the resultant small term containing $k_{13} + k_{14}$ gives, for 4050 Å.

$$\frac{1}{\Phi_{C_4H_9NO_2}} = 1 + \frac{k_{12}}{k_{31}} + \frac{2.7k_{10}(NO_2)}{k_{31}(C_4H_{10})} \qquad (33)$$

In this case the variation in quantum yield with isobutane pressure, or with the $(NO_2)/(C_4H_{10})$ ratio, is more straightforward than that predicted at 3130 Å. The dependence on pressure indicated by the yields in Table III suggests that, when $M = i\text{-}C_4H_{10}$, k_{12}/k_{13} is small, and the absolute yields suggest that $k_{10}/k_{31} \approx 10^2$, but the experimental values are so rough that this cannot be stated with certainty. To a first approximation, the yield at 4050 Å. will exceed that at 3130 Å. if $2.7k_{10}/k_{31} < k_3k_6(M)/2k_{27}k_4$, and in the investigated pressure range this would appear to be the case. The postulated mechanisms thus permit both a higher yield and a greater dependence on isobutane pressure at 4050 relative to 3130 Å.

The observations of Sato and Cvetanović[2] on the photoöxidation of 1-butene by nitrogen dioxide, where again the major products were identical but the product yields at 4050 Å. appeared to equal or exceed those at shorter wave lengths, may be explained by postulating that O atoms and NO_2' react with 1-butene to yield the same first product

$$3130\ \text{Å.}: O + C_4H_8 \longrightarrow C_4H_8O \quad k_{34} \qquad (34)$$

$$4050\ \text{Å.}: NO_2' + C_4H_8 \longrightarrow NO + C_4H_8O \quad k_{35} \qquad (35)$$

The resulting quantum yield equations will resemble (30) and (33), with appropriate substitutions and elimination of the factor 2 in (30). Cvetanović's value of k_{34} is 1.1×10^9 l. mole^{-1} sec.$^{-1}$ and the pressures used by Sato and Cvetanović were 3 mm. of NO_2 and 30 mm. of $i\text{-}C_4H_8$. For these values eq. 30 properly revised gives $\Phi_{34} = 0.45$. The yield at 4050 Å. and the same pressures will exceed this value if $(k_{12} + 0.27k_{10})/k_{35} < 1.2$.

Acknowledgment.—The authors are grateful to the Air Pollution Control District, Los Angeles County, and to the National Institutes of Health, U. S. Public Health Service, for funds granted in partial support of this research.

[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL, OTTAWA, CAN.]

The Photo-oxidation of Azoethane[1]

BY H. CERFONTAIN[2] AND K. O. KUTSCHKE

RECEIVED JUNE 13, 1962

The photo-oxidation of azoethane has been studied over the temperature range 28° to 152° at various oxygen and azoethane pressures and over a wide range of intensities. Nitrogen, acetaldehyde and ethanol are major products at all temperatures. The amount of nitrogen formed is greater than in the photolysis of azoethane in the absence of oxygen and increases with decreasing oxygen pressure within given limits, especially at high temperatures, where nitrous oxide and ethylene become important products. A mechanism for the formation of ethylene, nitrous oxide and additional nitrogen is proposed. At temperatures above 100° acetaldehyde is produced, in part, by oxidation of ethoxy radicals. At high conversion several C_1-products are formed. The acetyl radical is an intermediate in the formation of these products from acetaldehyde. It was not possible to determine a rate constant for the reaction of ethyl radicals with oxygen.

Introduction

In the photolysis of azoethane no evidence was found for the existence of $C_2H_5N_2$ radicals.[3] Azoethane was therefore expected to be a convenient source of ethyl radicals for a study of the reaction between these radicals and molecular oxygen.

The oxidation of ethyl radicals has been the subject of several investigations. Jones and Bates[4] have studied the photo-oxidation of ethyl iodide. They followed the course of the reaction manometrically, and concluded that acetaldehyde and ethanol are the main products. Finkelstein and Noyes[5] and, later, Jolley[6] have made an extensive study of the photo-oxidation of diethyl ketone. It seems well established that ethyl, propionyl and pentanonyl radicals are involved in the oxidation. Carbon monoxide, carbon dioxide and acetaldehyde were the major products detected. No analysis was made for ethanol. Tracer experiments showed that carbon monoxide was formed solely from the carbonyl group and that a certain fraction of the carbon dioxide, especially at higher temperature, originated from the α-ethyl carbon atom.

Ethyl hydroperoxide is the major product in the mercury-photosensitized oxidation of ethane under some conditions.[7] The results show that ethyl hydroperoxide is not formed by hydrogen abstraction of the $C_2H_5O_2$ radical from the parent compound. Turner, Callear and Cvetanović, who studied the oxidation of ethyl radicals produced from mercury-photosensitized hydrogenation of ethylene arrived at the same conclusion.[8] The main reaction producing ethyl hydroperoxide was thought to be

$$C_2H_5O_2 + HO_2 \longrightarrow C_2H_5O_2H + O_2$$

Experimental

Azoethane, prepared by Merck, Sharpe and Dohme, Montreal, was redistilled and degassed several times and the middle fraction collected and stored as a liquid in a blackened tube behind a mercury cut-off. The oxygen was

---

(1) Issued as N.R.C. No. 7079.

(2) National Research Council Postdoctoral Fellow 1955–1957; present address: Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, Netherlands.

(3) H. Cerfontain and K. O. Kutschke, *Can. J. Chem.*, **36**, 344 (1958).

(4) L. T. Jones and J. R. Bates, *J. Am. Chem. Soc.*, **56**, 2285 (1934).

(5) A. Finkelstein and W. A. Noyes, Jr., *Disc. Faraday Soc.*, **14**, 82 (1953).

(6) J. E. Jolley, *J. Am. Chem. Soc.*, **79**, 1537 (1957).

(7) J. S. Watson and B. de B. Darwent, *J. Phys. Chem.*, **61**, 577 (1957).

(8) A. H. Turner, A. B. Callear and R. J. Cvetanović, unpublished work.

prepared by heating potassium permanganate and purified by passage through two traps at liquid nitrogen temperature.

A Hanovia S 500 medium pressure mercury arc, run off a stabilized a.c. supply, was used as a light source. The reaction cell was filled with a parallel light beam, produced by two quartz lenses and one stop. The incident light intensity was varied by the use of neutral density filters. A Corning filter No. 5860, 4.0 mm. in thickness, limited the incident radiation to the 3340 and 3660 Å. wave lengths. Jones and Steacie[9] have shown that under similar experimental conditions about 96% of the radiation absorbed by azomethane consists of the 3660 Å. group of lines; a similar limit of absorption was assumed here. Acetaldehyde is transparent at 3660 Å. and has an absorption band between 3480 and 2300 A.[10,11] The maximum extinction coefficients of acetaldehyde and azoethane are of the same order of magnitude.[3,10] It is therefore assumed that there is no photolysis of acetaldehyde under our experimental conditions. Absorption measurements were made with a photocell, coupled to a sensitive galvanometer.

