1% and a negative value, thus establishing the highest average chemical yield from the isomeric transition observed up to that time. They concluded that their results were consistent with the interpretation that every transition causes bond rupture, just as every transition was known to involve internal conversion. It now appears, from the data of Table I, that the two highest values of the retention in this earlier work were more nearly correct than the lower values.

Acknowledgment.—This work was supported in part by the Atomic Energy Commission and in part by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation.

MADISON 6, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

The Photolysis of Azoethane[1]

BY J. L. WEININGER[2] AND O. K. RICE

RECEIVED MAY 22, 1952

The photolysis of azoethane was investigated by measurement of the production of nitrogen. The quantum yield was observed to decrease with increasing pressure of azoethane; at the maximum pressure investigated, 1.73 atm., it had fallen to 60% of its low pressure value, which, within the experimental error, can be considered to be unity. The minimum life-time of activated azoethane was calculated to be 2.5×10^{-11} second, on the assumption of a collision efficiency of unity for deactivation by collision and of a collision diameter of 7 A. for the azoethane molecule. A smaller efficiency for deactivation by collision would correspond to a longer life-time for the excited molecule.

Introduction

The photolysis of azomethane has been studied by many investigators because of its relative simplicity. From the work of Cannon and Rice[3] and others[4] it is known that up to a pressure of 630 mm. the quantum yield at 3660 Å. remains approximately unity. Although some of the excitation energy in photochemical decomposition is initially electronic, it is possible that the mechanism of decomposition involves its transfer to vibrational energy and the eventual accumulation of vibrational energy in a particular bond. If this is the case, collisions should deactivate the molecule and the quantum yield should decrease at sufficiently high pressures. No such decrease has been observed in the case of azomethane at pressures obtainable at room temperature.

Azoethane possesses a larger number of vibrational degrees of freedom than azomethane; one may thus logically expect that an excited azoethane molecule would have a longer life-time than a correspondingly excited azomethane molecule. An investigation of the pressure dependence of the photolysis of azoethane was undertaken for this reason. The data for pressures up to 230 mm. (the vapor pressure at 30°) showed evidence for such a decrease, obscured by the scatter of the measurements. Experiments at still higher pressures, obtained by raising the temperature, confirmed the decrease. Extrapolation from the experimental results indicates that the quantum yield decreases to about 50% of its low pressure value at a pressure of 2 atm., the result being uncertain to an extent of ±10%.

Experimental Part

Preparation of Azoethane.—Diformyl hydrazine[5] was ethylated and subsequently hydrolyzed with hydrochloric acid to diethylhydrazine dihydrochloride. This was oxidized with cupric chloride to the corresponding cuprous chloride azoethane addition product. Azoethane was then prepared by heating the addition compound, a method analogous to that employed by Jahn[6] in preparing azomethane. The azoethane was purified by drying, liquefaction and repeated distillation.

Vapor pressure determinations were performed from −70 to 27° (room temperature). The extrapolated value of the boiling point at atmospheric pressure was found to be 58.3°. The heat and entropy of vaporization at 0° were, respectively, 7,200 cal. deg./mole and 26 cal./mole. Several molecular weight calculations from vapor density measurements gave a mean molecular weight of 87.0 ± 2.0, as compared to expected molecular weight of 86.1.

Optical System.—The same optical system was employed which was used in the photolysis of azomethane.[3] The 3660 Å. line of a medium pressure mercury arc[7] was isolated by the monochromator designed by Cannon and Rice.[8] The lamp was operated at 90–100 volts d.c. Consequently, the monochromatic intensities behind the exit slit (3.97×10^{15} to 1.16×10^{16} quanta per minute) were somewhat smaller than in the previous work. The intensity was measured by a thermopile, which gave a direct reading on a low resistance moving-coil galvanometer of high sensitivity. Corrections for first-order reflections from quartz–gas interfaces and lenses were made for all measurements, as explained below. The correction varied with azoethane pressure; its maximum was 7% of the absorbed intensity.

The absorption coefficient of azoethane was obtained by measuring the transmitted intensity of the 3660 Å. radiation at various pressures. It was found to be 6.82 l.-mole^{-1}-cm.$^{-1}$.

Reaction and Analysis System.—Azoethane was illuminated in a horizontal quartz cell, 9.8 cm. long, with a diameter of 2.5 cm. and windows 1 mm. thick. A chromel heating wire was wound around the cell, which was thermally insulated by means of "Insulag" cement. The temperature of the heated cell was measured by an iron–constantan

---

[1] This work was performed with financial aid from the Research Corporation and was presented at the Spring Meeting of the A.C.S., Buffalo, March, 1952.

