

similar to that of the aureomycin molecule in aureomycin hydrochloride. The hydroxyl group OH(5) has, however, been placed equatorially with respect to ring B, *i.e.*, *trans* to OH(6). The published set of positional parameters leads to distances of about 3.75 Å. from OH(5) to the nearest chloride ion and of more than 4 Å. for OH(5) . . . OH(6); both of these distances are much too long for hydrogen bonding to take place. The evidence presented by Takéuchi and Buerger consists of a minimum function that contains many spurious peaks and of an electron density projection down the *a*-axis (11.2 Å.) in which severe overlapping of many of the atoms occurs. This evidence cannot be regarded as constituting conclusive proof of the correctness of their proposed structure. The structure is probably correct in its general lines but the published projection is just as compatible with the alternative *cis* relationship of OH(5) and OH(6) which would allow a satisfactory intramolecular hydrogen bond to be formed.

Thus although the X-ray information on the configuration at C(5) in terramycin is incomplete and does not permit an unequivocal conclusion to be drawn, a strong case can be made for the *cis* relationship between OH(5) and OH(6), in agreement with the tentative chemical assignment.¹¹

Acknowledgment.—Partial support for this work was provided by the U. S. Army Research Office, Durham (Grant G237). The calculations were done at the Computing Facility of the University of California at Los Angeles. We wish also to thank those who have been helpful at various stages of these studies, including Prof. R. A. Woodward for communication of unpublished chemical results, Prof. W. N. Lipscomb for the crystallographic results on 4-epiaureomycin, Dr. P. K. Gantzel for assistance with some of the computing, Dr. W. Keller-Schierlein for the biological tests, and Mrs. Maryellin Reinecke for preparation of the figures.

[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS, 10, OHIO]

A Study of the Ethyl-Oxygen Reaction by Flash Photolysis

BY DAVID P. DINGLEY AND JACK G. CALVERT

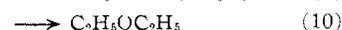
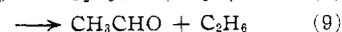
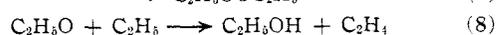
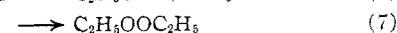
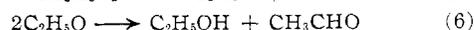
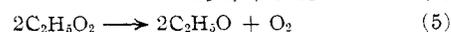
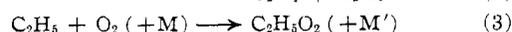
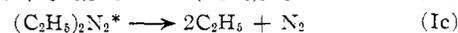
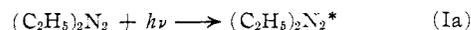
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Ethyl radicals were formed by the flash photolysis of azoethane in both fused quartz and Pyrex systems and with and without additions of moderating gas and oxygen. Flash photolyses in the fused quartz system formed thermally non-equilibrated radicals even with the addition of relatively large quantities of moderating gas (up to 9.5 cm. of methanol). Similar photolyses in the Pyrex system with moderating gas resulted in thermal equilibration of the ethyl radicals as judged by the normal, thermal value obtained for the disproportionation to combination ratio of the ethyl radicals (0.11 ± 0.01). The "hot" radicals in the flash photolyses in the fused quartz system have their origin in the absorption of the short wave length ultraviolet by azoethane.

For the pressure range 0.48–10.3 cm. at 22°, the reaction $C_2H_5 + O_2 \rightarrow C_2H_5O_2$ (3) was shown to be second order with a rate constant, $k_3 = 6.9 \times 10^{-12}$ cc./molecule-sec. The values of this rate constant derived from previous work on diethyl ketone-oxygen mixture photolyses are considerably lower than the present estimate probably because of the importance of C_2 -product forming reactions other than H-abstraction from ketone. The present work shows the possible reaction $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ (4) to be unimportant compared to reaction 3 for thermally equilibrated radicals at 22°.

The association reaction of the methyl radical with oxygen was shown to obey third-order kinetics^{1–3} in the usual pressure range encountered (up to 31 cm. of neopentane). It is of both theoretical and practical interest to establish the degree of complexity in the initial reaction product (RO_2) of a radical (R) with oxygen for the transition to the region of second-order kinetics to occur. Estimates of the rate constant for the ethyl-oxygen reaction are available^{4,5}; however, the reaction system from which these were derived was very complex, and the results could not be expected to be of high accuracy. The previous estimates lie in the range $k_3 = 10^{-13} - 10^{-14}$ cc./molecule-sec.^{4,5} These values are low in comparison with the rate constants calculated for the assumed second-order kinetics in the methyl-oxygen reaction in the same pressure range: 7×10^{-12} cc./molecule-sec.³ Therefore in this study we have attempted to redetermine both the order and the rate constant for the ethyl-oxygen reaction by measurement of the competitive reaction of radical combination following the flash photolysis kinetic techniques employed by Sleppy and Calvert.³ Since the radical concentration must be very high for the combination reaction to proceed measurably when in competition with the reaction with oxygen, flash photolysis generation of the radicals is an essential

part of the method. Azoethane was our choice of ethyl radical source because of its convenient absorption region and the demonstrated simplicity of the photochemistry of this compound. However, in view of the previous studies of the alkyl and alkoxy radical reactions, it was anticipated that the reactions involved in the photooxidation of azoethane could be much more complex than those encountered in the azomethane photooxidation; in fact, it seemed likely that consideration of the following rather involved reaction sequence would be necessary in this case.