The quartz reaction cell was 10 cm. long and 5 cm. in diameter with a volume of 180 cm.^{3} The total volume of the reaction system was 282 cm.^{3}, including the reaction cell, a magnetically driven stirrer, a U-tube trap and connecting tubing. The reaction system was contained in a thermostated air oven and separated from the storage and analytical line by two Hoke diaphragm valves (No. 413). Direct heat on the cell was avoided by blowing the air from the heating compartment into the reaction cell compartment with a fan. The temperature gradient along the cell did not exceed 0.5° and the temperature was maintained to within 0.5° during an experiment.

By means of a dosing Toepler pump, known quantities of oxygen could be introduced into the reaction cell. Since constant oxygen pressures were desired at pressures less than 1.0 mm., doses of oxygen were added during the run as frequently as necessary. The number of doses required was determined in trial experiments. Only those experiments are reported in which the initial and final oxygen pressures agreed within 10%, except at oxygen pressures lower than 0.1 mm., where the agreement was better than 25%.

The Ward still analysis was carried out as follows. Noncondensables—nitrogen, carbon monoxide and oxygen—were removed at −215° and analyzed by means of a copper-copper oxide furnace at 270°. The C_2-hydrocarbons were removed at −184°; the carbon dioxide-nitrous oxide-formaldehyde fraction was removed at −154°, and the acetaldehyde–butane fraction was removed at −125°. These three fractions were analyzed mass spectrometrically. The remaining products, together with the bulk of unreacted azoethane, will be referred to as "liquid products." Mass spectrometric analysis of the "liquid products" from high conversion experiments showed the presence of ethanol, methanol and water. The amounts of ethanol and methanol were estimated by gas phase infrared analysis. The accuracy of this method is 0.02 cm.^{3} N.T.P. for ethanol and 0.05 cm.^{3} N.T.P. for methanol. A reasonable accuracy was therefore obtained only for high conversion experiments. An absorption band at 1750 cm.$^{-1}$ was attributed to acetic acid, since this peak could be removed by condensing the "liquid products" on solid potassium hydroxide.

Peroxides were determined by the ferrous thiocyanate method.[12] Azoethane interferes since monoethyl hydrazine, formed in an acid-catalyzed hydrolysis, reduces ferric thiocyanate. The azoethane was therefore removed from the "liquid products" by passing a stream of oxygen-free nitrogen through its aqueous solution.

The photolysis of azoethane in the absence of oxygen was used as an actinometer.

Results

The quantum yield of nitrogen formation in the photolysis of azoethane in the absence of oxygen depends on temperature and azoethane pressure.[3] It is therefore convenient to express the amount of nitrogen formed in the photooxidation as a ratio to the amount of nitrogen formed in the photolysis without oxygen under otherwise identical conditions. This ratio will be referred to as the quantum ratio of nitrogen formation, $^{r}\Phi_{N_2}$. The amounts of other products formed in the photo-oxidation are expressed relative to the amount of nitrogen produced in the same experiment. These ratios will be referred to as product ratios X/N_2.

The thermal reaction between oxygen and azoethane could not be neglected at 152°. At that temperature the chains are still very short so that the thermal and photo-chemical reactions may be assumed to be additive. Uncorrected values are shown in parentheses in the tables.

All pressures listed are reduced to 0°. The precision of the quantum and product ratios is not expected to be better than ±8%.

Table I shows the quantum ratio of nitrogen and the product ratios of the other products as functions of the exposure at 28° and 152°. Most noteworthy is the fact that with increasing exposure the product ratios of acetaldehyde and nitrous oxide decrease, while the product ratios of carbon dioxide, carbon monoxide and methanol increase. At 152° the quantum ratio of nitrogen decreases with increasing exposure; this effect exceeds that due to the consumption of azoethane. Nitrous oxide is not formed at room temperature, but becomes a major product at 152°, especially at low conversions. The C_2-hydrocarbon fraction is largely ethylene, even at very low oxygen pressure. Traces of acetylene were detected. Small amounts of formaldehyde were detected in all high conversion experiments.

The results of experiments with various oxygen pressures are listed in Table II. The quantum ratio of nitrogen formation increases with decreasing oxygen pressure and increasing temperature. With constant exposure the product ratio of nitrous oxide passes through a maximum as the oxygen pressure increases.

Variation in light intensity has little effect on the quantum and product ratios (Table III), although the product ratios of carbon dioxide and carbon monoxide show a slight increase with decrease in light intensity; at low light intensities the conversion was slightly greater and this trend in the ratios may be explicable on this basis.

The quantum ratio of nitrogen formation and the product ratios of nitrous oxide and acetaldehyde increase with increasing azoethane pressure (Table IV); the product ratios of carbon dioxide and carbon monoxide, on the other hand, show a decrease with increasing azoethane pressure.

Peroxides were sought in experiments at 28° only; experimental conditions were: azoethane 14.1 mm., oxygen 2.0 mm. and $I_a \sim 1.3 \times 10^{13}$ quanta cm.$^{-3}$ sec.$^{-1}$. For exposures of 30, 77, 150 and 230 minutes the product ratios for peroxides were 0.0071, 0.0059, 0.0057 and 0.0046, respectively. The peroxide was not positively identified in view of the small yields, although

---

(9) M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, 21, 1018 (1953).

(10) J. H. C. Smith, *Carnegie Inst. Reports*, 27, 178 (1928).

(11) P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.*, 55, 1767 (1933).

(12) Sir A. C. Egerton, A. J. Everett, G. J. Minkoff, S. Rudrakanchana and K. C. Salooja, *Anal. Chim. Acta*, 10, 422 (1954).

