AIP | The Journal of Chemical Physics

Photolysis of Ethane at 1470 A

M. H. J. Wijnen

Citation: The Journal of Chemical Physics **24**, 851 (1956); doi: 10.1063/1.1742620
View online: http://dx.doi.org/10.1063/1.1742620
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/24/4?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 24, NUMBER 4 APRIL, 1956

Photolysis of Ethane at 1470 A*

M. H. J. Wijnen†
Division of Pure Chemistry, National Research Council, Ottawa, Canada

(Received July 19, 1955)

The photolysis of ethane at 1470 A has been investigated in the temperature range 25° to 240°C and over a wide range of initial ethane pressures. As reaction products were found mainly H_2, CH_4, C_3H_8, and C_4H_{10}. Traces of ethylene and, not identified, higher hydrocarbons were also detected. The results indicate that the primary step in the photolysis of ethane is

$$C_2H_6+h\nu\rightarrow C_2H_5+H.$$

The amounts and ratios of products, formed during the photolysis, indicate that the reaction mechanism of the photolysis is similar to that of the Hg photosensitized decomposition of ethane.

A few experiments on the photolysis of CO_2 at 1470 A indicate that φCO increases with increasing temperatures.

INTRODUCTION

VERY little work has been done so far on the direct photolysis of ethane. The main reason for this is undoubtedly the fact that ethane does not absorb above 1620 A.[1]

A direct photolysis of compounds, absorbing in the Schumann ultraviolet, was made possible by the development of the xenon lamp by Harteck and Oppenheimer[2] which lamp was improved by Groth.[3]

An easier to operate type of xenon lamp was later developed by Dacey and Hodgins.[4]

Both types of lamps, however, have the disadvantage that it is extremely difficult to carry out investigations at different temperatures. In the present investigation we have studied the photolysis of ethane over the temperature range 25° to 240°C. This was made possible by the use of a new type of xenon lamp which is described in detail in the experimental section.

It has been suggested by Groth[3] to use CO_2 as actinometer for the photolysis at 1470 A. Since the photolysis of CO_2 has so far only been studied at room temperature, it seemed important to carry out a few experiments photolyzing CO_2 at higher temperatures. The results of these experiments in regard to the usefulness of CO_2 as actinometer for 1470 A light will be discussed.

EXPERIMENTAL

The xenon lamp is separated from the reaction cell by a vacuum chamber. Since the lamp heats up considerably when in use, the vacuum chamber serves to prevent heat transfer from lamp to cell which would make it impossible to obtain a constant temperature over the full length of the reaction vessel. The light reaches into the cell via two quartz bubble windows (thickness of the windows is in the order of 20 microns). Due to their shape the bubble windows stand up to pressures of about 1 atmosphere if the pressure is exerted toward the concave side of the bubble window. It is therefore possible to fill the reaction cell up to pressures of 1 atmosphere while the vacuum chamber is evacuated. On the other side small pressure differences of 5 mm or more will break the windows if the pressure is higher at the convex side of the windows. It is advisable to connect the lamp to the vacuum chamber in order to prevent breaking of the bubble window between lamp and vacuum chamber while evacuating the lamp. Throughout this investigation an operating pressure of about 1.5 mm of xenon in the lamp has been used. This pressure has been shown[5] to give an optimum yield of 1470 A light in the Dacey-Hodgins type of xenon lamp. It has also been observed[5] that during the operation of the lamp the xenon slowly disappeared, probably due to "cleanup" as observed in electrodeless discharge of gases. To prevent any pressure change during its operation the lamp was connected to a ballast volume of 1 liter. The lamp is operated on a 60 cycle current from a 6000-v transformer whose primary windings are connected to a variac. An operating current of about 40 ma was used throughout the investigation. The electrodes are commercial neon-sign electrodes. Lamp and vacuum chamber are made out of quartz. The Pyrex reaction vessel, with a volume of 200 cc, is attached to the vacuum chamber by a graded Pyrex quartz seal.

Reaction vessel and vacuum chamber were surrounded by an aluminium block furnance. The temperature was measured by means of copper-constantan thermocouples and controlled to within 1°C by a photoelectric relay operating on the light beam from the potentiometer galvanometer.