Other reactions involving hydroperoxide formation may also contribute to the mechanism. Although the complexity of the possible reaction scheme is great, it has been possible to sort out the kinetic data for

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TABLE I
 PRODUCT YIELDS FROM THE FLASH PHOTOLYSIS OF AZOETHANE

| Run | Pressure, cm. | | Yields, μ moles | | | | 1/3 | 2/3 | $\frac{3 + (1 + 2)/2}{4}$ |
|---|------------------|-------------------------|---------------------|----------|-------------|--------------------|-------|-------|---------------------------|
| | $(C_2H_5)_2N_2$ | Added gas | C_2H_6 | C_2H_4 | C_4H_{10} | N_2 | | | |
| (a) Flash photolysis in the quartz system | | | | | | | | | |
| 1 | 1.04 | 2.74(neohexane) | 0.42 | 0.48 | 1.92 | 2.50 | 0.22 | 0.25 | 0.95 |
| 2 | 0.93 | 3.38(neohexane) | .44 | 0.61 | 2.29 | 2.71 | .19 | .27 | 1.04 |
| 3 | 1.5 | 7.9(neohexane) | .85 | 1.38 | 4.93 | 6.76 | .17 | .28 | 0.89 |
| 4 | 0.72 | 9.47(CH_3OH) | .36 | 0.39 | 1.77 | — | .20 | .22 | — |
| 5 | 1.15 | 3.3($C_2H_5OC_2H_5$) | .99 | 1.73 | 4.42 | 6.18 | .22 | .39 | 0.94 |
| 6 | 1.3 | 3.7($C_2H_5OC_2H_5$) | 1.50 | 2.33 | 9.32 | 11.31 | .16 | .25 | .99 |
| 7 | 1.4 | 5.2($C_2H_5OC_2H_5$) | 0.86 | 1.25 | 3.88 | 6.44 | .22 | .32 | .77 |
| 8 ^a | 1.3 | 3.7($C_2H_5OC_2H_5$) | .16 | 0.13 | 1.31 | 1.16 | .12 | .10 | 1.25 |
| 9 ^b | 1.4 | 4.2($C_2H_5OC_2H_5$) | .29 | 0.24 | 2.75 | 2.65 | .11 | .09 | 1.14 |
| 10 ^c | 3.9 ^c | 0 | 1.89 | 2.20 | 8.10 | 12.50 ^c | .23 | .27 | 0.82 ^c |
| (b) Flash photolysis in the Pyrex-filtered system | | | | | | | | | |
| 11 | 0.3 | 0 | 0.110 | 0.096 | 0.863 | 0.723 | 0.127 | 0.111 | 1.34 |
| 12 | 0.8 | 0 | .130 | .137 | 1.069 | 1.212 ^d | .122 | .128 | (1.00) ^d |
| 13 | 1.2 | 0 | .217 | .231 | 2.295 | 2.526 | .095 | .100 | 1.00 |
| 14 | 1.25 | 0 | .268 | .268 | 2.240 | 2.439 | .120 | .120 | 1.03 |
| 15 | 1.28 | 0 | .252 | .233 | 1.930 | 2.759 | .131 | .121 | 0.79 |
| 16 | 1.3 | 0 | .220 | .206 | 2.276 | 2.490 ^d | .097 | .091 | (1.00) ^d |
| 17 | 2.55 | 0 | .467 | .457 | 4.520 | 4.984 ^d | .103 | .101 | (1.00) ^d |
| 18 | 0.84 | 1.16($C_2H_5OC_2H_5$) | .166 | .158 | 1.286 | 1.542 | .129 | .123 | 0.94 |
| 19 | 0.96 | 1.09($C_2H_5OC_2H_5$) | .125 | .128 | 1.160 | 1.265 | .108 | .110 | 1.02 |
| 20 | 1.24 | 1.20($C_2H_5OC_2H_5$) | .276 | .228 | 2.198 | 2.400 | .126 | .104 | 1.02 |
| 21 | 1.25 | 1.25($C_2H_5OC_2H_5$) | .254 | .227 | 2.132 | 2.354 | .119 | .106 | 1.01 |
| 22 ^e | 1.27 | 1.28($C_2H_5OC_2H_5$) | .205 | .195 | 1.660 | 1.916 | .123 | .117 | 0.97 |
| 23 ^f | 1.27 | 1.35($C_2H_5OC_2H_5$) | .148 | .117 | 1.265 | 1.371 | .117 | .092 | 1.02 |
| 24 | 1.19 | 1.36($C_2H_5OC_2H_5$) | .123 | .087 | 1.197 | 1.370 | .103 | .073 | 0.95 |
| 25 | 1.32 | 1.10($C_2H_5OC_2H_5$) | .219 | .209 | 1.707 | 1.871 | .128 | .122 | 1.03 |
| 26 ^g | 1.3 | 2.6($C_2H_5OC_2H_5$) | .094 | .082 | 0.779 | 0.875 | .121 | .105 | 0.99 |
| 27 | 1.3 | 2.6($C_2H_5OC_2H_5$) | .246 | .239 | 1.882 | 2.126 ^d | .132 | .127 | (1.00) ^d |
| 28 ^g | 1.20 | 4.11($C_2H_5OC_2H_5$) | .138 | .131 | 1.345 | 1.487 | .103 | .097 | 1.00 |
| 29 | 1.35 | 4.1($C_2H_5OC_2H_5$) | .168 | .158 | 1.700 | 1.814 | .099 | .093 | 1.03 |
| 30 | 1.4 | 4.5($C_2H_5OC_2H_5$) | .227 | .205 | 1.975 | 2.240 | .115 | .104 | 0.98 |