TABLE I: PHOTO-OXIDATION OF AZOETHANE; DEPENDENCE ON EXPOSURE

Oxygen press., mm.	Exposure, sec.	N_2, cm.^{3} N.T.P.	$^r\Phi_{N_2}$	$\frac{-O_2}{N_2}$	$\frac{CH_3CHO}{N_2}$	$\frac{CO_2}{N_2}$	$\frac{CO}{N_2}$	$\frac{CH_3CO_2H}{N_2}$	$\frac{C_2H_5OH}{N_2}$	$\frac{CH_3OH}{N_2}$	$\frac{N_2O}{N_2}$	$\frac{C_2H_4}{N_2}$	$\frac{C_2H_6}{N_2}$	Carbon balance	Hydrogen balance	Oxygen balance
$T = 28°$, azoethane pressure = 18.3 mm., $I_a = 0.64 \times 10^{13}$ quanta cm.$^{-3}$ sec.$^{-1}$																
1.1	900	0.054	1.41	1.73	0.88	0.16	0.009	...	..	..	...	0.026	...	1.90	4.6	0.60
1.1	1800	.109	1.43	1.62	.77	.22	.013	...	..	..	0.009	.021	...	1.88	4.3	.66
1.1	4300	.248	1.41	1.74	.61	.35	.015	...	..	..	...	.020	...	1.77	4.2	.63
1.1	7200	.398	1.41	1.82	.46	.46	.021	...	+[a]	+[a]	.020	.018	0.0002	1.70	4.1	.66
1.1	10800	.556	1.37	1.87	.32	.53	.026	0.03	0.88	0.19	.012	.018	.0011	1.58	3.7	.65
$T = 28°$, azoethane pressure = 13.7 mm., $I_a = 1.3 \times 10^{13}$ quanta cm.$^{-3}$ sec.$^{-1}$																
1.1	200	0.0247	1.50	..	0.92	0.11	0.008	...	..	..	...	0.031	...	2.0	4.7	..
1.1	900	.107	1.38	1.65	.79	.24	.009	...	..	..	...	.026	...	1.88	4.5	0.73
1.1	3600	.378	1.39	1.84	.45	.48	.028	...	0.90	0.21	...	.019	...	1.70	3.9	.68
3.8	14000	1.08	1.19	1.81	.28	.57	.017	0.043	0.75	0.34	...	.016	...	1.55	3.6	.72
$T = 152°$, azoethane pressure = 10.0 mm., $I_a = 1.1 \times 10^{13}$ quanta cm.$^{-3}$ sec.$^{-1}$																
1.2	150	0.0235	2.10(2.36)[b]	..	1.38	..	0.093	...	..	..	...	0.149	...	1.52	3.4	..
1.2	300	.044	1.99(2.20)	3.0	1.18	0.13	.114	...	..	..	0.59	.124	...	1.53	3.4	0.51
1.1	500	.067	1.84(2.05)	2.9	1.08	.18	.142	...	..	..	.59	.126	0.004	1.48	3.3	.54
1.2	700	.081	1.64(1.76)	2.8	0.87	.23	.151	...	..	..	.44	.117	...	1.39	3.3	.52
1.1	800	.090	1.57(1.72)	2.9	1.08	.30	.169	...	..	..	.38	.119	...	1.72	3.4	.54
1.0	1100	.116	1.63(1.69)	2.8	..	..	.196	...	0.80	..	..	...	...	..	..	..
1.1	1300	.140	1.51(1.66)	2.8	0.76	0.30	.214	...	.88	0.15	0.40	0.111	.005	1.48	3.3	0.51
1.2	2200	.227	1.51(1.60)	2.7	.71	.38	.235	...	.97	.26	.33	.099	.009	1.67	3.8	.59
1.3	3300	.318	1.47(1.53)	2.6	.59	.44	.268	...	.84	.53	.26	.094	.002	1.69	3.9	.65
1.1	4400	.444	1.55(1.64)	2.4	.45	.44	.198	0.12	.95	.64	.22	.083	...	1.84	4.4	.75
2.7	11500	.944	1.37(1.41)	2.3	.28	.47	.178	0.11	.68	.62	.15	.063	...	1.55	3.7	.67

[a] Positively identified mass spectrometrically. [b] Values in parentheses are not corrected for the dark reaction.

TABLE III

PHOTO-OXIDATION OF AZOETHANE; DEPENDENCE ON LIGHT INTENSITY

I_a, quanta cm.$^{-3}$ sec.$^{-1}$ $\times 10^{-13}$	Exposure, sec.	N_2, cm.^{3} N.T.P.	$^r\Phi_{N_2}$	$\frac{-O_2}{N_2}$	$\frac{CH_3CHO}{N_2}$	$\frac{CO_2}{N_2}$	$\frac{CO}{N_2}$	$\frac{N_2O}{N_2}$	$\frac{C_2H_4}{N_2}$
$T = 28°$, azoethane pressure = 13.9 mm., oxygen pressure = 1.2 mm.									
1.35	900	0.107	1.48	1.65	0.79	0.24	0.0093	..	0.026
0.137	9000	.100	1.41	1.69	.71	.29	.010	..	.020
0.0159	57600	.086	1.61	1.65	.77	.28	.014	..	.021
$T = 118°$, azoethane pressure = 10.7 mm., oxygen pressure = 1.1 mm.									
1.16	600	0.050	1.37	2.6	0.92	0.23	0.076	0.30	0.084
0.85	1000	.061	1.35	2.6	.84	.26	.112	.32	.067
.243	3500	.061	1.33	2.6	.84	.27	.112	.33	.082
.054	14400	.076	1.45	2.8	.85	.34	.144	.37	.081
.054	14400	.076	1.45	2.8	.98	.32	.144	.33	.079

TABLE II

PHOTO-OXIDATION OF AZOETHANE; DEPENDENCE ON OXYGEN PRESSURE[a]

Oxygen press., mm.	Exposure, sec.	N_2, cm.³ N.T.P.	$^{r}\Phi_{N_2}$	$\frac{O_2}{N_2}$	$\frac{CH_3CHO}{N_2}$	$\frac{CO_2}{N_2}$	$\frac{CO}{N_2}$	$\frac{N_2O}{N_2}$	$\frac{C_2H_4}{N_2}$	$\frac{C_2H_6}{N_2}$	$\frac{C_4H_{10}}{N_2}$
T = 28°, azoethane pressure = 13.9 mm., I_a = 1.3 × 10^{13} quanta cm.$^{-3}$ sec.$^{-1}$											
7.7	900	0.090	1.24	..	1.02	0.08	0.002	0.0077	0.025	...	0.005
5.8	900	.092	1.27	..	0.98	.10	.002	.0065	.024	...	.012
1.28	900	.107	1.40	1.65	.82	.25	.009	.0073	.026	...	.012
0.79	900	.109	1.50	1.60	.79	.28	.011	...	.026	...	.006
.45	900	.109	1.51	1.61	.74	.29	.014	...	.027	...	.008
.19	900	.110	1.52	1.63	.69	.31	.017	...	.029	...	.003
.082	900	.110	1.51	1.69	.62	.37	.019	...	.031	...	.017
.091	200	.0253	1.53	1.62	.90	.18	.011	...	.025	...	.035
.058	200	.0253	1.53	1.58	.82	.16	.010	...	.025	...	.025
.029	200	.0251	1.52	1.60	.82	.16	.011	...	.025	...	.038
T = 118°, azoethane pressure = 10.7 mm., I_a = 1.1 × 10^{13} quanta cm.$^{-3}$ sec.$^{-1}$											
8.6	800	0.074	1.41	..	1.35	0.28	0.059	0.141	0.055	...	...
4.5	800	.075	1.43	..	1.03	.28	.061	.161	.063	...	...
3.2	800	.075	1.44	2.8	1.07	.31	.068	.189	.065	...	...
1.4	800	.074	1.43	2.6	0.93	.34	.089	.244	.065	...	...
0.78	800	.075	1.44	2.6	.83	.35	.098	.240	.059	...	...
.51	800	.080	1.54	2.5	.81	.31	.100	.277	.059	...	...
.27	800	.087	1.70	2.4	.72	.32	.107	.235	.054	0.003	...
.22	200	.0246	1.85	2.6	1.17	.072	.036	.392	.066	.007	...
.092	200	.0322	2.42	2.5	1.22	.044	.050	.447	.065	.004	...
.059	200	.0317	2.40	2.4	1.12	.063	.043	.366	.060	.008	...
.031	200	.0344	2.63	2.2	1.11	.051	.040	.334	.061	...	...
T = 152°, azoethane pressure = 10.0 mm., I_a = 1.1 × 10^{13} quanta cm.$^{-3}$ sec.$^{-1}$											
9.1	700	0.071	1.36(1.46)[a]	..	1.16	0.23	0.072	0.17	0.076	...	0.05
5.7	700	.080	1.54(1.65)	..	1.11	.23	.104	.23	.084	...	.01
3.1	700	.087	1.65(1.80)	2.9	0.98	.26	.128	.28	.091	...	.03
1.21	700	.081	1.65(1.74)	2.8	.87	.24	.151	.44	.117	...	...
1.02	700	.110	2.04(2.26)	3.0	.90	.34	.158	.32	.109	0.005	...
0.79	700	.109	2.06(2.25)	2.9	.84	.30	.162	.34	.106	.005	0.02
.54	700	.106	2.06(2.18)	2.9	.95	.30	.169	.33	.115	.003	.02
.31	150	.037	2.77(3.46)	3.4	1.28	.16	.095	.56	.146	...	.01
.25	150	.037	2.81(3.48)	3.1	1.25	.13	.089	.51	.146	...	...
.13	150	.030	2.39(2.84)	2.5	1.16	...	.086	...	.151	.012	.04
.057	150	.032	2.65(2.93)	2.3	0.94	...	.079	...	.138	.004	.07
.057	150	.035	2.86(3.27)	2.5	1.11	.082	.078	.33 (.40)	.148	.011	.03
.024	150	.030	2.54(2.75)	2.0	0.97	.071	.075	.20 (.25)	.130	.007	.04

