Appendix

Errors in Activation Enthalpies and Entropies.—The Arrhenius activation energy is given by

$$\Delta E_a = \frac{RT_1T_2 \ln (k_2/k_1)}{T_2 - T_1}$$

Consider the errors (or precision measures) of k_2 and k_1 as $\pm r_2$ and r_1, respectively. Then

$$\ln (k_2 \pm r_2) = \ln \left[k_2 \left(1 \pm \frac{r_2}{k_2}\right)\right]$$

but r_2/k_2 is small compared to one so

$$\ln (k_2 \pm r_2) = \ln k_2 \pm r_2/k_2$$

and similarly for k_1 and r_1. Thus the Arrhenius activation energy becomes

$$\Delta E_a = \frac{RT_1T_2}{T_2 - T_1} \ln (k_2/k_1) \pm \frac{RT_1T_2}{T_2 - T_1} [(r_2/k_1)^2 + (r_1/k_2)^2]^{1/2}$$

The second term in this equation is the statistical error in the activation energy. Consider, for example, the temperature interval 25-35°. The term $RT_1T_2(T_2 - T_1)$ has the numerical value of 18,260 cal. mole^{-1} and thus errors of 1% in both k_2 and k_1 will lead (irrespective of the values of k_2 and k_1) to errors in ΔE_a of ± 256 cal. mole^{-1}. Two per cent. errors in both k_2 and k_1 lead to twice as great an error in ΔE_a (± 512), 3% three times (± 768), etc. The error may be decreased by increasing the temperature interval (provided the Arrhenius eq. is followed). Thus a 20° interval instead of a 10° interval (at about the same mean temperature) will give essentially half the error, a 30° interval one-third, etc. It is to be noted that the statistical error does not give the maximum error. Thus in the example cited above appropriately distributed errors of 1% will lead to a maximum error of ± 365 cal. mole^{-1}. In as much as it is not uncommon to find rate data reported in the literature as accurate to 5%, it is apparent from this discussion that differences in energies of activation obtained from a 10° interval (near room temperature) are commonly insignificant (*i.e.*, within experimental error) unless greater than 1.5 kcal. The inherent difficulty in obtaining precise enthalpies of activation is particularly well emphasized when one considers that if other factors were equal this 1.5 kcal. factor would introduce better than one power of ten difference in rates. The entropy of activation and its statistical error is given by

$$\Delta S^\ddagger = \frac{RT_2 \ln k_2 - RT_1 \ln k_1}{T_2 - T_1} - R \ln \frac{kT}{h} - R \pm \frac{R}{T_2 - T_1} \sqrt{\left(T_2 \frac{r_2}{k_2}\right)^2 + \left(T_1 \frac{r_1}{k_1}\right)^2}$$

The above discussion applies as well to equilibrium constants, enthalpy and entropy changes and their errors.

STATE COLLEGE, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

The Photolysis of Acetaldazine

BY R. K. BRINTON

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The products of the photolysis of acetaldazine have been investigated at 30, 100 and 170°, over the wave length region 3340 to 2380 Å. These products listed in order of their importance are acetonitrile, ammonia, nitrogen, methane, ethane and 2-butene. In order to explain the variation of the quantum yields with experimental conditions it is necessary to propose several primary mechanisms, the two most important being $CH_3CH{=}N{-}N{=}CHCH_3 + h\nu \rightarrow CH_3CN + CH_3CH{=}NH$ (2), $CH_3CH{=}N{-}N{=}CHCH_3 + h\nu \rightarrow CH_3 + CH{=}N{-}N{=}CHCH_3$ (3). The large amounts of acetonitrile ($\Phi \sim 0.5$ at longer wave lengths) are apparently formed exclusively by (2) along with ethylidineimine which evidently forms a linear type addition polymer capable of liberating part of its nitrogen as ammonia either in the system or at the low pressures used in the collection procedures. The methyl radicals liberated in (3) may abstract hydrogen atoms from the azine to form methane, combine to form ethane, or initiate a radical polymerization by addition to the conjugated azine molecule. The 2-butene and some of the nitrogen produced must be the result of $CH_3CH{=}N{-}N{=}CHCH_3 + h\nu \rightarrow N_2 + CH_3CH{=}CHCH_3$ although the nitrogen is always considerably in excess of the 2-butene and appears to be a product of some radical reaction especially at high temperatures.