^a Double strength window glass was placed between the flash tube and the cell. ^b Single strength window glass was placed between the flash tube and the cell. ^c Diethyl ketone was used in this experiment in place of azoethane and three flashes of the same reactant were made before analysis; the non-condensable fraction is CO in this case. ^d Nitrogen yields calculated from an assumed mass balance in these runs. ^e 9500 v. flash used in this run. ^f 8200 v. flash used in this run. ^g These runs had a low total yield of products (probably due to improper mixing of the ether and azoethane) and were not used in constructing Fig. 2.

reaction 3 and obtain other useful information about the ethyl-oxygen reaction system at 22° in the present work.

Experimental

Apparatus.—The fused quartz photolysis system was essentially that described by Sleppy and Calvert³ except that the flash tube, filled with xenon at 25 cm. pressure, was operated at 10,000 v. through a capacitance bank of six 120 μ f. capacitors arranged to give a 4000-joule flash at full potential. This resulted in flashes which rose to a peak in 100 μ sec. with a time from initiation to peak/e intensity of 330 μ sec. The Pyrex system contained a 1-m. Pyrex photolysis cell, 20 mm. o.d., 227-cc. volume, which was shielded by a surrounding 1-m. Pyrex tube, 25 mm. o.d.

The rate of change of flash intensity with time was measured by directing filtered radiation from the flash on to a RCA 918 photocell. Through the use of glass plates and Corning filters the radiation entering the phototube was filtered; the wave length dependence of the filter transmission and the response of the phototube combined to match almost exactly the first absorption band of azoethane. The signal from the phototube circuit triggered the sweep on a Tektronix type 541 oscilloscope. Internal circuit timing fixed the sweep at 10 μ sec. per grid division and a photograph of the oscilloscope trace then was used to measure the change in flash intensity with time. Neutral density filters of 53 and 15% transmission (metal on quartz) were used in different flashes to evaluate the linearity of the response of the light detection system and ensure against overloading of the photocell. This intensity-time plot and the product analyses provided the basis for estimation of the rate of ethyl radical formation.

Materials.—Azoethane was obtained from Merck and Co., Ltd., of Montreal, Que., in 5-g. lots and was stored at Dry Ice temperature. The material as obtained contained small quan-

ties of butane and was purified in small batches before use by fractionation in the Leroy-Ward still at -90°; the purified samples, stored at liquid nitrogen temperature, were shown by chromatographic analyses to be free from impurities that might interfere with the product analysis. Since accurate analysis for very small quantities of butane was demanded in the present work, precautions to avoid the photolysis of azoethane in the room light had to be taken; all storage was in covered Dewars, and the fluorescent room lights were turned off during transfers and runs. Ethyl ether used was anhydrous analytical reagent (Mallinckrodt); small batches were purified as with azoethane and stored at liquid nitrogen temperature. Nitrogen and oxygen gases were Liquid Carbonic high purity cylinder material which were used without further purification. Ethylene, ethane and butane were Phillips research grade. Absolute ethyl alcohol and acetaldehyde (Eastman) were used as chromatographic standards without further purification.

Product Analysis.—After the photolysis in runs where oxygen was not added, the condensable products were frozen out in a trap at liquid nitrogen temperature. The non-condensables were pumped out of the system through the Toepler pump, measured in a Blacet-Leighton gas microburet, and analyzed in a Consolidated mass spectrometer (model 21-620). The condensables were injected into a gas chromatographic analytical system of the type described by Kerr and Calvert,⁶ using programmed heating of a column of 1% squalene on 30-60 mesh activated alumina; excellent separations of the hydrocarbon products and excess azoethane and ether were possible. For runs where oxygen was added, the non-condensable products and the excess oxygen reactant were pumped off through the vacuum system and discarded, and the condensables analyzed as before. For ethanol analysis the chromatographic column adsorbent was polyethylene glycol 400 on firebrick⁷ and for acetaldehyde

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TABLE II
 PRODUCT YIELDS FROM THE FLASH PHOTOLYSIS OF AZOETHANE-OXYGEN MIXTURES