[a] Values in parentheses are not corrected for the dark reaction.

polarographic identification was attempted. No fouling of the mercury surfaces, often noted when peroxides are handled in systems containing mercury, was observed, even after operation for two years. It is felt therefore that the yields quoted are maximum values.

The material balance was calculated for the experiments, listed in Table I, from the equations

carbon balance =

$$\frac{CH_3CHO + C_2H_5OH + C_2H_4 + {}^1/_2CO_2 + {}^1/_2CO + {}^1/_2CH_3OH + CH_3CO_2H}{N_2 + N_2O}$$

hydrogen balance =

$$\frac{2CH_3CHO + 3C_2H_5OH + 2CH_3OH + 2C_2H_4 + 2CH_3COH}{N_2 + N_2O}$$

oxygen balance =

$$\frac{{}^1/_2CH_3CHO + {}^1/_2C_2H_5OH + CO_2 + {}^1/_2CO + {}^1/_2N_2O + {}^1/_2CO{}^1/_2CH_3OH + CH_3CO_2H}{-O_2}$$

The assumption was made that the product ratio of ethanol is 1.0, as seems to be warranted by extrapolation from the estimated product ratio of ethanol for high conversion experiments. The carbon, hydrogen and oxygen balances should be equal to 2, 5 and 1, respectively. The values observed are somewhat less than these numbers (Table I); this might be explained by the formation of water and formaldehyde, which products were detected positively by mass spectrometric analysis, although no estimates of their quantities

TABLE IV

PHOTO-OXIDATION OF AZOETHANE; DEPENDENCE ON AZOETHANE PRESSURE

Azoethane,[a] press., mm.	I_a, quanta cm.$^{-3}$ sec.$^{-1}$ $\times 10^{-13}$	Exposure, sec.	N_2, cm.^{3} N.T.P.	$^r\Phi N_2$	$-\frac{O_2}{N_2}$	$\frac{CH_3CHO}{N_2}$	$\frac{CO_2}{N_2}$	$\frac{CO}{N_2}$	$\frac{N_2O}{N_2}$	$\frac{C_2H_4}{N_2}$
				$T = 28°$, oxygen pressure = 1.2 mm.						
80.2	5.04	200	0.090	1.90	1.57	0.93	0.091	0.003	..	0.024
38.8	3.20	200	.062	1.85	1.56	.92	.089	.003	..	.025
13.8	1.33	900	.107	1.38	1.65	.79	.24	.009	..	.026
13.8	1.33	200	.025	1.50	..	.92	.11	.008	..	.030
4.5	0.39	2700	.109	1.32	1.8	.77	.31	.015	..	.024
2.1	.19	2700	.050	1.28	1.8	.88	.23	.016	..	.039
1.5	.13	2700	.040	1.33	1.7	.88	.19	.012	..	.040
				$T = 152°$, oxygen pressure = 1.1 mm.						
30.6	2.68	250	0.132	2.64(3.1)[b]	2.9	1.10	0.17	0.107	0.50	0.116
18.4	1.70	300	.097	2.34(2.8)	3.3	1.05	.25	.107	.49	.126
10.0	1.09	700	.110	2.03(2.2)	3.2	0.92	.32	.167	.34	.109
2.9	0.25	2400	.070	1.33(1.4)	2.7	0.80	.35	.224	.24	.125

[a] The azoethane pressures are accurate to ±0.15 mm., and introduce a large error in $^r\Phi_{N_2}$ at low azoethane pressures.
[b] Values in parentheses are not corrected for the dark reaction.

were made. Addition reactions of oxygenated radicals to azoethane might serve as another explanation of the low material balance. However, mass spectrometric analysis of high conversion experiments (~15%) showed no indication of the products of such reactions.

Discussion

The mechanism of the photo-oxidation of azoethane must be complex, since so many reaction products are formed. A detailed mechanism fully substantiated in all respects, could not be obtained. However, certain restrictions can be placed on the modes of formation of some of the products. Reactions, consistent with these restrictions and other data available, are suggested here. To facilitate the discussion it seems advisable to list at one point all the steps which will be considered.