The Photolysis of Acetaldazine.—Evidence that the ethylidene biradical, CH_3CH, enters into the thermal and photochemical decomposition mechanism of diazoethane has been given in two previous papers.[1,2] Since it is probable that isomerization is slow enough to allow formation of 2-butene by a radical combination reaction, a more detailed study of the reactions of the ethylidene radical would be of interest. Inasmuch as considerable difficulty was encountered with the unstable and sometimes explosive diazoethane, another means of generating ethylidene radicals would be desirable. Such a possibility is suggested by the photolysis of acetaldazine if a primary step such as

$$CH_3CH{=}N{-}N{=}CHCH_3 + h\nu \longrightarrow 2CH_3CH + N_2 \tag{1}$$

occurs. Although this reaction is no more than 30 kcal. endothermic, several preliminary photolyses showed that it did not occur to any appreciable extent. The main decomposition products were identified as acetonitrile and ammonia. In view of these unexpected results the study of the photolysis of acetaldazine was carried out in some detail.

Experimental

Acetaldazine was prepared from acetaldehyde and hydrazine hydrate according to the method described by

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[1] D. H. Volman, P. A. Leighton, F. E. Blacet and R. K. Brinton, *J. Chem. Phys.*, **18**, 203 (1950).

[2] R. K. Brinton and D. H. Volman, *ibid.*, **19**, 1394 (1951).

Curtius and Zinkeisen.[3] Following an initial simple distillation to eliminate the ether extraction solvent, the product was fractionated in a column of about ten theoretical plates at the reflux ratio used. The fraction boiling at 96.3 to 97.0° (uncorrected n^{24}_{D} 1.4400) was stored over anhydrous calcium oxide.

Figure 1 shows molar extinction coefficients of acetaldazine in hexane as measured on a Beckman Model DU ultraviolet spectrophotometer. Qualitative measurements of the gas phase absorption made on a large Bausch and Lomb Littrow spectrograph did not reveal any banded structure which may have been concealed in the liquid phase determination.

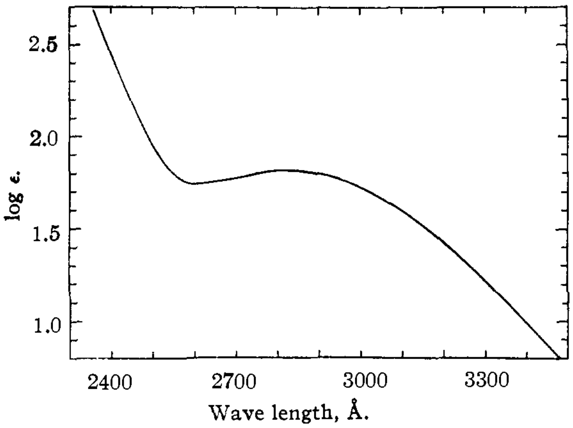

Fig. 1.—The molar extinction coefficients of acetaldazine in hexane solvent.

All irradiations were made with a 500-watt A. C. Hanovia Type A medium pressure arc stabilized by Amperex ballast tubes and an electronic voltage regulator. Monochromatic light used in the various photolyses was obtained from the arc by use of crystal quartz monochromator. Uranyl oxalate actinometry and integration methods using a thermopile measuring circuit[4] were used to measure the light intensities.

The majority of the photolyses at 30° were conducted in a cylindrical silica cell 31 mm. diameter by 247 mm. long. A similar cell (197 mm.) enclosed in a 210-cm. aluminum sleeve wrapped with chromel resistance wire served for that series of photolyses in which the temperature was varied. In all cases the light beam from the monochromator essentially filled the cell volume.

The products of the photolyses which were measured in the gas phase at low pressures were separated by a toepler pump into four fractions: those volatile at (a) −120°, (b) −80°, (c) −35°, and (d) 0°. A small amount of yellow polymer remained in the cell after this treatment. Each fraction was analyzed on a Consolidated mass spectrometer. The analyses of fraction (b) composed mainly of ammonia along with small amounts of acetonitrile and residual acetaldazine were of rather poor accuracy presumably because of adsorption effects. However the normalization factors of 1.0 ± 0.1 indicate that the accuracies are at least as good as +10%.

In order to obtain sufficient sample necessary for an accurate estimation of acetonitrile in mixture with the residual acetaldazine it was necessary to carry the photolyses to 4-8% completion. Since none of the products identified absorb in the spectral region under investigation and in addition, the polymer deposited on the cell window produced negligible absorption, the rather high conversion should not produce any complications.