| Run | Pressure, cm. | | | Product, yield, μ moles | | | C_2H_4/C_4H_{10} |
|-----------------|-----------------|---------------|-------|-----------------------------|--|--------------|--------------------|
| | $(C_2H_5)_2N_2$ | $(C_2H_5)_2O$ | O_2 | C_2H_6 | C_2H_4 | C_4H_{10} | |
| 31 | 1.07 | 1.07 | 1.27 | — | CH ₃ CHO, 2.08 | — | — |
| 32 | 1.10 | 1.12 | 1.09 | — | C ₂ H ₅ OH, 2.27 | — | — |
| 33 | 1.16 | 1.22 | 1.04 | — | C ₂ H ₅ OH, 2.02 | — | — |
| 34 | 0.483 | 0 | 0.284 | — | 0.052 | 0.0014 | 37 |
| 35 | 0.670 | 0 | .288 | 0.0039 | .089 | .0034 | 26 |
| 36 | 1.25 | 1.36 | .069 | .14 | .13 | .144 | 0.9 |
| 37 | 1.24 | 1.28 | .070 | .13 | .12 | .116 | 1.0 |
| 38 | 1.25 | 1.31 | .203 | .039 | .080 | .028 | 2.9 |
| 39 | 1.25 | 2.30 | .216 | .012 | .061 | .019 | 3.2 |
| 40 | 1.26 | 1.29 | .278 | .017 | .065 | .020 | 3.3 |
| 41 | 1.25 | 1.73 | .321 | .011 | .062 | .0103 | 6.0 |
| 42 | 1.25 | 1.33 | .685 | — | .048 | .0139 | 3.5 |
| 43 | 1.25 | 1.28 | 1.76 | — | .031 | \leq .0021 | 15 |
| 44 | 1.18 | 1.25 | 2.06 | — | .038 | \leq .0034 | 11 |
| 45 | 1.20 | 1.39 | 4.07 | — | .022 | \leq .0015 | 15 |
| 46 | 1.24 | 4.30 | 6.87 | — | .006 | \leq .0030 | 2 |
| 47 ^a | 1.21 | 1.21 | 8.95 | — | .024 | \leq .0041 | 5.9 |
| 48 | 5.99 | 4.28 | 0.315 | 0.49 | 1.06 | .455 | 2.3 |

^a 9500-v. flash used in this run.

analysis a 75–25% mixture of 30% dinonyl phthalate on firebrick and 5% glycerol on firebrick.⁵

The Flash Photolysis of Azoethane without Oxygen.—In Table I the results of the flash photolysis of azoethane in the oxygen-free system are given; the first seven runs were made in the unfiltered system with various added gases, neohexane, methanol and diethyl ether. In these runs with unfiltered flash, the very high ratio of ethylene/butane suggests the importance of non-thermally equilibrated ethyl radicals. Reasonable pressures of added gases were ineffective in lowering this ratio. In runs 8 and 9 glass plates were inserted between the cell and the flash tube. Here the near normal C_2H_4/C_4H_{10} ratios show that this procedure of ethyl radical formation realizes thermal equilibration. In view of these results the quartz photolysis cell was replaced with a Pyrex cell and filter combination. Data for runs 11–30 are from photolyses using this flash system. In run 10 diethyl ketone was used as the ethyl radical source in the quartz system.

The Flash Photolysis of Azoethane-Oxygen Mixtures.—The results are shown in Table II. In runs 31–33 analysis for the oxygenated products of the reaction was made; the chromatographic columns employed did not allow analysis for the hydrocarbon products in these runs. In runs 34–48 only hydrocarbon analysis was made. It can be noted that the reaction of ethyl radicals with oxygen is so fast that very little butane is formed in all oxygen-containing mixtures. However, the amounts of the hydrocarbon products are accurately determinable in the runs below 1-cm. oxygen pressure; butane yields from runs containing above 1 cm. of oxygen are near the detection limit of the equipment employed and the yields shown represent possible maximum values.

The selection of a suitable moderating gas to test the order of the oxygen-ethyl radical reaction was based on consideration of several properties of the possible material: chemical inertness to the ethyl radicals under flash photolysis conditions, lack of light absorption in the range produced by the flash, non-interference with the analytical procedures, and sufficient volatility to provide a wide range of useful pressures at room temperature. Several perfluoro- and other compounds were tried, but most of them failed to have at least one of the desired properties. Neohexane, methanol and ethyl ether were satisfactory and were used in our experiments. Ethyl ether was chosen for quantitative studies because of its close structural resemblance to azoethane. This indicated that it would probably be as effective as azoethane as a third body and therefore treatment of the results would be simplified, since summation of the total azoethane and ether pressures would give the third body pressure.

Discussion

The Mechanism of the Flash Photolysis of Azoethane.

There are two rather striking differences between the product distribution from the flash photolysis of azoethane in the unfiltered quartz system (runs 1–7 of Table I) and that obtained from the azoethane photolysis in steady illumination at 3660 Å. and 25°: (1)

(8) Suggested by K. O. Kutschke, National Research Council, Ottawa, Ont.; private communication.

the ratio of C_2H_4/C_4H_{10} is far from that expected from the best estimates of the disproportionation to combination ratio for thermally equilibrated radicals; see Table III; (2) the C_2H_4/C_2H_6 ratio is much above

