of this kind are not uncommon appears recently from several sources. For example, O. K.

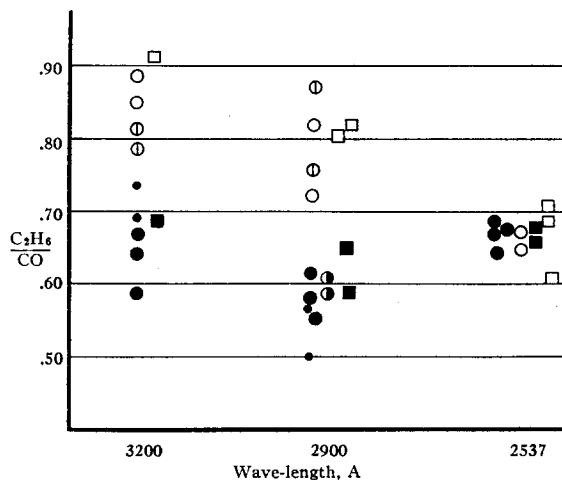


FIG. 2. C_2H_6/CO ratio as a function of wave-length. For legend see Fig. 1.

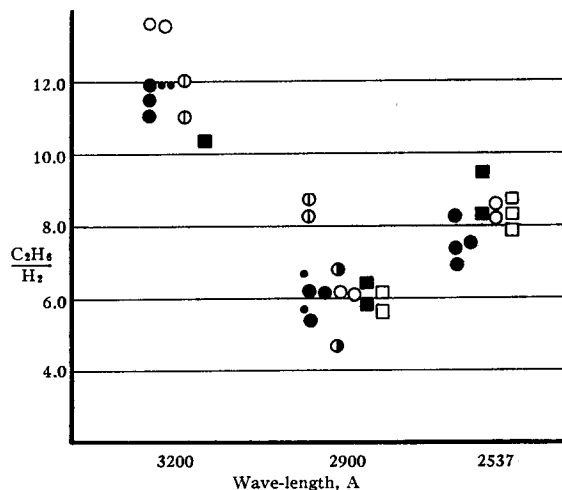
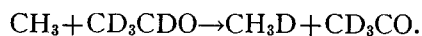


FIG. 3. C_2H_6/H_2 ratio as a function of wave-length. For legend see Fig. 1.

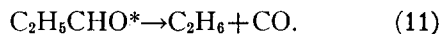
¹⁶ H. A. Taylor and M. Burton, J. Chem. Phys. 7, 414 (1939).

Rice and Hayden¹⁷ have stated that the relatively stable HCO radical may be an even more effective chain carrier than CH₃ in the high temperature photolysis of acetaldehyde. Also, although Burton, Ricci, and Davis¹⁸ found that free radicals are produced in the pyrolysis of acetaldehyde even at the lowest temperatures studied, Morris¹⁹ obtained the apparently contradictory result that mixed deuterio-methanes were not found as products in the pyrolysis of mixtures of normal- and deuterio-acetaldehyde. The contradiction follows from the assumption of a Rice-Herzfeld²⁰ chain-continuing step, e.g.,



However, if the chain-continuing step is an induced predissociation, as in reaction 4, there is no contradiction in the two sets of results.

Induced predissociation of this type requires an activation energy which is ordinarily available only at high temperature. However, the radicals, when produced, possess considerable excess energy (i.e., they are quite "hot") and retain this energy until their first collision. Thus, if the first collision is with a molecule like C₂H₅CHO in this case, there may be enough energy for the induced predissociation. Recently O. K. Rice and Hayden¹⁷ have estimated ~11 kcal. for the energy of the chain-continuing step in acetaldehyde, a figure which indicates that the excess energy available in R' in this case is of the order of magnitude required to produce the effects noted, particularly at shorter wave-lengths. For this reason, the apparent "chain length" of this step (which can in no event exceed unity according to the explanation given) must decrease as the wave-length is increased. We shall see that it is this *theoretical* requirement which suggests the necessity for an ultimate molecule step, at least at longer wave-length,



Reaction 5 is offered without further discussion to account for the butane reported by Leighton

¹⁷ O. K. Rice and W. L. Hayden, J. Chem. Phys. **10**, 445 (1942).

¹⁸ Burton, Ricci, and Davis, J. Am. Chem. Soc. **62**, 265 (1940).

¹⁹ J. Morris, J. Am. Chem. Soc. **63**, 2535 (1941).

²⁰ F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

TABLE V. Calculated and observed C₂H₆/CO ratios at 2537A.

Expt.	Temp.	C ₂ H ₆ /CO		Discrepancy % calc.
		Calc.	Obs.	
117	30°C	0.52		
127		.41		
142		.46	0.37	—0.20
143		.50	.37	— .26
139	100°C	.48	.32	— .33
140		.52	.34	— .34
Average				— .28

and Blacet.¹ We have not been concerned with this feature of the yield in our work.