Table I lists the experimental conditions and quantum yields of products of the acetaldazine photolyses. Positions in the table filled in by a line represent analyses that involved various experimental difficulties. Photolyses listed with two wave lengths were illuminated with the exit slit of the monochrometer opened to include two lines of the mercury arc source. A more precise technique for measuring the fraction of light absorbed was employed on all photolyses following no. 8. For earlier photolyses the quantum yield of any product relative to the yields of the other products of that same photolysis is valid but absolute quantum yields are high by an unknown amount.

The variation of quantum efficiency with intensity, wave length and temperature is shown in Figs. 2, 3 and 4, respectively. Results from photolyses 20, 26, 32 and 33 on ammonia yield as a function of temperature are not included in Fig. 4 because of the wide variation of the ammonia analyses between the two 100° experiments. This poor agreement in ammonia analyses among duplicate runs at higher temperatures was common to several other photolyses not shown in Table I and was also true to a lesser extent in the duplicate 30° runs. In spite of their poor reproducibility it seems certain that the ammonia yields do not vary to any very large degree with temperature and lie within the range 0.06 to 0.20, in the 30 to 170° region.

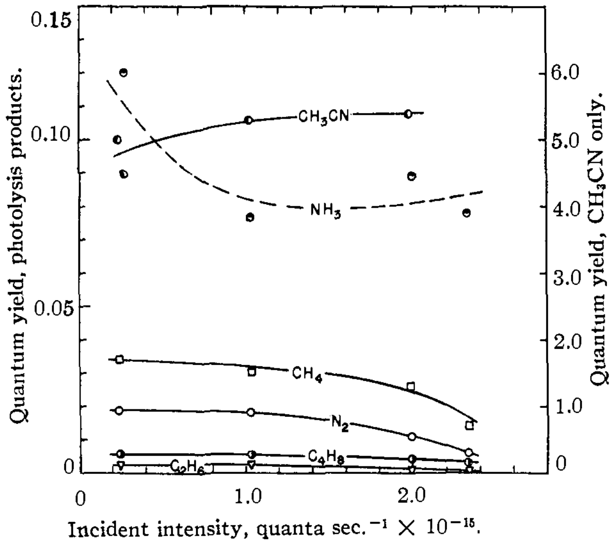

Fig. 2.—The variation in quantum yield with intensity at 30° and 3020–3130 Å. The data shown include photolyses 9, 10, 11 and 12 at 3020–3130 Å. and photolysis 16 at 3020 Å.

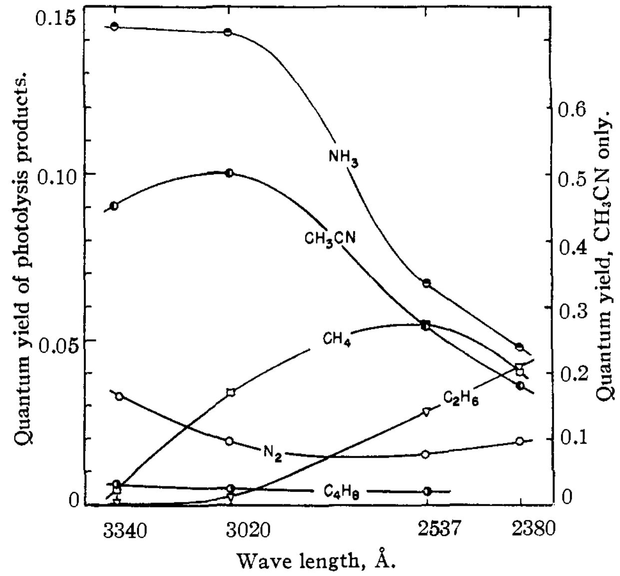

Fig. 3.—The variation of quantum yield with wave length at 30°. The intensities of photolyses 13, 14, 15 and 16 which are included in this figure vary about fourfold.

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[3] T. Curtius and E. Zinkeisen, *J. prakt. Chem.*, **58**, 325 (1898).

[4] R. K. Brinton and C. T. O'Konski, *Rev. Sci. Istr.*, **24**, 1102 (1953).