[2] Department of Chemistry, Polytechnic Institute of Brooklyn.

[3] C. V. Cannon and O. K. Rice, THIS JOURNAL, **59**, 1038 (1937).

[4] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 232.

[5] Either formyl or benzoyl groups can be used to assure symmetrical ethylation. The diformyl hydrazine is more easily prepared and gives better yields.

[6] F. P. Jahn, THIS JOURNAL, **59**, 1761 (1937).

[7] F. Daniels and L. J. Heidt, *ibid.*, **54**, 2381 (1932).

[8] C. V. Cannon and O. K. Rice, *Rev. Sci. Instruments*, **13**, 513 (1942).

thermocouple placed against the outside of the quartz wall near the center of the cell. From the bottom of the cell, at the center, projected a closed tube, about two inches in length, heated with the cell. The cell itself could be isolated from the vacuum system by a mercury seal stopcock. In the experiments above room temperature, excess azoethane was condensed into the protruding tube, the cell then isolated and the desired vapor pressures attained by heating. Thus it was possible to obtain higher than atmospheric pressures. At the completion of an experiment all condensable gases were frozen out with liquid air or liquid nitrogen. The latter was used to ascertain that, within the limits of experimental error, the small amounts of ethane which may have been produced during the photolysis were completely condensed by the more readily available liquid air. The amount of the remaining non-condensable gas, presumably nitrogen, was measured in a combined Toepler pump and McLeod gage.[9] The non-condensable gases of several experiments were collected for the purpose of a mass spectrographic analysis.

Results

The data and results of all experiments except some preliminary ones and a few which gave unreliable results for known reasons are filed with the American Documentation Institute.[10] Figure 1 shows the results, the pressure dependence of the quantum yield.

Experiments up to a pressure of 235 mm. were performed at room temperature; experiments at higher pressures (690 and 1310 mm.) correspond to higher reaction temperatures (328 and 348°K.).

For the experiments at room temperature I/I_0, the ratio of the intensity of the radiation transmitted by the gas (I) to the intensity of the radiation when the reaction cell was evacuated (I_0), was calculated from the temperature and pressure of the gas and its absorption coefficient. The number of quanta absorbed during the experiment was then calculated from the equation

$$N_q = 1.703 \times 10^{15} (1 + 0.123\, I/I_0) \times \frac{1 - I/I_0}{I/I_0} \times It$$

where N_q is the number of quanta absorbed and t the time of radiation. The numerical constant is the product of the calibration constant of the thermopile–galvanometer assembly (equal to 1.522 $\times$ 10^{15} quanta-min.$^{-1}$-(cm. deflection)$^{-1}$) and a factor (1.1197) relating the intensity of the radiation passing through the gas to that impinging on the thermopile. This factor, together with the expression in the bracket, accounts for first-order reflections. The equation was derived by applying the general argument of Farkas and Melville[11] to the optical system described above. The evaluation of the number of quanta absorbed by this equation was preferred to direct reading of the galvanometer because I_0 could be measured only before and after an experiment, which does not take into account fluctuations in the intensity of the light source.

In the case of the high pressure experiments, however, all of the radiation was absorbed. Consequently, N_q for these experiments was calculated from the value of I_0, the deflection of the galvanometer when no gas was present and the time of radiation, t, by means of the relation

$$N_q = 1.522 \times 10^{15} \times I_0 t$$

where 1.522 $\times$ 10^{15} is the calibration constant of the galvanometer–thermopile assembly in quanta-min.$^{-1}$ (cm. defl.)$^{-1}$.

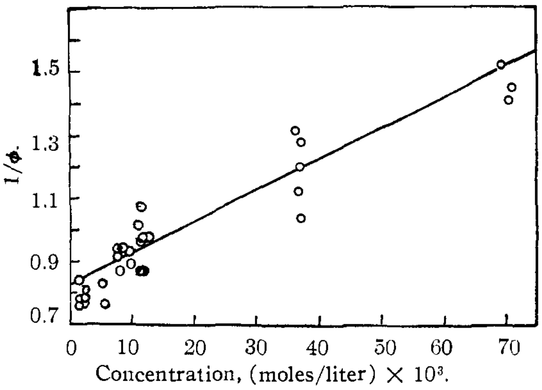


Fig. 1.—Reciprocal quantum yield *versus* concentration.