As main reaction products were found H_2, CH_4, C_3H_8 and C_4H_{10}. Traces of ethylene and higher hydrocarbons were also detected. H_2 and CH_4 were separated from the residual ethane at $-210°C$ in a liquid nitrogen pump-

---

* National Research Council No. 3908.

† Present address: Celanese Corporation of America, Clarkwood, Texas.

[1] H. Sponer, *Molekul Spektren* (Verlag Julius Springer, Berlin, Germany, 1935, 1936), Vol. I (tables), Vol. II (text).

[2] P. Harteck and F. Oppenheimer, Z. physik. Chem. **B16**, 77 (1932).

[3] W. Groth, Z. physik. Chem. **B37**, 307 (1937).

[4] J. R. Dacey and J. W. Hodgins, Can. J. Research **B28**, 90 (1950).

[5] M. H. J. Wijnen and H. A. Taylor, J. Chem. Phys. **21**, 233 (1953).

TABLE I. Photolysis of CO_2.

No.	P_{CO_2} in mm	Temp. °C	$CO+O_2$ mole/sec	CO mole/sec
1	23.6	25	0.98 10^{14}	0.87 10^{14}
3	72.7	25	0.96 10^{14}	0.87 10^{14}
2	25.1	270	1.65 10^{14}	1.28 10^{14}
4	72.0	270	1.65 10^{14}	1.17 10^{14}

down trap. The ratio H_2/CH_4 was then determined by mass spectrometric analysis. The residual ethane containing all other reaction products was then analyzed in the mass spectrometer. Due to the small percentage of C_3H_8 and C_4H_{10} in the residual ethane and due to interference, caused by the presence of some not identified higher hydrocarbons, the analysis for C_4H_{10} and in particular for C_3H_8 cannot be considered to be very accurate.

In all experiments the conversion was less than 5%.

The research grade ethane was obtained from Phillips Petroleum Company.

RESULTS AND DISCUSSION

CO_2

To explain the formation of CO and O_2 in the photolysis of CO_2 at 1470 A, Groth[3] proposed the following reactions:

$$CO_2+h\nu\rightarrow CO+O \tag{a}$$

$$O+O+M\rightarrow O_2+M. \tag{b}$$

Based on the assumption that at 1470 A the quantum yield for the decomposition of NH_3 would be equal to 0.17 as observed by Wiig and Kistiakowsky[6] at about 2100 A, and that the quantum yield of ozone formation in O_2 would be equal to two as found by Vaughan and Noyes[7] in the region of 1720 to 1900 A. Groth obtained quantum yields of 0.98 for the production of CO and of 1.47 for the production of $CO+O_2$ in the photolysis of CO_2 at 1470 A.

Assuming φCO to be equal to 0.98, Wijnen and Taylor[5] recently found that the quantum yield for the decomposition of NH_3 increased from 2 to 12 with increasing NH_3 pressure. Since these results could not be reconciled with those of Groth, the authors suggested that there is no certainty about the actual value of φCO and $\varphi(CO+O_2)$.

A few experiments have been carried out to obtain some more information regarding the usefulness of CO_2 as actinometer for photolysis at 1470 A. The results of these experiments, which were xenon photosensitized in order to obtain complete absorption of all 1470 A light, are given in Table I.

Two observations may be made from these experiments: (1) the ratio $(CO+O_2)/CO$ is temperature dependent and especially at room temperature considerably smaller than 1.5 as suggested by reactions (a) and (b), and as observed by Groth; (2) the quantum yield of CO production increases with increasing temperature. At room temperature we obtain $(CO+O_2)/CO=1.1$. Groth's value of 1.5 for this ratio is not necessarily in contradiction with our results. According to reaction (b) O_2 is formed via recombination of O atoms in a triple collision. The intensity of the xenon lamp used by Groth is of the order of 10^{16} quanta/sec, while ours is of the order of 10^{14} quanta/sec. If we accept as a possible explanation for our O_2 deficiency, disappearance of O atoms on the wall, then it is clear that at high O atom concentrations the recombination reaction may be more important. Summarizing these results, this author comes to the conclusion that there is little evidence indicating that φCO in the photolysis of CO_2 is equal to unity. Since it is extremely difficult to carry out direct measurements on the intensity of 1470 A light, CO_2 may be used as a "relative" actinometer. However in doing so, calculations should be based on the production of CO (not on the production of $CO+O_2$) and it should be taken into account that φCO increases with increasing temperature.