Reactions 6a and 6b are adopted as the only reactions involving two formyl radicals in this case. Frankenburger and his co-workers,²¹ working with the mercury-photosensitized reaction between hydrogen and carbon monoxide (at pressures considerably higher than employed by us), found formaldehyde and glyoxal, formed presumably by reactions involving HCO, in the ratio of 4 : 1. On the other hand, Zemany²² has adduced evidence that in the photolysis of glyoxal at pressures of a few millimeters the reaction between HCO radicals yields principally CO, H₂, and HCHO and a negligible quantity of (HCO)₂. Since our conditions are more nearly similar to those of Zemany and, in any event, the neglect of the possible formation of glyoxal does not introduce any serious error into our considerations, we make the simplifying assumption that the only significant reactions involving two free HCO radicals are 6a and 6b. The internal consistency of this assumption in our work can be seen by an arithmetical examination of the data at 2537A.

If we limit ourselves only to the reactions so far considered, we see that possible reactions at 2537A producing our measured products are: 3 producing R'; 4 and 11 producing C₂H₆ and CO; 6a producing H₂ and CO; and 6b producing CO. Let us represent the total cm of C₂H₆ by *x*, CO by *y*, and H₂ by *z*.²³ The number of cm produced in any particular reaction or group of

²¹ Frankenburger, Klinkhardt, Steigenwald, and Zimmerman, Zeits. f. Elektrochemie **36**, 757 (1930).

²² P. Zemany and M. Burton, unpublished work.

²³ Moles of a gas are proportional to the pressure registered by a fixed volume in the Saunders-Taylor apparatus.

reactions will be indicated by the appropriate subscript. Thus,

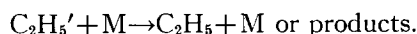
$$\begin{aligned} x &= x_{4,11} = y_{4,11}, & 1 \\ \text{and} & & \\ y_{6b} &= y - x - 2z. & 2 \end{aligned}$$

The number of cm decomposed to give free radicals is $2(y-x-z)$ and consequently the calculated C_2H_5/CO ratio (r_{calc}) should be $2(y-x-z)/y$. The results at 2537A are compared with the observed ratios ($r_{obs} = C_2H_5/CO$ in Table III) in Table V. In the last column the discrepancy is noted as a fraction of the calculated value. This fraction should be equal to the fraction of radicals which have disappeared before reaching the mirror. This latter may be calculated from our knowledge of the half-life of the C_2H_5 radicals ($\sim 4.0 \times 10^{-3}$ sec.), the length of the irradiated zone (10 cm), the distance of the mirror from the edge of the irradiated zone (0 cm), and the streaming velocity (1120 cm/sec.). The result is 31 percent, a value which is in better agreement with the average discrepancy shown in Table V than can reasonably be expected from the accuracy of the analyses (± 5 percent).

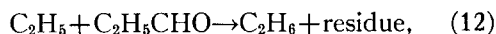
Other Reactions

It must be emphasized that the data so far considered furnish no criterion for a choice between reactions 4 and 11. Either one or both may be the source of C_2H_6 . Further conclusions necessitate examination of the data at longer wave-lengths, the striking features of which are best illustrated in Figs. 1 to 3. For example, the C_2H_5/CO ratio (Fig. 1) reaches a maximum at some intermediate wave-length. If reaction 4 is the principal source of C_2H_6 , the result is easily accounted for; we conclude merely that at longer wave-length reaction 4 is less frequent since less energy is available in R' . The existence of a maximum at intermediate wave-lengths can then be interpreted on the basis of a preconceived notion that the more complicated process of rearrangement involved in reaction 11 takes place with greater probability at longer wave-length.¹³ This conclusion is supported also by the CO/H_2 and C_2H_6/H_2 ratios which increase markedly at shorter wave-lengths, indicating the incidence of a mechanism which does not yield H_2 .

This conclusion of itself is not sufficient to account for the other results. The C_2H_6/CO ratios at 2900A and 3200A are clearly sensitive to the presence or the absence of a mirror (cf. Fig. 2). Such a result indicates that C_2H_5 radicals at these wave-lengths (but not at 2537A) react with some substance, most probably C_2H_5CHO , to yield C_2H_6 without yielding CO .²⁴ Obviously, the reaction cannot involve the ("hot") C_2H_5' radicals since they do not survive a first collision; i.e.,

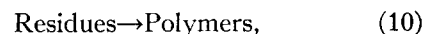
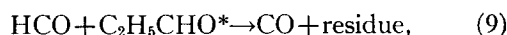
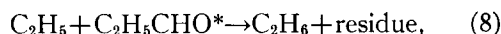


Neither can it involve a reaction such as

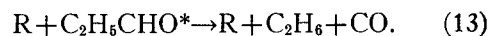


where the assumption is that the activation energy is very low, for on such an assumption C_2H_6/CO should increase also at 2537A.