TABLE III

ESTIMATES OF THE RATIO OF THE DISPROPORTIONATION TO COMBINATION FOR ETHYL RADICALS

| Radical source | k_2/k_1 | Ref |
|---|-----------------|--------------|
| $2C_2H_5 \rightarrow C_4H_{10}$ | | (1) |
| $\rightarrow C_2H_4 + C_2H_6$ | | (2) |
| (1) $(C_2H_5)_2Hg$, photolysis (100°), full Cd Lamp ($\lambda \geq 2288 \text{ \AA.}$) | 0.43 | 9 |
| full Hg Lamp | 0.38 | 9 |
| $(C_2H_5)_2Hg$, pyrolysis (320–370°) | 0.25 | 13 |
| (2) $Hg(^3P_1)$ -sensitized hydrogenation of C_2H_4 (25°) | 0.15 ± 0.01 | 15 |
| (2) $Hg(^3P_1)$ -sensitized hydrogenation of C_2H_4 (25°) | 0.11 | 20 |
| (2) $Hg(^3P_1)$ -sensitized hydrogenation of C_2H_4 (25°) | 0.14 | 21 |
| (3) $(C_2H_5)_2CO$, photolysis (25–101°) | 0.11 ± 0.02 | 11 |
| (3) $(C_2H_5)_2CO$, photolysis (100–250°) | 0.12 | 16 |
| (3) $(C_2H_5)_2CO$, photolysis (50–150°) | 0.13 ± 0.01 | 17 |
| (3) $(C_2H_5)_2CO$, photolysis (25–225°) | 0.14 ± 0.02 | 18 |
| (3) $(C_2H_5)_2CO$, photolysis (110°) | 0.13 ± 0.01 | 24 |
| $(CH_3CD_2)_2CO$, photolysis (24–138°) | 0.10 ± 0.02 | 10 |
| $(CD_3CD_2)_2CO$, photolysis (50–197°) | 0.10 ± 0.01 | 23 |
| (4) C_2H_5CHO , photolysis (25°) | 0.10 ± 0.01 | 12 |
| (4) C_2H_5CHO , photolysis (50–215°) | 0.15 | 22 |
| (5) $(C_2H_5)_2N_2$, photolysis (3660 Å., 26–178°) | 0.13 ± 0.02 | 14 |
| $(C_2H_5)_2N_2$, photolysis (27–175°) | 0.12 ± 0.01 | 19 |
| $(C_2H_5)_2N_2$, flash photolysis (22°) | 0.11 ± 0.01 | Present work |

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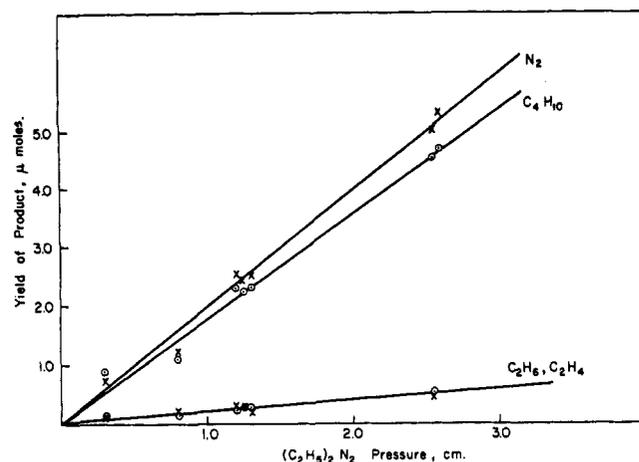


Fig. 1.—Yields of products in the flash photolysis of azoethane as a function of azoethane pressure: oxygen-free, Pyrex-filtered system; no added moderating gas; 4000-J. flash; temperature, 22°

unity, the value anticipated if reactions 1 and 2 are dominant for ethyl radicals in this system. Note that the data of run 10 in which diethyl ketone was used as the free radical source shows very similar results. Others have also observed these effects recently in solution²⁵ and gas phase photolyses²⁶ of azoethane in fused quartz systems. From the data of runs 1-7 of Table I it can be seen that the addition of relatively large amounts of moderating gas has little, if any, effect on the product distribution (up to 9.5 cm. of CH₃OH). These unexpected results disappear as a short wave length filter is placed between the cell and the flash tube (runs 8 and 9 of Table I), and the product distribution for experiments with the Pyrex-filtered system (runs 11-30) is just that expected for the occurrence of the mechanism I, 1 and 2. The results suggest that a highly excited ethyl radical may be formed in azoethane photolysis at the short wave lengths. An intense absorption band begins in azoethane below about 2300 Å., and it seems likely that absorption in this region of the flash is responsible for the excited radicals; at 2300 Å. the decomposition of azoethane is about 45 kcal. more exothermic than at 3600 Å. Presumably a highly vibrationally excited ethyl radical (C₂H₅^{*}) formed in the primary act could decompose as in 11



or disproportionate in (2') at a much faster rate than that characteristic of thermallized ethyl radicals.²⁷



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(27) Dr. B. C. Roquette has found hydrogen as a product of azoethane flash photolysis in a quartz system to the extent of about 1% of the nitrogen formed when ethylene was 10% higher than the ethane yield. If account is taken of the fact that H-atom addition to the azoethane double bond system may occur in part following 11, these results are in accord with reaction 11.

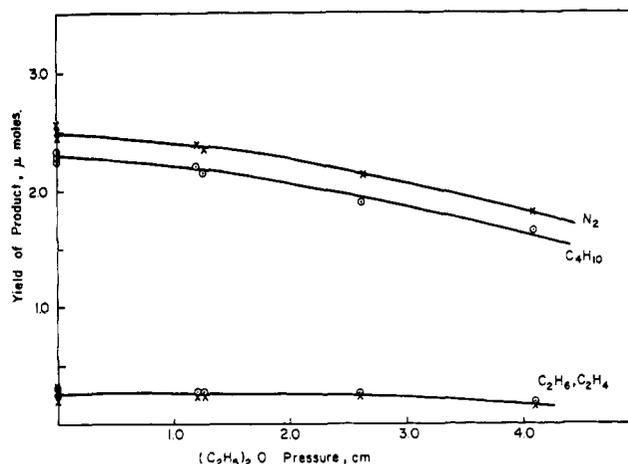


Fig. 2.—Yields of products of the flash photolysis of azoethane as a function of ethyl ether pressure: oxygen-free, Pyrex-filtered system; azoethane pressure, about 1.3 cm.; 4000-J. flash; temperature, 22°.