$$A + h\nu \longrightarrow A^* \qquad (1)$$
$$A^* \longrightarrow N_2 + 2C_2H_5 \qquad (2)$$
$$A^* + A \longrightarrow 2A \qquad (3)$$
$$C_2H_5 + O_2(+M) \longrightarrow C_2H_5O_2(+M) \qquad (4)$$
$$C_2H_5O_2 \longrightarrow C_2H_5O + {}^1/_2O_2 \qquad (5)$$
$$\longrightarrow CH_3CHO + OH \qquad (6)$$
$$C_2H_5O + C_2H_5N_2C_2H_5 \longrightarrow C_2H_5OH + C_2H_5N_2C_2H_4 \qquad (7)$$
$$OH + C_2H_5N_2C_2H_5 \longrightarrow H_2O + C_2H_5N_2C_2H_4 \qquad (8)$$
$$C_2H_5N_2C_2H_4 \longrightarrow C_2H_5 + N_2 + C_2H_4 \qquad (9)$$
$$C_2H_5N_2C_2H_4 + O_2 \longrightarrow C_2H_5 + N_2O + CH_3CHO \qquad (10)$$
$$\longrightarrow C_2H_5O + N_2 + CH_3CHO \qquad (11)$$
$$\longrightarrow C_2H_5O_2 + N_2 + C_2H_4 \qquad (12)$$
$$C_2H_5O + C_2H_5O \longrightarrow C_2H_5OH + CH_3CHO \qquad (13)$$
$$C_2H_5O + O_2 \longrightarrow CH_3CHO + HO_2 \qquad (14)$$
$$C_2H_5N_2C_2H_4 + C_2H_5O_2 \longrightarrow C_2H_5N_2C_2H_4O + C_2H_5O \qquad (15)$$
$$C_2H_5N_2C_2H_4O \longrightarrow C_2H_5 + N_2 + CH_3CHO \qquad (16)$$
$$C_2H_5O + CH_3CHO \longrightarrow C_2H_5OH + CH_3CO \qquad (17)$$
$$OH + CH_3CHO \longrightarrow H_2O + CH_3CO \qquad (18)$$
$$CH_3O + CH_3CHO \longrightarrow CH_3OH + CH_3CO \qquad (19)$$
$$CH_3CO \longrightarrow CH_3 + CO \qquad (20)$$
$$CH_3 + O_2 \longrightarrow CH_3O + {}^1/_2O_2 \qquad (21)$$
$$CH_3CO + O_2 \longrightarrow CH_3O + CO_2 \qquad (22)$$
$$CH_3O + C_2H_5N_2C_2H_5 \longrightarrow CH_3OH + C_2H_5N_2C_2H_4 \qquad (23)$$
$$CH_3O + C_2H_5O \longrightarrow C_2H_5OH + CH_2O \qquad (24)$$
$$\longrightarrow CH_3OH + CH_3CHO \qquad (25)$$
$$CH_3O + CH_3O \longrightarrow CH_3OH + CH_2O \qquad (26)$$
$$R + CH_2O \longrightarrow RH + CHO \qquad (27)$$
$$CHO + O_2 \longrightarrow CO + HO_2 \qquad (28)$$
$$\longrightarrow CO_2 + OH \qquad (29)$$

A represents azoethane and R is some radical in the system. The radical HO_2 is assumed to be essentially inert in the system and its formation represents termination. The over-all process described by reaction 5 is discussed below.

The oxidation is characterized by a marked effect of exposure, *i.e.*, time of illumination if I_a is constant, on the product ratios (Table I). The trends are reminiscent of those found in the photo-oxidation of azomethane[13,14] and will be explained in similar terms.

At moderate oxygen pressures the early stages of the reaction can be represented by reactions 1 to 13 except for the effect of intensity (Table III) which suggests that the termination is first order in radicals rather than second order as required by reaction 13. Thus the ethyl radicals formed in the primary act, after oxidation in 4, 5 and 6, initiate a short chain *via* 7 and 8. This chain is continued by oxidation and degradation of the large azoalkyl radical, reactions 9 to 12, which also regenerate ethyl or ethoxy chain centers. The major products during this stage are ethanol and acetaldehyde along with nitrous oxide, nitrogen, ethylene and some water; the oxides of carbon are absent.

At later stages the reaction is inhibited, probably by the acetaldehyde formed, leading to the formation of C_1-products; this inhibition is described by reactions 17 to 26. It is probable that the formaldehyde formed also acts as an inhibitor as suggested by reactions 27 to 29.

---

(13) (a) R. L. Strong and K. O. Kutschke, *Can. J. Chem.*, **37**, 1456 (1959); (b) F. Wenger and K. O. Kutschke, *ibid.*, **37**, 1546 (1959).
(14) M. Shahin and K. O. Kutschke, *ibid.*, **37**, 73 (1961)

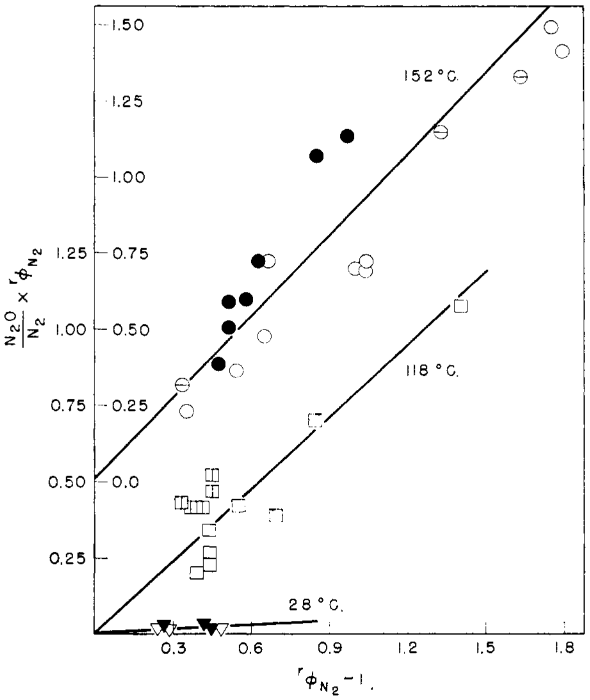

Fig. 1.—Relation between nitrous oxide and secondary nitrogen: variation of oxygen pressure, ○, □, ▽; variation of exposure, ●, ■, ▼; variation of azoethane pressure, ⊖, ⩡; variation of light intensity, ◫, ⧩; triangles, 28°; squares, 118°; circles, 152°; note scale change for data at 152°.

Reasons for the introduction of 14, 15 and 16 are considered in the detailed sections below.

Formation of Nitrous, Nitrous Oxide and Ethylene.—The quantum ratio of nitrogen formation ($^r\Phi_{N_2}$) is greater than unity under all experimental conditions and varies with temperature, oxygen and azoethane pressures. This suggests that nitrogen is not formed by reaction 2 only. The amount of nitrogen not formed in the primary process will be referred to as secondary nitrogen, $(N_2)_s$, while that from the primary process will be designated as $(N_2)_p$. It is unlikely that this secondary nitrogen is formed by a reaction of excited azoethane molecules and oxygen as can be seen from the following two considerations. The variation of $^r\Phi_{N_2}$ with oxygen pressure is in the opposite sense to that required if excited azoethane were induced to decompose by collision with oxygen. Secondly, at 152° $^r\Phi_{N_2}$ reaches values as high as 2 for high azoethane pressures (Table IV) and for short exposures (Table I), where the quantum yield of nitrogen formation in the absence of oxygen is near unity.[3] Under these conditions two molecules of nitrogen are formed per quantum absorbed and, consequently, at least two molecules of nitrogen per excited azoethane molecule. Thus if any nitrogen-producing reaction between excited azoethane and oxygen occurs, it is completely obscured by other reactions producing nitrogen. Appreciable deactivation of excited azoethane molecules by oxygen is unlikely, since $^r\Phi_{N_2}$ is greater than unity at high oxygen pressures at room temperature,[15] where no evidence exists for a chain reaction.

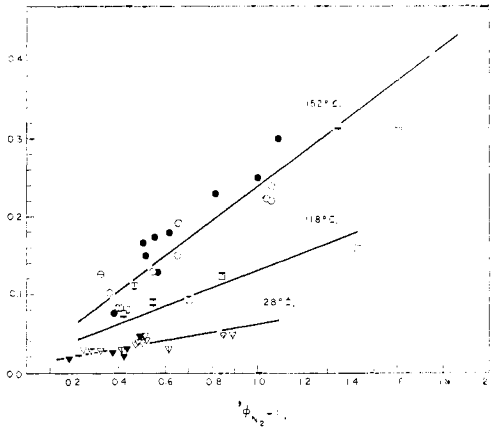

Fig. 2.—Relation between ethylene and secondary nitrogen; for explanation of symbols see Fig. 1.