TABLE I

QUANTUM YIELDS OF PRODUCTS IN ACETALDAZINE PHOTOLYSES

Photolysis no.	Concn. azine, mole cc.$^{-1}$ × 10^6	Incident intensity, quanta sec.$^{-1}$ × 10^{-15}	Absorbed energy, quanta × 10^{-19}	Temp., °C.	Wave length, Å.	Quantum yields N_2	CH_4	C_2H_6	C_4H_8	NH_3	CH_3CN	H_2
4	1.52	0.93	4.20	27	3130	0.012	0.023	0.0055	....	0.149	0.74	0.0010
5[a]	1.95	1.82	11.2	25	3130 3020	.013	.038	.0039	0.0072	.117	.79	.0012
6[a]	1.81	0.74	10.6	26	2537 2650	.022	.111	.074	.0051	.157	.53	.0040
7	1.86	1.81	2.99	92	3130 3020	.030	.035	.0016	.0073	.181	.70	....
8	1.97	0.72	2.62	100	2537 2650	....	....	....	.0086	.131	.43	....
9	2.79	0.27	5.70	29	3130 3020	....	....	....	.0030	.121	.45	....
10	2.92	1.03	5.82	31	3130 3020	.018	.030	.0029	.0052	.077	.52	....
11	2.78	1.99	5.27	31	3130 3020	.011	.026	.0011	.0041	.089	.54	.0009
12	2 70	2 33	4.40	30	3130 3020	.0062	.014	.0010	.0034	.078	..	.0005
13	2.22	0.16	3.90	28	2380	.019	.040	.042	....	.048	.18	.0016
14	2.28	.36	7.13	28	2537	.015	.055	.028	.0040	.067	.27	.0032
15	2.31	$.08^{6}$	3.18	28	3340	.033	.0043	.0004	.0050	.144	.45	.0011
16	2.08	.24	3.74	27	3020	.019	.034	.0024	.0055	.142	.50	.0004
18[b]	1.84	.75	3.67	27	3130	.011	.0056	....	....	...	.39	....
19[c]	1.90	.77	3.84	27	3130	....	....	....	.0025	.081	.53	....
20	2.39	.71	2.74	29	3130	.015	.013	.0004	.0047	.072	.54	.0003
26	2.44	.78	2.39	98	3130	.026	.015	[e]	.0045	.201	.55	....
32[d]	2.01	.72	1.47	170	3130	.155	.031	[e]	.013	.065	.42	.0012
33	2.34	.78	2.42	102	3130	.020	.014	[e]	.0037	.113	.51	.0007

[a] *Ca.* 50% decomposition. [b] Contained added CO_2 (2.95 × 10^{-5} mole cc.$^{-1}$). [c] Contained added N_2 (3.29 × 10^{-5} mole cc.$^{-1}$). [d] A small correction was made in the yields of N_2 and NH_3 for the dark reaction at 170°. [e] Ethane yield less than 0.0001.

No attempt was made to determine a product balance on experiments carried to 4–8% completion because of the inaccuracy in determining small amounts of azine decomposed from a difference in the analyses of large amounts of azine present both before and after irradiation. Stoichiometry of the reaction is indicated by data shown in Table II for three photolyses taken to a high percentage completion.

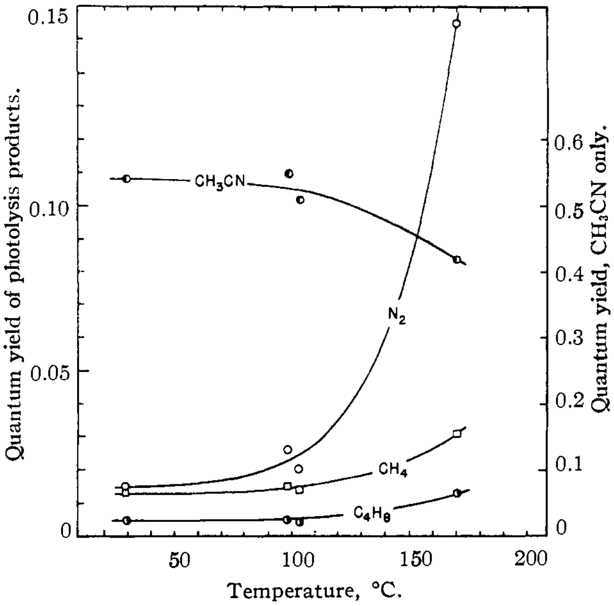


Fig. 4.—The variation of quantum yield with temperature at 3130 Å.