Possible acceptable explanations of the results may involve reactions such as



and, in addition to those,



The latter reaction for example, might account for the increases in CO/H_2 and C_2H_6/H_2 already noted at 3200A. However, a detailed consideration of any of these reactions is certainly not justified on the basis of the data at hand. The statement should, however, be made that if excited molecules such as $C_2H_5CHO^*$ are involved in reactions such as 8 and 9 (where 8 accounts for the C_2H_6/CO effects already noted), then the half-life implicitly required for the excited state is $> 10^{-3}$ sec., as judged from the time required for the radicals to pass from the irradiated zone into the remoter portions of the reaction tube.²⁵

²⁴ Note the approximate constancy of CO/H_2 ratios indicated at 2537 and 2900A.

²⁵ Cf. R. Spence and W. Wild, J. Chem. Soc. 590 (1941), who have recently arrived at a similar conclusion regarding the excited state of acetone.

Conclusion on Mechanism of Photolysis

The major conclusion from the data here presented is that a free radical decomposition occurs at all wave-lengths. An ultimate molecule decomposition may also occur but, if it does, its probability is greatest at the longer wave-lengths. On the other hand, it is possible to devise an exclusively free radical process (involving a reaction such as 13) which may account for the results at longer wave-lengths. The data are not sufficiently extensive to warrant a critical evaluation of the possible mechanisms.

Mechanism of Energy Transfer

The simplest possible mechanism after reaction 1 would seem to be a spontaneous predissociation transition starting from the excited state represented by $C_2H_5CHO^*$ and ending with *any* repulsive or weakly attractive state whose dissociation level is less than 90 to 112 kcal. above the ground state. According to the bond strengths we have assumed,²⁶ H atoms could then appear at 2900 and 2537Å and free CH_3 radicals might be expected at all wave-lengths. The failure to observe the latter at all indicates that geometric factors are important.

According to Mulliken,²⁷ the excited electron is a $2p$ non-bonding one on the oxygen atom. The experimental results here reported would indicate that although this excited state can interact with a state involving excitation of an adjacent bond it cannot do so with a state involving excitation at a more remote bond. The failure to observe atomic hydrogen in any substantial amount must then be attributed to another factor.

The conditions bearing on the decomposition into C_2H_6 and CO have already been discussed for the parallel case of acetaldehyde.²⁸ In regard to the alternative decompositions yielding H or C_2H_5 in the primary step, it is not unreasonable

to assume that the ~ 20 kcal. difference in the dissociation levels may be reflected by a large difference in the heights of the intersections of the repulsive (or perhaps weakly attractive) states representing dissociation into H and C_2H_5 , respectively, with an excited state of propionaldehyde (a state, incidentally, which may be different from that to which the original excitation occurred). Such a difference might markedly favor the predissociation process yielding C_2H_5 radicals²⁹ but it is impossible to arrive at any better interpretation of the results without a more precise knowledge of the potential energy relationships. For example, conditions have been indicated where (unlike this case) decomposition to products on the higher dissociation level may be favored.²⁹

That ~ 20 kcal. may be more than sufficient to inhibit a decomposition even when there is sufficient energy available is well illustrated by the case of crotonaldehyde. In that case, the conjugated double bond may strengthen the R-CHO bond by perhaps 10 kcal.³⁰ No photodecomposition can be detected at room temperature at wave-lengths from 3130 to 2380Å.³¹ Neither the R-CHO bond nor the remote CH_3-C bond is broken even though more than enough energy is available for either process. The fact that the CH_3-C bond in this case is not broken indicates that in the case of a "long-chain" aldehyde we are not dealing with possible competition between two or more possible mechanisms (i.e., breaks at various C-C bonds) but with only one possible rupture process,¹³ the break of the C-C link adjacent to the excited atom.

Acknowledgment

The authors wish to express their appreciation to Professor John E. Ricci and to Dr. R. D. Present for many stimulating discussions concerning this paper.

²⁶ M. Burton, J. Chem. Phys. **6**, 818 (1938). See, however, Andersen, Kistiakowsky, and Van Artsdalen, *ibid.* **10**, 305 (1942); also D. P. Stevenson, *ibid.* **10**, 291 (1942).

²⁷ R. S. Mulliken, J. Chem. Phys. **3**, 564 (1935).

²⁸ T. W. Davis and M. Burton, J. Chem. Phys. **7**, 1075 (1939).

²⁹ G. K. Rollefson and M. Burton, J. Chem. Phys. **6**, 674 (1939).

³⁰ Cf. the case of glyoxal, reference 26.

³¹ F. E. Blacet and J. E. Lu Valle, J. Am. Chem. Soc. **59**, 2375 (1937); F. E. Blacet and J. G. Roof, *ibid.* **58**, 73 (1936); H. W. Thompson and J. W. Linnett, J. Chem. Soc. 1425 (1935).