C_2H_6

In Table II we give the results obtained on the direct photolysis of C_2H_6 at 1470 A. At each temperature the results are arranged according to increasing initial C_2H_6 pressure. The number in the first column indicates the sequence in which the experiments were carried out. By R_x we indicate the rate of production of the compound X.

The following two reactions have been suggested as primary steps in the photolysis of C_2H_6.

$$C_2H_6+h\nu\rightarrow 2CH_3 \tag{1a}$$

$$C_2H_6+h\nu\rightarrow C_2H_5+H. \tag{1b}$$

Reaction (1b) was rejected by Faltings[8] because of an almost negative indication of formaldehyde production when photolyzing mixtures of C_2H_6 and CO, while HCHO was definitely formed in irradiating H_2-CO mixtures. As pointed out by Groth and Scharfe[9] this evidence is not conclusive since, in the presence of C_2H_6, H atoms may react with C_2H_6 to form H_2 and C_2H_5 rather than react with CO to form HCHO. As evidence for reaction (1a), Faltings pointed out that acetone was found as a reaction product when photolyzing C_2H_6 in presence of CO. Several experiments were carried out by us, in which we photolyzed C_2H_6 in presence of CO. No positive indication could, however, be obtained regarding the production of acetone and/or diethyl ketone. Furthermore, if reaction (1a) would be

---

[6] E. O. Wiig and G. B. Kistiakowsky, J. Am. Chem. Soc. **54**, 1806 (1932).

[7] W. E. Vaughan and W. A. Noyes, Jr., Am. Chem. Soc. **52**, 559 (1930).

[8] K. Faltings, Ber. deut. chem. Ges. **72**, 1206 (1939).

[9] W. E. Groth and G. Scharfe, Z. physik. Chem. N.F. **2**, 142 (1954).

TABLE II. Photolysis of C_2H_6.

No.	(C_2H_6) in mole/cc ×10^{-17}	In mole/cc sec ×10^{-12} R_{H_2}	R_{CH_4}	$R_{C_3H_8}$	$R_{C_4H_{10}}$	R_{H_2}/R_{CH_4}
			25°C			
16	5.80	2.10	2.14	1.45	0.60	0.98
13	6.07	1.64	1.74	1.03	0.53	0.94
14	14.85	4.54	2.95	2.01	1.40	1.54
17	22.19	5.51	2.63	2.74	2.74	2.09
18	41.79	8.48	2.08	2.18	3.19	4.08
15	75.75	14.19	2.89	2.51	5.02	4.92
19	82.27	11.80	2.20	1.52	4.57	5.37
			58°C			
12	3.41	1.78	1.54	0.94	0.53	1.16
8	10.31	4.18	2.85	1.95	1.19	1.47
9	20.85	7.67	1.96	1.49	2.75	3.91
11	31.74	13.83	3.65	3.82	4.92	3.78
10	59.81	19.53	2.60	3.18	4.43	7.50
			99°C			
24	3.14	2.91	3.72	1.20	0.50	0.78
23	3.76	3.54	2.60	1.25	0.67	1.36
27	16.02	9.31	2.67	2.19	2.93	3.49
21	24.48	18.40	3.28	2.83	4.65	5.61
26	30.67	21.85	3.69	3.19	5.54	5.92
22	51.96	29.30	2.76	2.16	6.73	10.61
25	63.42	35.43	2.31	2.64	4.99	15.34
			240°C			
29	2.09	6.01	1.48	0.96	2.22	4.06
31	3.80	9.94	1.37	1.19	3.57	7.26
26	5.64	12.35	1.81	1.87	3.33	6.83
28	8.46	20.14	1.34	1.95	8.79	15.01
30	19.21	11.51	0.59	0.00	9.10	19.62
32	35.21	24.27	1.26	0.00	34.74	19.31

the primary step, it would be expected that the production of CH_4 would increase with increasing initial C_2H_6 pressure according to the reaction $CH_3+C_2H_6\rightarrow CH_4+C_2H_5$. As may be seen in Table II, no such increase is observed at any of the temperatures at which our experiments were carried out.