Thus it will be assumed that the primary process in the photolysis of azoethane is unaffected by oxygen and that the observed values of $^r\Phi_{N_2}$ greater than unity are caused by the formation of nitrogen from secondary processes.

From the results in Tables I, II, III and IV it is seen that at oxygen pressures greater than 0.1 mm. the amount of secondary nitrogen shows a trend which is parallel to that of nitrous oxide. A similar relation is observed between ethylene and secondary nitrogen. The estimated quantum and product ratios are not expected to be more accurate than 8%, which means an uncertainty up to 30% in the amount of secondary nitrogen for low quantum ratios. Taking this into account it is approximately correct to state that the amount of secondary nitrogen is proportional to the amount of nitrous oxide for a given temperature, at oxygen pressures between 0.1 and 9 mm. and varying azoethane pressures, exposures and light intensities (Fig. 1). This strongly suggests that nitrous oxide and secondary nitrogen are formed in similar types of reaction. It is likely that nitrous oxide is formed in a manner similar to that suggested for its formation in the photo-oxidation of azomethane[16]; hence reaction 10 is chosen here. The approximate linearity between the rate of nitrous oxide formation and the azoethane pressure supports this choice (Table IV). The relation described above between the yields of secondary nitrogen and nitrous oxide then requires that reactions like 11 and 12 be used for the formation of secondary nitrogen.

Reactions 15 and 16 are included to account for the decrease of the $N_2O/(N_2)_s$ ratio at very low oxygen pressures. The amount of nitrous oxide will decrease relative to the amount of secondary nitrogen at these low oxygen pressures, as observed, if reactions 4 and 15 are fast in comparison with 10.

The amount of ethylene produced is found to be proportional to the amount of secondary nitrogen as well. This is illustrated in Fig. 2; the small intercepts may be explained by reaction 9. The constancy of the $C_2H_4/(N_2)_s$ at a given temperature implies that ethylene is produced mainly from the same reactants as those producing secondary

---

[15] At 28°, 16 mm. oxygen, 18 mm. azoethane and I_a = 0.9 × 10^{13} quanta cm.$^{-3}$ sec.$^{-1}$, $^r\Phi_{N_2}$ was found to be 1.18.

[16] G. R. Hoey and K. O. Kutschke, *Can. J. Chem.*, 33, 496 (1955).

nitrogen; reaction 12 is proposed. It is difficult to see how ethylene could be formed from a reaction between $C_2H_5N_2C_2H_4$ and $C_2H_5O_2$ and, hence, most of the secondary nitrogen cannot be formed through 15 and 16. The formation of ethylene by a reaction of ethyl radicals with oxygen is unlikely at these temperatures.[5,7,16a]

If nitrous oxide, secondary nitrogen and ethylene are produced only by reactions 10, 11 and 12, the following relations may be deduced

$$k_{12}/k_{11} = C_2H_4/((N_2)_s - C_2H_4)$$
$$k_{10}/k_{11} = N_2O/((N_2)_s - C_2H_4)$$

The ratios of the rate constants have been calculated from the slopes of the plots in Figs. 1 and 2. They are, for k_{10}/k_{11}, 0.91 ± 0.16 (118°) and 1.23 ± 0.20 (152°); for k_{12}/k_{11} 0.05 ± 0.02 (28°), 0.12 ± 0.04 (118°) and 0.29 ± 0.05 (152°). The values of k_{12}/k_{11} lead to an activation energy difference of $E_{12} - E_{11} = 3.6 \pm 1.5$ kcal./mole.

The dependence of the formation of secondary nitrogen and of nitrous oxide on the oxygen pressure suggests that the formation of secondary nitrogen is inhibited by oxygen. Since oxygen is essential to chain propagation, the inhibition must be indirect, in such a way that the formation of $C_2H_5N_2C_2H_4$ will be impeded with increasing oxygen pressures. A reaction between ethoxy radicals and oxygen (reaction 14) would have this effect, provided that hydrogen abstraction by $C_2H_5O_2$ radicals is slow; it has been suggested for a similar reason in the photo-oxidation of diethyl ketone.[6] The effect of exposure has been mentioned and will be discussed in more detail below.

Reaction of Ethyl Radicals with Oxygen.—It is generally considered that reaction 4 represents the first step in the reaction of ethyl radicals with oxygen. It is not possible to use the present data to obtain reliable values for the over-all rate constant of reaction 4 nor to determine whether a third body is required as it is in the comparable reactions of methyl radicals.[17-19] This situation arises because of the very small amounts of ethane and butane found even at the lowest oxygen pressure used. Hence the usual technique of competing reactions could not be employed with any confidence.

The observation of even small amounts of butane ($^r\Phi_{C_4H_{10}} < \sim 0.05$) in this system is rather surprising. It might be explained as an experimental artifact since the fraction analyzed for butane unavoidably contained some azoethane whose slow pyrolysis prior to analysis might have produced the butane observed. On the other hand, it is not impossible that a small fraction of the primary process leads to molecular butane and nitrogen directly, without the intervention of ethyl radicals. The latter interpretation is supported by recent work on the photolysis of azomethane in the presence of oxygen where an analogous molecular decomposition has been observed.[20]

Whatever its precise value, the absence of the usual products of the reactions of ethyl radicals indicates that reaction 4 is fast. The ethylene found cannot arise from disproportionation of ethyl radicals and its mode of formation has been discussed above. The major oxidation products observed in the early stages are acetaldehyde and ethanol which suggests that, in common with many other oxidation systems, a mechanism is required for the conversion of alkyl peroxy to alkoxy radicals. Reaction 5 gives the over-all reaction; some regeneration of oxygen is required to account for the low relative yields of oxygen consumption at room temperature. Several mechanisms have been offered to describe this general type of reaction[16,21]; since the present data cannot be used to distinguish between the various suggestions, these will not be discussed here. It will be assumed that the conversion represented by 5, although of unknown order, is fast and efficient for all conditions used here. In particular, it will be assumed that ethyl hydroperoxide is not formed in significant amounts. In view of the sensitivity of the hydroperoxide to surface decomposition, the fact that only very small yields of peroxidic substances were detected here is not a conclusive reason to omit consideration of its formation. However, that evidence is supported by recent work on the photo-oxidation of azomethane in which methyl hydroperoxide has been identified[22]; it has been shown that the product probably is not of great importance in the mechanism.[23]

Formation of Acetaldehyde and Ethanol.—In the early stages of the reaction acetaldehyde and ethanol are produced in the chain steps 7, 10, 11 and 12 and in the termination step 13. Because of the formation of OH in 6, it is predicted that the yield of acetaldehyde would exceed that of ethanol; the data are insufficiently precise, especially for ethanol, to permit a test of this prediction. At higher conversions where ethanol could be determined with some accuracy by the methods used, the oxidation was inhibited by the aldehyde and the yield of ethanol exceeded that of acetaldehyde.