While vibrational excitation of the ethyl radical would be expected to enhance the rate of reaction 2, it should lower the rate of 1 and thus lead to the observed high ratio of C₂H₄/C₄H₁₀. The ineffectiveness of added gas in moderating the excited ethyl radicals supports the motion that the excitation is largely vibrational. The suggested mechanism of "hot" radical participation in the unfiltered flash experiments is consistent with the observations of others who have studied the reactions of vibrationally excited ethyl radicals (*e.g.*, see the work of Turner and Cvetanovic²¹).

The mass balance shown in the last column of Table I is near unity in the filtered flash experiments and the mechanism of product formation seems unambiguous in these experiments. The results can be used with some confidence to obtain a reliable estimate of the rate constant ratio, $k_2/k_1 = 0.11 \pm 0.01$. In Table III it can be seen that the present estimate is consistent with the previous estimates of this quantity derived from the photolysis of diethyl ketone, propionaldehyde and azoethane; they lie in the range, $k_2/k_1 = 0.12 \pm 0.02$. Only in those cases where participation of excited radicals is likely (Hg(C₂H₅)₂ and H + C₂H₄ studies) is a "high" ratio found.

Some details of the mechanism of the primary process of azoethane photolysis are evident from the variation of the product yields with azoethane pressure and added ether; see Fig. 1 and 2. The quantum yield of azoethane decomposition has been shown to be near unity for the lowest azoethane pressures used in our work.¹⁹ Since the light path is very short in our system and the absorption by azoethane is weak, light absorption should be nearly proportional to the pressure of azoethane. Deactivation (Ib) is only a minor process up to 2.5 cm. of azoethane, so the near linear relation of Fig. 1 can be rationalized.¹⁹ However, when large pressures of ether are added to fixed pressure of azoethane, clear evidence for the deactivation of excited azoethane is obtained; see Fig. 2.

All of the results found in the Pyrex-filtered flash photolysis of azoethane support the simple mechanism Ia,b,c, followed by reactions 1 and 2, and prove that the system is a convenient source of high concentration, near thermally equilibrated ethyl radicals.

The Mechanism of the Flash Photolysis of Azoethane-Oxygen Mixtures.—Product data from the Pyrex-filtered flash photolysis of azoethane-oxygen mixtures, summarized in Table II, show that acetaldehyde and ethanol are the major products under our conditions. These products are formed in approxi-

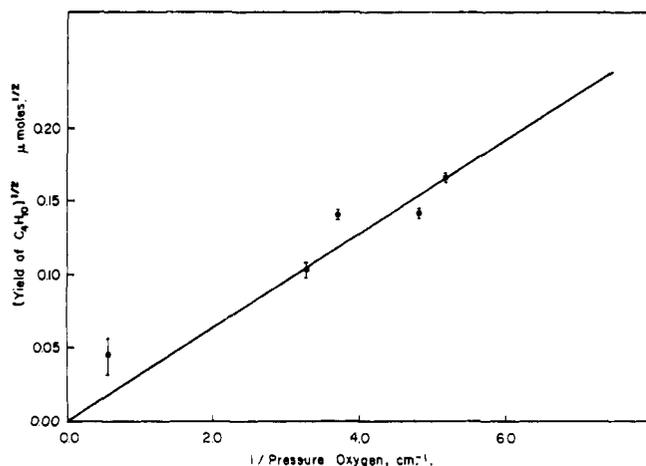
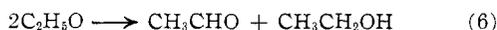


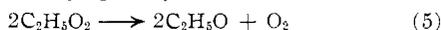
Fig. 3.—Butane yields from the flash photolysis of azoethane with added oxygen as a function of oxygen pressure: Pyrex-filtered system; azoethane pressure about 1.3 cm.; ether pressure 1.3–2.3 cm.; 4000-J. flash; temperature, 22°; the length of the pips on the experimental points show the error introduced due to uncertainty in the measurement of the butane yields. Data from run 43 at 1.76 cm. O_2 has been used at the lowest $1/P_{O_2}$ point shown; a relatively large error is apparent in this run; although the high O_2 pressure runs were consistent with the mechanism within the large experimental error, they were not used in deriving estimates of the rate constant k_3 . The straight line through the origin is the theoretical locus of points for $k_3 = 6.9 \times 10^{-12}$ cc./molecule-sec., assuming the mechanism I-10 is operative.

mately equal amounts: CH_3CHO , 2.08; C_2H_5OH , 2.14 μ moles in the near identical runs 31–33. Furthermore, the yields of these products account well for the majority of the ethyl radicals formed in this system; thus the expected number of radicals formed for the condition used in runs 31–33 can be estimated from the data of Fig. 1 and 2 to be about 4.1 μ moles, in reasonably good agreement with the observed average of 4.2 μ moles of ethanol plus acetaldehyde found in the products. It is attractive to assume that these products arise in the disproportionation reaction between ethoxyl radicals



The alternative competitive combination reaction 7 appears to be at least one-twelfth that of 6²⁸ so that it is not surprising that there is almost a complete account of the ethyl radicals produced in the flash through the ethanol and the acetaldehyde products.