For experiments below 235 mm. the value of I/I_0 varied from 0.82 to 0.15 depending on the pressure of azoethane. The time of radiation varied from 150 minutes to 25 minutes according to the amounts of products which were desired. This resulted in a value of N_q which varied for different experiments from 0.92 $\times$ 10^{17} to 10.08 $\times$ 10^{17} quanta.

The calculation of the number of molecules of nitrogen was based on the assumption that nitrogen was the only non-condensable gas. This value varied from 1.04 $\times$ 10^{17} to 9.67 $\times$ 10^{17} for different experiments. In conjunction with the quantity N_q the quantum yield for the azoethane decomposition is obtained if for each azoethane molecule which decomposes one molecule of nitrogen is produced. The quantum yield varied with some scatter from a maximum of 1.32 for a low pressure experiment to a minimum of 0.66 for a high pressure experiment. Figure 1 is a least-squares fit of the reciprocal value of the quantum yield *versus* pressure.

The non-condensable gas products of several experiments were collected for mass spectrographic analyses in two separate samples.[12] The results for one of these are given in Table I.

TABLE I

ANALYSIS OF NON-CONDENSABLE GAS PRODUCTS

Component	Mole per cent.	Component	Mole per cent.
Butane	0.2	Oxygen	0.1
Propane	.1	Nitrogen	94.5
Ethane	.6	Water	3.3
Acetylene	.1	Azoethane	None
Ethylene	.7	Methane	None
Carbon dioxide	.4	Carbon monoxide	None

The data refer to the products of relatively high pressure experiments (181.4 to 219.3 mm.) with azoethane near its vapor pressure at room tempera-

---

(9) W. L. Haden and E. S. Luttropp, *Ind. Eng. Chem., Anal. Ed.*, **13**, 571 (1941).

(10) For copies of these data order Document 3680 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D.C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(11) A. Farkas and H. W. Melville, "Experimental Methods in Gas Reactions," The Macmillan Co., New York, N. Y., 1939, p. 247.

(12) For these analyses we are indebted to Dr. Fred L. Mohler of the National Bureau of Standards.

ture. The other smaller sample containing products of low pressure experiments (25.4 to 50.7 mm.) gave erratic results (*e.g.*, 31.0% water). These results were discarded in the belief that water vapor and possibly other gases may have been introduced in the sealing of the flask containing the sample.

By a comparison with the photolysis of azomethane a quantum yield of unity was to be expected for the low pressure experiments on azoethane. The value of $\Phi = 1.22$ for the extrapolation of Φ to zero concentration (see Fig. 1) may be due to incorrectness of the manufacturers' calibrations of the thermopile and galvanometer, which were accepted and used.

Another possible source of error was introduced by the necessity of raising the temperature of the reaction system for the high pressure experiments. The temperature had to be raised to 348°K. in order to attain the maximum pressure of about 1,300 mm. of pure azoethane. There was, therefore, a maximum temperature difference of 48 degrees between low pressure experiments (at about 300°K. room temperature) and high pressure experiments. It is, however, assumed that this temperature difference did not have any appreciable effect on the quantum yield of the reactions.

Discussion

As in the previous work on azomethane[3] it is assumed that the decomposition of azoethane can be followed by the production of nitrogen. The primary step in the photochemical decomposition involves the excitation of azoethane

$$C_2H_5N{=}NC_2H_5 + h\nu \longrightarrow C_2H_5N{=}NC_2H_5^*$$

which is followed by dissociation steps, either successive or perhaps simultaneous

$$C_2H_5N{=}NC_2H_5^* \longrightarrow C_2H_5N{=}N + C_2H_5$$

$$C_2H_5N{=}N \longrightarrow C_2H_5 + N_2$$

unless deactivation of the activated molecule occurs.

The ethyl radicals may then react either by recombination or disproportionation.[13] By analogy with the postulated mechanism of azomethane decomposition,[3] it is possible that radicals and addition compounds of the type $(C_2H_5)_2NNC_2H_5$ and $(C_2H_5)_2NN(C_2H_5)_2$ may also be formed. These secondary reactions would not, however, affect the validity of using the quantum yield of nitrogen production as a measure of the amount of azoethane decomposed in the primary act, provided the addition compounds are stable. Their stability is indicated by the absence of any evidence of a chain reaction. Their concentration must also have been small as only 1 or 2% of azoethane was decomposed in any one experiment. On the other hand, if the dissociation were a two-step process, and if the first step were reversible

$$C_2H_5N_2 + C_2H_5 \longrightarrow C_2H_5N{=}NC_2H_5^*$$

the yield of nitrogen would fall below the amount of dissociation actually begun, though not below the amount completed. This possibility appears quite unlikely because of the small concentrations of the radicals involved and the probable instability of the radical $C_2H_5N_2$.