The amount of acetaldehyde formed in reactions 6, 13, 14 and 25, *i.e.*, not arising from the $C_2H_5N_2$-C_2H_4, can be estimated on the basis of the following assumptions, all of which are reasonable in the range of conditions used. (a) The acetaldehyde formed in 10 is equal to the total nitrous oxide found. (b) The acetaldehyde formed in 11 can be taken as the difference between secondary nitrogen and ethylene. (c) Each acetaldehyde attacked by radicals leads to a molecule of CO_2, *i.e.*, the oxygen pressure is high enough so that the acetyl radical reacts only *via* 22 and not 20. (d) The oxygen pressure is sufficiently large that 9 is negligible. (e) The conversions are low enough that the amount of carbon dioxide arising from attack on formaldehyde is negligible. On this basis

$$(CH_3CHO)_{6,13,14,25}/(N_2)_p \equiv Y_{CH_3CHO}$$
$$= [((CH_3CHO + CO_2 + C_2H_4 - N_2O)/N_2) - 1]\ ^r\Phi_{N_2} + 1$$

(16a) J. A. Gray, *J. Chem. Soc.*, 3150 (1952).

(17) D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, **53**, 1102 (1957).

(18) M. I. Christie, *Proc. Roy. Soc. (London)*, **A224**, 411 (1958).

(19) W. C. Sleppy and J. G. Calvert, *J. Am. Chem. Soc.*, 81, 769 (1959).

(20) P. Ausloos, private communication.

(21) P. L. Hanst and J. G. Calvert, *J. Am. Chem. Soc.*, **63**, 71 (1959).

(22) M. Shahin and K. O. Kutschke, *J. Phys. Chem.*, **65**, 2277 (1961).

(23) N. R. Subbaratnam and J. G. Calvert, *J. Am. Chem. Soc.*, **84**, 1113 (1962).

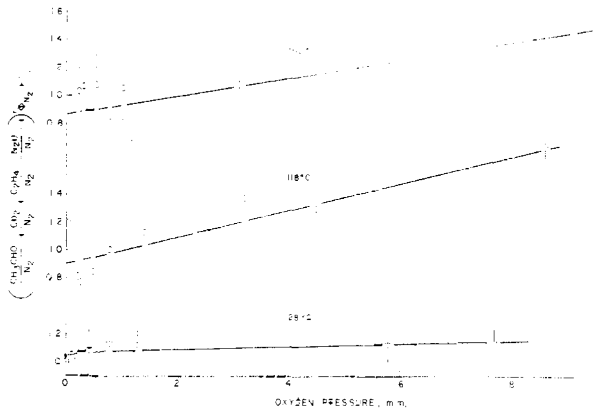

Fig. 3.—Dependence of Y_{CH_3CHO} on oxygen pressure: ∇, 28°, pressure of azoethane 13.9 mm., $I_a = 1.3 \times 10^{13}$ quanta cm.$^{-3}$ sec.$^{-1}$; □, 118°, pressure of azoethane 10.7 mm., $I_a = 1.1 \times 10^{13}$ quanta cm.$^{-3}$ sec.$^{-1}$; O, 152°, pressure of azoethane 10.0 mm., $I_a = 1.1 \times 10^{13}$ quanta cm.$^{-3}$ sec.$^{-1}$.

The function Y_{CH_3CHO} is listed in Table V and plotted against the pressure of oxygen in Fig. 3 where it is shown to be almost independent of $[O_2]$ at 28°, but approximately linear in $[O_2]$ at the higher temperatures. This observation is taken as support for 14 as a mode of formation of acetaldehyde. Additional evidence in its support was presented in connection with the discussion of the inhibition of the nitrogen, etc., yields by oxygen. The quantity $(CH_3CHO)_{14}/(N_2)_p$ can thus be obtained from each experiment by subtracting the pertinent intercept of Fig. 3 from Y_{CH_3CHO}. In fact, values of Y_{CH_3CHO} obtained at low oxygen pressure are almost indistinguishable from the intercept, so that only those values of $(CH_3CHO)_{14}/(N_2)_p$ calculated from data taken at higher pressures of oxygen are listed in Table V.

The decrease of Y_{CH_3CHO} at increased pressures of azoethane at 152° presumably reflects the increased fraction of ethoxy radicals which undergo the abstraction reaction 7 to form ethanol. If the contribution of 8 and 23 to the formation of $C_2H_5N_2C_2H_4$ can be neglected, and if the latter radical disappears only in 10, 11 and 12, then the yield of ethanol from 7 is given as

$$(C_2H_5OH)_7/(N_2)_p = [(N_2O + N_2)/N_2]\,{}^r\Phi_{N_2} - 1$$

Probably reaction 23 can be neglected at the lower conversions, but no estimate can be made of the contribution of 8. Hence the $(C_2H_5OH)_7/(N_2)_p$ reported in Table V are maximum values.

Data are thus available to calculate approximate values of

$$k_7/k_{14} = [(C_2H_5OH)_7/(CH_3CHO)_{14}][O_2]/[A]$$

The average values given in Table V suggest that k_7/k_{14} is near unity and that $E_7 - E_{14}$ is small. A result of this kind was, of course, necessary in order to explain the rather large inhibiting effect of $[O_2]$, especially at 152° where the chain, as measured by ${}^r\Phi_{N_2}$, is relatively well developed

The Acetyl Radical.—A number of C_1-products are found in the photo-oxidation, especially at the higher conversions. Their formation is assumed to proceed *via* the acetyl radical. The results in Table I show that the acetaldehyde concentration approaches a steady value at high conversion and that carbon dioxide, carbon monoxide, methanol and acetic acid formed in secondary processes.

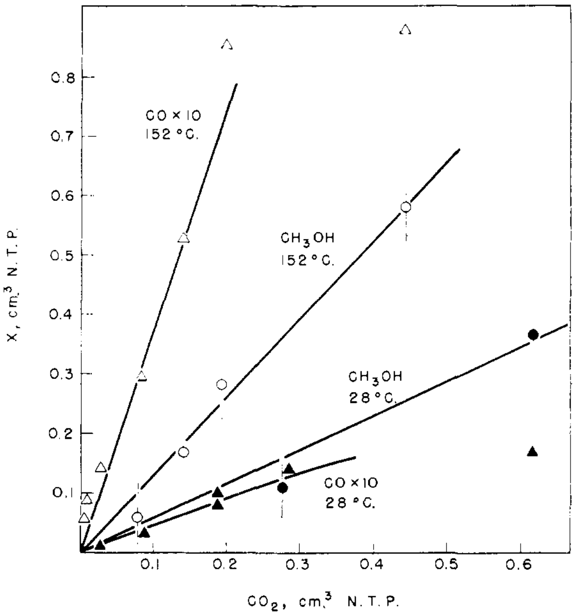

Fig. 4.—Relation between methanol, carbon monoxide and carbon dioxide yields.