Presumably ethoxyl radicals have their origin in the reaction between ethyl peroxy radicals



while the ethyl peroxy radicals are formed in the primary step (3) of the oxidation sequence



In all runs except those at the lowest oxygen-azoethane ratios (36, 37, 48) less than 5% of the ethyl radicals produced react to form hydrocarbon products. It is likely that reaction 1 is the only source of butane in this system. However, the relatively large C_2H_4/C_4H_{10} ratios suggest that ethylene is formed in some reactions in addition to (2). Furthermore, note in Table II that the C_2H_4/C_4H_{10} ratio is largest for the experiments with the least moderating gas present. In similar experiments 45 and 46 a rather dramatic decrease in the C_2H_4/C_4H_{10} ratio (15 \rightarrow 2) is had on increasing the ether pressure by a factor of three. The results are not consistent with the hypothesis that the major C_2H_4

forming reaction is (2), (4) or (8) involving thermally equilibrated radicals since added ether should have no effect on the C_2H_4/C_4H_{10} ratio in this case. Rather it appears that the ethylene formation in runs at the higher O_2 pressures arises largely from a reaction involving a small fraction of the ethyl radicals which are non-thermally equilibrated



C_2H_5' represents an ethyl radical in one of the lower energy vibrational, rotational or translational modes of excitation which is not sufficient to promote reaction 11 (~ 40 kcal. endothermic) but does favor the near thermally neutral (and probably low activation energy) reaction 4. The fraction of the ethyl radicals formed in the Pyrex-filtered flash which are sufficiently energy-rich to react by 4' is about 1% with the usual experiment conditions employed; at the highest pressures of moderating gas only about 0.1% of the radicals react by 4'.

The reaction of ethyl radicals with oxygen appears to be complicated further in experiments at the lowest oxygen pressures employed (36, 37 of Table II). The relatively high yield of C_2H_4 and C_2H_6 suggests the importance of reactions 8 and 9; however, Wijnen²⁹ has found that $k_8/k_{10} = 2.3$ and $k_9/k_{10} = 1.3$; therefore $k_8/k_9 = 1.8$, so that if 8 and 9 do occur then an additional source of ethane is also required to reach the near equal rates of C_2H_4 and C_2H_6 found in runs 36 and 37. It is not clear what the source might be; one obvious possibility is a H-abstraction from azoethane or ether by hot ethyl radicals. Reactions involving the ethyl peroxy and ethyl radicals would favor ethylene rather than ethane formation. The reaction mechanism is obviously most complex and incompletely understood in these runs with the lowest oxygen pressures.

Estimation of the Rate Constant for Reaction 3.—

From the previous discussion it is concluded that reaction 3 is the major reaction which destroys ethyl radicals under our conditions of flash photolysis of azoethane-oxygen mixtures; less than 5% of the ethyl radicals react by other paths except at the lowest oxygen pressures employed. We may use the butane yields in these runs as a monitor of the ethyl radical concentration together with the measured value of the rate constant k_1 to estimate, in the fashion of Sleppy and Calvert, the rate constant for the reaction 3. Assuming the mechanism I-10 the differential equation 12 describes the rate of change of ethyl radical concentration with time in our flash system

$$d[C_2H_5]/dt = 2I_a\phi_1 - [C_2H_5][O_2][M]k_3 - [C_2H_5]^2(k_1 + k_2) - [C_2H_5][O_2]k_4' - [C_2H_5][C_2H_5O](k_8 + k_9 + k_{10}) \quad (12)$$

Product analysis suggest that the first two terms are dominant and, to a first approximation, determine the ethyl radical concentration at any given time; for our conditions the other three terms may be neglected in evaluation of $[C_2H_5]$. The rate of ethyl radical formation, $2I_a\phi_1$, can be calculated from the time dependence of the flash intensity and a knowledge of the total ethyl radicals formed in experiments at similar reactant and ether pressures but in the absence of oxygen. In the actual calculations an arbitrary value of the rate constant k_3 was assumed and $[C_2H_5]$ was calculated for each 10- μ sec. interval of the flash. From this information a curve or $[C_2H_5]^2$ was constructed. The area under the curve multiplied by k_1 (4.27×10^{-11} cc./molecule-sec.)²⁹ and the cell volume σ_{ave} a theoretical butane yield. A new choice of k_3 was made and the entire calculation repeated until the theoretical and

(29) We have assumed no temperature dependence to the rate constant data of Shepp and Kutschke¹⁷ and have used the average value of all their data: $k_1 = 4.27 \times 10^{-11}$ cc./molecule-sec.