If we assume that the dissociation of an activated molecule of azoethane always proceeds to completion with liberation of a molecule of nitrogen, and that nitrogen is produced by no other process, we may estimate the minimum mean life-time of an activated azoethane molecule by comparison of the number of molecules activated with the number of molecules of nitrogen produced, together with assumptions as to the rate of the process of collisional deactivation.

By the method of the stationary concentration of the activated molecule Φ can be related to k_1 and k_2, the rate constants of dissociation and deactivation, and the concentration of azoethane by the equation

$$\frac{1}{\Phi} = 1 + \frac{k_2}{k_1}(C_2H_5N{=}NC_2H_5)$$

A least-squares fit of the data was made for $1/\Phi$ *versus* the concentration of azoethane, which was expressed in moles per liter. The graph of these data is shown in Fig. 1. [It should be noted that at concentrations of 0.037 and 0.070 mole per liter the experiments were performed at a higher temperature. Since the concentration is inversely proportional to the temperature and the frequency of collision is directly proportional to the square root of the temperature, $1/\Phi$ should be plotted *versus* concn. $\times \sqrt{T}$ to take into account the temperature differences. For the relatively small temperature range covered, however, it may be shown that this correction is negligible in view of the scattering of the data.]

The equation of the straight line is

$$1/\Phi = 0.822 + 9.704 \text{ (azoethane)}$$

The slope is given in units of liter-moles^{-1} and the concentration of azoethane in moles-liter^{-1}. A numerical value is thus obtained for the ratio of the two rate constants k_2/k_1.

The rate constant for deactivation, k_2, may be calculated simply from the collision theory on the assumption of zero activation energy; then $k_2 = ZQ$. Z is the collision frequency for the collisions $A + A^*$, and Q the collision efficiency factor. Assuming Q to be unity we may calculate values of k_2 corresponding to various assumed values of σ, the kinetic theory diameter of the azoethane molecule. From k_2 and the slope of the $1/\Phi$ curve, values of k_1 and of $\tau = 1/k_1$, the mean life of an activated azoethane molecule may then be calculated.

VALUES OF THESE QUANTITIES CORRESPONDING TO SEVERAL ESTIMATES FOR σ

σ, A	k_2, liter·moles^{-1} sec.$^{-1}$	k_1, sec.$^{-1}$	τ, sec.
7	3.9×10^{11}	4.0×10^{10}	2.5×10^{-11}
8	5.0×10^{11}	5.2×10^{10}	1.9×10^{-11}
9	6.4×10^{11}	6.6×10^{10}	1.5×10^{-11}

If the efficiency factor Q is in fact smaller than unity, the true values of k_2 and k_1 are smaller than estimated and the true value of τ is proportionately larger.

Thus, the values of τ, given above, represent the

---

[13] K. J. Ivin and E. W. R. Steacie, *Proc. Roy. Soc.* (*London*), **A208**, 25 (1951).

minimum mean life-time of an activated azoethane molecule, depending on the efficiency of deactivation by collision and the validity of the values chosen for the collision diameter of the molecule. τ may serve as a useful criterion in estimating the order of magnitude of the life-time of excited molecules in other unimolecular reactions.

We would like to thank Professor R. A. Marcus for several helpful suggestions.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Kinetics of the Decompositions of Ethyl, Isopropyl and *n*-Propyl Bromides

BY ARTHUR T. BLADES AND GEORGE W. MURPHY

RECEIVED JUNE 30, 1952

The decompositions of ethyl, isopropyl and *n*-propyl bromides have been studied in a flow system with toluene as a carrier gas. First-order kinetics are obeyed, and the conclusion is reached that the reaction is intramolecular in each case. The rate expressions are: k(ethyl bromide) $= 7.3 \times 10^{12} \exp -(52{,}300/RT)$; k(isopropyl bromide) $= 4.0 \times 10^{13} \exp -(47{,}700/RT)$ and k(*n*-propyl bromide) $= 1.0 \times 10^{13} \exp -(50{,}700/RT)$ sec.$^{-1}$. The nature of the transition state is discussed.