A strong indication for reaction (1b) as primary step is given by our results which show clearly a marked increase in H_2 and C_4H_{10} production with increasing initial C_2H_6 pressure. A similar increase in H_2 and C_4H_{10} production with increasing initial C_2H_6 pressure has also been observed in the Hg photosensitized reaction of ethane where the following reaction is accepted as primary step[10]

$$Hg(^3P_1)+C_2H_6\rightarrow C_2H_5+H+Hg(^1S_0).$$

Reaction (1b) has also been suggested by Groth and Scharfe[9] in analogy to their results obtained in the direct photolysis of propane.

Accepting, therefore, reaction (1b) as primary step, we suggest the following reaction mechanism to explain our results:

$$C_2H_6+h\nu\rightarrow C_2H_5+H \tag{1}$$

$$H+C_2H_6\rightarrow H_2+C_2H_5 \tag{2}$$

$$2C_2H_5\rightarrow C_4H_{10} \tag{3}$$

$$2C_2H_5\rightarrow C_2H_4+C_2H_6 \tag{4}$$

$$H+H+M\rightarrow H_2+M \tag{5}$$

$$H+C_2H_5\rightarrow C_2H_6^* \tag{6}$$

$$C_2H_6^*\rightarrow 2CH_3 \tag{7}$$

$$C_2H_6^*+M\rightarrow C_2H_6+M \tag{8}$$

$$CH_3+C_2H_5\rightarrow C_3H_8 \tag{9}$$

$$CH_3+C_2H_5\rightarrow CH_4+C_2H_4 \tag{10}$$

$$2CH_3\rightarrow C_2H_6 \tag{11}$$

$$CH_3+C_2H_6\rightarrow CH_4+C_2H_5 \tag{12}$$

$$CH_3+H+M\rightarrow CH_4+M \tag{13}$$

$$C_2H_4+R\rightarrow C_2H_4R. \tag{14}$$

Reactions (2), (3), (4), and (5) do not warrant any discussion since they are generally accepted reactions of the radicals, produced by the primary step, among themselves or with the parent compound. The fact that CH_4 and C_3H_8 are found as reaction products strongly suggests that CH_3 radicals are formed during the reaction. The results also indicate that relative to the production of H_2 and C_4H_{10} the production of CH_4 and C_3H_8 is favored in the region of low initial ethane pressures (see R_{H_2}/R_{CH_4} in Table II). To explain the formation of methyl radicals we propose reactions (6), (7), and (8). These reactions have also been suggested to explain the formation of CH_4 in the Hg photosensitized decomposition of ethane. From reactions (6), (7), and (8), it is clear that the formation of methyl radicals and subsequently the formation of methane and propane will decrease with increasing initial ethane pressure as is observed in our experiments. Following the production of CH_3 radicals via reaction (7), propane may be formed by reaction (9). Reaction (10) is similar to the disproportionation reaction of two ethyl radicals and has been shown to occur by Ausloos and Steacie[11] and by Wijnen.[12] Reaction (10) plays only a negligible role in the formation of CH_4, however, since it has been shown[11] that its methane formation is equal to about 4/100 of the propane formation by reaction (9). To account for the formation of methane we therefore propose reactions (12) and (13). Since reaction (12) has an activation energy of about 11.2 kcal[13] it seems unlikely that especially at the lower temperatures this reaction would be the sole source of methane production. This is even more so when we consider that the production of methyl radicals via reaction (7) is favored in the region of low initial ethane pressures, a region which is not favorable to reaction (12).

Accepting our reaction mechanism thus far suggested

---

[10] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1954), Second edition, Vol. 1, Section V-35.

[11] P. Ausloos and E. W. R. Steacie, Can, J. Chem. **33**, 1062, (1955).

[12] M. H. J. Wijnen, J. Chem. Phys. **22**, 1631 (1954).

[13] M. H. J. Wijnen, J. Chem. Phys. **23**, 1357 (1955).

TABLE III. Values of $R_{CH_4}/R_{C_3H_8}\cdot R_{C_4H_{10}}^{\frac{1}{2}}/(C_2H_6)$.