Table V

Formation of Acetaldehyde and Ethanol

Temp., °C.	Azoethane press., mm.	Oxygen press., mm.	$(C_2H_5OH)_7$ / N_{2prim}	Y_{CH_3CHO}	$(CH_3CHO)_{14}$ / N_{2prim}	k_{7a}/k_{14}
28	13.9	7.7	0.25	1.14	0.07	
		5.8	.28	1.13	.06	
		1.28	.41	1.12	.05	
		0.79		1.13		
		.45		1.09		
		.19		1.04		
		.082		1.03		
118	10.7	8.6	0.61	1.75	0.84	0.6
		4.5	.66	1.30	.37	.8
		3.2	.71	1.37	.44	.5
		1.4	.78	1.13	.20	.5
		0.78	.78	1.00	.07	.8
		.51	.96	0.85		
		.27	1.1	.76		
		.22	1.6	.85	Av.	0.6 ± 0.3
152	10.0	9.1	0.59	1.41	0.54	1.0
		5.7	0.89	1.29	.42	1.2
		3.1	1.12	1.08	.31	1.1
		1.2	1.38	0.66		
		1.02	1.7	1.06		
		0.79	1.8	0.81		
		.54	1.8	1.08		
		.31	3.3	1.07		
		.25	3.2	1.04	Av.	1.1 ± 0.4
28	80.2	1.36	0.90	1.07		
	38.8	1.13	1.85	1.05		
	13.8	1.28	1.38	1.08		
	4.5	1.16	0.32	1.13		
	2.1	1.15	.28	1.18		
	1.5	1.11	.33	1.14		
152	30.6	1.03	3.0	0.70		
	18.4	0.99	2.5	0.85		
	10.0	1.02	1.7	1.02		
	2.9	1.12	0.65	1.05		

Reactions 20 and 22 are suggested for the formation of carbon monoxide and carbon dioxide. Some data on the photolysis of acetone in the presence of O^{18}-enriched oxygen can be interpreted[24] to yield $E_{20} - E_{22} \sim 9$ kcal. mole^{-1} with log $A_{20}/A_{22} \sim 19.1$ when concentrations are expressed in molecule/ml.

Hence at oxygen pressures of 1 mm. or higher it is unlikely that much of the carbon monoxide is formed by decomposition of the acetyl radical. It seems more probable that a substantial portion of the carbon monoxide arises from attack on formaldehyde (reactions 27, 28 and 29). The methyl radicals formed by reaction 20 eventually will be oxidized to methoxy radicals.[16,21] These methoxy radicals and those formed by reaction 22 will form methanol and formaldehyde by reactions similar to those suggested for the disappearance of ethoxy radicals. Acetic acid is likely to be formed from the acetyl radical as well. No mechanism for its formation is proposed since only a few approximate estimations of the amounts of the acid were made.

According to the mechanism proposed for the disappearance of the acetyl radicals the ratios CO/CO_2 and CH_3OH/CO_2 should be independent of exposure for a given temperature and azoethane and oxygen pressure. This is observed, as is illustrated in Fig. 4. The product ratio of carbon monoxide falls rapidly for conversions greater than 12%, probably because hydrogen abstraction from ethanol and methanol compete with the hydrogen abstraction from formaldehyde. This may be the explanation of the observed decrease in the product ratios of the alcohols at highest conversion (Table I).

From the foregoing discussion it may be deduced that the total amount of acetaldehyde formed will be equal to the sum of the estimated amounts of acetaldehyde, carbon dioxide, acetic acid and the amount of carbon monoxide formed by reaction 20. At oxygen pressures greater than 0.1 mm. the amount of carbon monoxide formed by reaction 20 is small relative to the amount of carbon dioxide (< 5%) and can be neglected[24]; the amount of acetic acid is negligible in low conversion experiments also. Thus under these conditions the total amount of acetaldehyde formed will be nearly equal to the sum of the amounts of acetaldehyde and carbon dioxide determined, as was assumed earlier.

The formation of C_1-products at rather low conversions indicates that hydrogen abstraction from acetaldehyde is easier than from azoethane. This implies that the concentration of $C_2H_5N_2C_2H_4$ radicals, and hence the rate of formation of nitrous oxide, ethylene and secondary nitrogen, should decrease with increasing exposure until acetaldehyde concentration reaches a steady value. These effects are indeed observed as shown in Table I.

In over-all summary it is clear that the gross general features of the photo-oxidation can be explained by the type of mechanism proposed. Much remains to be done to improve the quantitative reliability of the data, especially at low conversion and low oxygen pressure, before detailed consideration can be given to the interaction of ethyl radicals with oxygen.

Acknowledgment.—The authors are indebted to the late Dr. E. W. R. Steacie for the interest he had throughout this work; they also wish to thank Mrs. Frances Kutschke and Mrs. R. H. Riem for the mass spectrometric analyses and Mr. R. Lauzon for the infrared analyses.

---

[24] H. Cerfontain, J. M. Vaerman and K. O. Kutschke, unpublished work.

[CONTRIBUTION FROM DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 20, N. Y., AND UNIVERSITY OF DELAWARE, NEWARK, DEL.]

A Comparison of the Radiolysis and Photolysis of Cyclopentanone

BY M. KATAYAMA, J. C. WHITMER AND C. N. TRUMBORE[1]

RECEIVED JULY 2, 1962

The major products of the γ-ray radiolysis of cyclopentanone are reported as hydrogen, carbon monoxide, ethylene and an oil. Yields of carbon monoxide and ethylene are uncertain because of secondary reactions setting in at about 0.001% conversion of the parent compound, but the hydrogen yield is constant with dose at $G(H_2) = 0.67$. The oil product has been characterized as having a molecular weight of about 200 and retains much of the parent cyclopentanone character. The gas phase radiolysis qualitatively resembles the liquid phase radiolysis. A comparison is given between the radiolysis and photolysis of cyclopentanone which points up the need for shorter wave length photolysis studies of this system.

The investigation reported here on the radiolysis of oxygen-free liquid and gaseous cyclopentanone by cobalt-60 γ-radiation was prompted by photochemical investigations of the same compound.[2,3] Srinivasan[3] suggested that the photolyzed gaseous system at 3130 Å. contained no detectable free radicals. The pressure and wave length dependence of the ratio of the photolysis products 4-pentenal: CO was attributed to the collisional deactivation of a vibrationally excited upper singlet electronic state. At high pressures the quantum yield of 4-pentenal was increased at the expense of the carbon monoxide yield, presumably the result of an internal isomerization in the ground vibrational state of of the excited electronic state. Photolysis of pure liquid cyclopentanone was used by Srinivasan to prepare 4-pentenal for identification purposes, but the quantum yield was not measured nor were quantum yields of other products measured.

According to the current theories of radiation chemistry, radiolysis presumably results in the

---

[1] Department of Chemistry, University of Delaware, Newark, Del.

[2] (a) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 80 (1942); (b) F. E. Blacet and H. Miller, *ibid.*, **79**, 4327 (1958).

[3] (a) R. Srinivasan, *ibid.*, **81**, 1546 (1959); (b) **83**, 4344 (1961); (c) **83**, 4348 (1961).