The decomposition of ethyl bromide has been the subject of extensive research.[1-5]

It was suggested by Goldberg and Daniels that additional evidence on which to base a mechanism for this decomposition might be provided by the toluene carrier gas technique which has been employed in this Laboratory for studying vinyl alkyl ether decompositions.[6] With an excess of toluene it should be possible to suppress chain reactions and focus attention on the intramolecular decomposition.[7]

Recent reports on the decompositions of isopropyl and *n*-propyl bromides have suggested that the same technique could assist in establishing these mechanisms also. Maccoll and Thomas[8] proposed an intramolecular mechanism for the pure isopropyl bromide decomposition but the reaction is complicated by a falling off of the rate constant in the latter stages. They attribute this to the reverse reaction. Agius and Maccoll[9] found that the decomposition of *n*-propyl bromide conformed best to a 3/2-order rate expression. They proposed a free radical type mechanism involving the initial break of the C–Br bond.

The present technique does not in itself enable us to analyze the sometimes complex kinetics in the decomposition of the pure bromides, but it does provide a means for isolating the intramolecular reaction. We shall show that the kinetics of all three decompositions under these conditions are similar.

Experimental

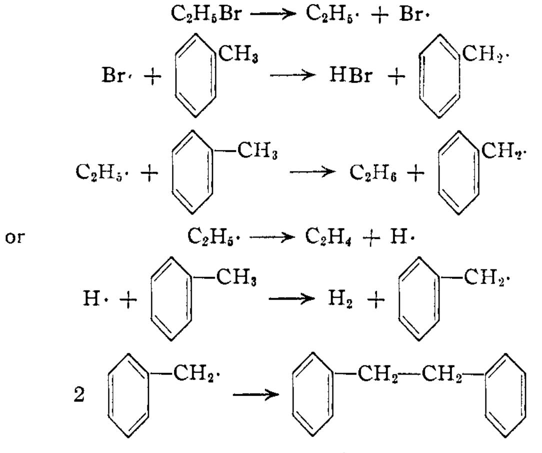
The apparatus is essentially the same as that described previously.[6] The aluminum block of the furnace has been replaced by an aluminum bronze block and the Pyrex reaction tube by a quartz tube of approximately the same dimensions. These changes were made in order to allow higher temperature studies.

The products of the pyrolyses were condensed in a liquid air trap and the course of the reaction followed by the amperometric titration of HBr. In the case of ethyl bromide, quantitative correspondence between the two products HBr and ethylene was checked by volumetric determination. In the other decompositions, identity of the propylene was established by infrared analysis but its total quantity was not determined.

The ethyl bromide was supplied by Dr. A. Goldberg from the same batch used in his own researches.[5] The isopropyl and *n*-propyl bromides were prepared by the method in reference 10 and were purified by fractionation in a 13-plate metal packed column. The isopropyl bromide boiled at 58.2° (745 mm.) and the *n*-propyl bromide at 70.0° (745 mm.).

Analytical Results and the Reaction Mechanism

Ethyl Bromide.—The products of this decomposition in the presence of toluene proved to be ethylene and HBr. If the reaction proceeded through a free radical mechanism, other products would be



expected. No hydrogen, ethane or dibenzyl nor any other products than ethylene and HBr were found. It must be concluded therefore that the reaction is intramolecular.

Isopropyl and *n*-Propyl Bromides.—If these decompositions proceeded through a radical mechanism in the presence of toluene, the products should include dibenzyl and one or more from the group hydrogen, methane, ethylene and propane, as may be shown by a reaction series similar to that of the

---

(1) E. T. Lessig, *J. Phys. Chem.*, **36**, 2335 (1932).

(2) E. L. Vernon and F. Daniels, THIS JOURNAL, **55**, 922 (1933).

(3) P. Fugassi and F. Daniels, *ibid.*, **60**, 771 (1938).

(4) F. Daniels and P. L. Veltman, *J. Chem. Phys.*, **7**, 756 (1939).

(5) A. Goldberg and F. Daniels, forthcoming publication.

(6) A. T. Blades and G. W. Murphy, THIS JOURNAL, **74**, 1039 (1952).

(7) During the course of this research Prof. Daniels received a communication from Prof. M. Szwarc reporting results on ethyl bromide from his laboratory which agree substantially with ours.

(8) A. Maccoll and P. T. Thomas, *J. Chem. Phys.*, **19**, 977 (1951).

(9) P. Agius and A. Maccoll, *ibid.*, **18**, 158 (1950).

(10) Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 25.