$10^{-17}(C_2H_6)$ mole/sec	$10^{12}(R_{CH_4}R_{C_4H_{10}}^{\frac{1}{2}}/R_{C_3H_8}(C_2H_6))$	$10^{6}(R_{H_2}/(C_2H_6))$
	25°C	
5.80	1.96	3.62
6.07	2.03	2.70
14.85	1.16	3.05
22.19	0.71	2.48
41.79	0.40	2.03
75.75	0.34	1.87
82.27	0.37	1.43
	58°C	
3.41	3.50	5.67
10.31	1.54	4.05
20.85	1.05	3.68
31.74	0.67	4.36
59.81	0.28	3.26
	99°C	
3.14	6.97	9.27
3.76	4.52	9.41
16.02	1.30	5.81
24.48	1.03	7.52
30.67	0.89	7.12
51.96	0.64	5.64
63.42	0.31	5.58
	240°C	
2.09	10.98	28.75
3.80	5.72	26.16
5.64	3.13	21.87
8.46	2.46	23.80

we obtain

$$\frac{R_{CH_4}R_{C_4H_{10}}^{\frac{1}{2}}}{R_{C_3H_8}(C_2H_6)}=\frac{k_3^{\frac{1}{2}}k_{12}}{k_9}+\frac{k_3^{\frac{1}{2}}k_{13}}{k_9}(H). \qquad (15)$$

According to Eq. (15) we should observe an increase in $R_{CH_4}R_{C_4H_{10}}^{\frac{1}{2}}/R_{C_3H_8}\cdot(C_2H_6)$ with increasing H atom concentration. Since H_2 is produced by reactions (2) and (5) it is difficult to obtain an accurate value for the H atom concentration. As an approximation we may, however, accept that H_2 is mainly produced by (2), in which case $H=1/k_2\cdot R_{H_2}/(C_2H_6)$. In Table III we give the values of $R_{CH_4}R_{C_4H_{10}}^{\frac{1}{2}}/R_{C_3H_8}(C_2H_6)$ and of $R_{H_2}/(C_2H_6)$ obtained at varying initial ethane pressures and at different temperatures. Even taking into account that our analysis for propane and butane was not too accurate, Table III shows without any doubt the general agreement between Eq. (15) and our experimental results and confirms, therefore, reaction (13).

As pointed out earlier, only traces of ethylene could be detected among the reaction products. According to our reaction mechanism ethylene is produced by reactions (4) and (10). Since $[R_{C_2H_4}$ produced by $(4)]/R_{C_4H_{10}}=k_4/k_5=0.13$,[14] and since $[R_{C_2H_4}$ produced by $(10)]/R_{C_3H_8}=k_{10}/k_9=0.04$[11] we obtain as maximum value for the rate of ethylene production $R_{C_2H_4}=0.14\,R_{C_4H_{10}}+0.04R_{C_3H_8}$. Considering the fact that part of the ethylene will undoubtedly disappear by reaction (14), it is not surprising that the amounts of ethylene produced during the reaction were too small to be determined.

It should be pointed out here that some ethylene might also be produced by the reaction $H+C_2H_5\rightarrow C_2H_4+H_2$. This reaction has not been taken up in our reaction mechanism since there is little evidence for its occurrence in general.

In reaction (14) R may be equal to H, CH_3 or C_2H_5. In the case of R being a methyl or ethyl radical it offers an explanation for the fact that traces of higher hydrocarbons were detected among the reaction products.

Summarizing our results, we believe there is little doubt that the primary step of the photolysis of ethane at 1470 A is $C_2H_6+h\nu\rightarrow C_2H_5+H$. Our results furthermore strongly indicate that the reaction mechanism of the photolysis of ethane is very similar if not identical to that of the Hg photosensitized decomposition of ethane.

ACKNOWLEDGMENTS

The author wishes to thank Miss Frances Gauthier and Mr. R. Pilon for the mass spectrometer analyses, and to thank Mr. G. Ensell especially for making the xenon lamp and reaction vessel used in this investigation.

---

[14] P. Ausloos and E. W. R. Steacie, Bull. soc. chim. Belges **63**, 87 (1954).