(28) J. Heicklen and H. S. Johnston, *J. Am. Chem. Soc.*, **84**, 4394 (1962).

actual experimentally measured butane yields were equal. The values of k_3 so obtained are summarized in Table IV for assumed second- and third-order kinetics of reaction 3. The results are consistent with a second-order law but vary greatly for the assumed third-order kinetics for 3. In Fig. 3 a test is made of the dependence of butane yield on oxygen pressure. The experimental points fall on the theoretical function calculated for $k_3 = 6.9 \times 10^{-12}$ cc./molecule-sec. within the experimental error, and are consistent with the theoretical first-order dependence of the reaction 3 on oxygen pressure and the mechanism assumed for butane formation. The data of runs 36 and 37 are not reliable since reactions other than 3 which destroy ethyl radicals become important here and these have been neglected in the calculation; the error is such as to lead to a high estimate. In run 42 at the highest O_2 pressure the butane yield is very low and near the detection limits of the equipment, so little weight can be given to the result.³⁰ The average of the seven other runs gives $k_3 = 6.9 \times 10^{-12}$ cc./molecule-sec.

TABLE IV

ORDER AND RATE CONSTANT ESTIMATES FOR THE REACTION:



| Run | —Pressure, cm.— | | k_3 , assuming | k_3 , assuming |
|-----|---------------------------|-------------------|---|---|
| | O_2 (avr.) ^a | $Et_2N_2 + Et_2O$ | 2nd order, × 10^{12} cc. /molecule-sec. | 3rd order, × 10^{10} cc. /molecule ² -sec. |
| 34 | 0.281 | 0.483 | 8.2 | 43.6 |
| 35 | 0.285 | 0.670 | 5.4 | 33.3 |
| 36 | 0.060 | 2.617 | (9.6) | (11.2) |
| 37 | 0.061 | 2.521 | (10.6) | (12.9) |
| 38 | 0.194 | 2.567 | 6.9 | 8.2 |
| 39 | 0.207 | 3.545 | 7.8 | 6.7 |
| 40 | 0.269 | 2.543 | 5.8 | 7.0 |
| 41 | 0.312 | 2.975 | 6.7 | 6.9 |
| 42 | 0.676 | 2.583 | (2.8) | (3.3) |
| 48 | 0.293 | 10.27 | 7.3 | 2.2 |

^a Average of initial and final O_2 pressure calculated assuming mechanism I, 1–10.

The estimate of k_3 derived in this work is 10^2 times higher than the rate constant determined by Jolley⁵ and 5×10^2 times that of Finkelstein and Noyes.⁴

(30) R. E. Reggert and P. Ausloos, *J. Phys. Chem.*, **66**, 2253 (1962), show that intramolecular formation of C_2H_5 in azomethane photolysis at 3660 Å. occurs with a quantum efficiency of about 0.004–0.007. Conceivably a very small intramolecular formation of butane may occur by an analogous process in azoethane photolysis in this study; at the highest oxygen pressure used the yield of butane is slightly higher than that expected from the assumption of reaction 1 to be the only source of butane. In any case, the accuracy of run 42 is very low, and it is not used in the calculations of k_3 ; if intramolecular formation of butane does occur, its quantum efficiency must be extremely small to fit the results found here, and it cannot affect the conclusions formed in this work.

Both of these values were based on relative rate measurements using the total C_2 -yields as the radical monitor in the photooxidation of diethyl ketone. The usual ethyl radical disproportionation and H-atom abstraction reactions were assumed to be the only sources of the C_2 -products by the earlier workers. Our work shows clearly that there are important sources of C_2 -products other than these, especially at the low O_2 pressures employed by the previous workers. It is likely in our opinion that the major difference between the previous values and the current estimate enters by this path. Since butane is used as the radical monitor in this work this source of difficulty is avoided here.

Since this work was completed we have become aware of a recent study of reaction 3 by Avramenko and Kolesnikova.³¹ The pressure and temperature ranges are quite different from those used in this study, so it is difficult to compare the results quantitatively. They estimate $k_3 \cong 2 \times 10^{-12}$ cc./molecule-sec. for the temperature range 348–575°K. and 4.2 mm. pressure. Ethyl radicals were formed in their system by the reaction, $H + C_2H_4 \rightarrow C_2H_5$, and at the low pressures employed, the hotness of the ethyl radical reactant is likely. They also report that the original energy-rich product, $C_2H_5O_2^*$, formed on bimolecular association of the ethyl radical and oxygen, decomposes 90% of the time at 1 mm. pressure of H_2 , 50% at 10 mm., and 10% at 100 mm. of H_2 . In our study, the molecules of $(C_2H_5)_2N_2$ and $(C_2H_5)_2O$ would act as much better energy transfer agents than H_2 , and our observation of second-order behavior of reaction 3 in the range of 4.8–103 mm. pressure is not inconsistent with their findings.

Our estimate of $k_3 = 6.9 \times 10^{-12}$ cc./molecule-sec. reported here is of reasonable magnitude for a very low activation energy reaction in the second-order region of kinetics; it is about one-fiftieth of the collision number calculated using the collision diameter of C_2H_5 equal to that of ethane. One may predict on the basis of this work that the higher alkyl free radicals which are more complex than ethyl will react with oxygen according to second-order kinetics in the usual pressure region.

Acknowledgment.—The authors gratefully acknowledge the financial support of this work by the United States Public Health Service, National Institutes of Health, Bethesda, Md. We wish to thank Drs. Julian Heicklen and Harold S. Johnston for access to manuscripts of papers now in press, Dr. B. C. Roquette for the useful exchange of information on related research in his laboratory, and Dr. Kenneth O. Kutschke for helpful discussions and suggestions during the course of this work.

(31) L. I. Avramenko and R. V. Kolesnikova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 806, 989 (1960).