TABLE II

PRODUCT BALANCE OF ACETALDAZINE PHOTOLYSES

Photolysis no.	Initial azine	Substances present (moles × 10^6) Final azine	CH_3CN formed	NH_3 formed	CH_3CN plus final azine
1[a]	930	467	467	48	934
5[b]	387	156	233	35	389
6[c]	397	256	102	30	358

[a] Full mercury arc with 2 mm. Pyrex filter (primarily 3020–3130 Å.). [b] 3020–3130 radiation. [c] 2537–2654 radiation.

An investigation of the dark reaction was made at 30, 100, 170 and 250°. No thermal decomposition could be detected at 30 and 100° in periods comparable to the longest photolyses. At 170° the small amounts of nitrogen, ammonia and acetonitrile formed necessitated approximately a 10% correction in ammonia and nitrogen analyses of the 170° photolyses. Products of the rather rapid thermal reaction at 250° for a six-hour pyrolysis conducted on acetaldazine at 2.5 × 10^{-6} mole cc.$^{-1}$ contained in the shorter silica cell are: H_2, nil; N_2, 37; CH_4, 12; C_2H_4, 2.1; C_2H_6, 0.2; C_3H_6, 0.9; C_3H_8, 6; C_4H_8, 9; NH_3, 10; CH_3CN, 31 μ moles, respectively.

Discussion

It is convenient to discuss the photolysis mechanism by a consideration of the following primary reactions

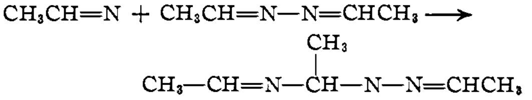
$$CH_3CH{=}N{-}N{=}CHCH_3 + h\nu \longrightarrow CH_3CN + CH_3CH{=}NH \quad (2)$$

$$\longrightarrow CH_3 + CH{=}N{-}N{=}CHCH_3 \quad (3)$$

$$\longrightarrow CH_4 + CH{=}N{-}N{=}CHCH_2 \quad (4)$$
$$\longrightarrow N_2 + CH_3CH{=}CHCH_3 \quad (5)$$
$$\longrightarrow N_2 + 2CH_3CH \quad (6)$$
$$\longrightarrow 2CH_3CH{=}N \quad (7)$$

The predominant decomposition must take place by intramolecular step (2) which at 3020 to 3340 Å. accounts for at least 90% of the azine molecules which decompose. The existence of (7) or, in fact, any other radical mechanism which produces nitrile must be considered very improbable for several reasons.

1. The data shown in Figs. 2 and 4 indicate that nitrile quantum yields are constant to within experimental error from 30 to 170° and with an intensity variation of ten-fold. This behavior is characteristic of an intramolecular primary dissociation but not consistent with a secondary radical reaction mechanism whereby the $CH_3CH{=}N$ radical may either form acetonitrile or add to the conjugated acetaldazine molecule.



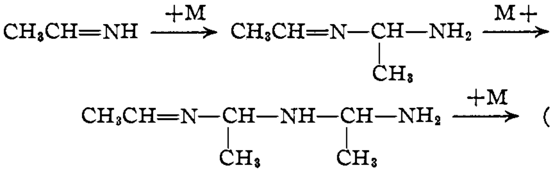
$$CH_3CH{=}N + CH_3CH{=}N{-}N{=}CHCH_3 \longrightarrow CH_3{-}CH{=}N{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}N{-}N{=}CHCH_3 \quad (8)$$

If the activation energy of reaction 8 is similar to the 3 to 5 kcal./mole[5] reported for radical addition to butadiene, this addition reaction would compete strongly with acetonitrile forming processes such as disproportionation of $CH_3CH{=}N$ radicals, donation of a hydrogen atom by this radical to acetaldazine, and decomposition of $CH_3CH{=}N$ to liberate hydrogen atom.

2. Stoichiometrical relations given in Table II indicate that 3020–3130 Å. radiations produce very nearly one acetonitrile molecule per acetaldazine molecule decomposed whereas 2537–2650 Å. radiations yield only 70% as much nitrile as would be predicted on a similar basis. Although a disproportionation between $CH_3CH{=}N$ radicals could well explain the long wave length stoichiometry, any reaction *via* path (8) would vary the one to one correspondence between the nitrile formed and azine decomposed. The discrepancy at short wave lengths probably reflects the effect of other primary reactions rather than a disappearance of azine by polymerization initiated by (8).

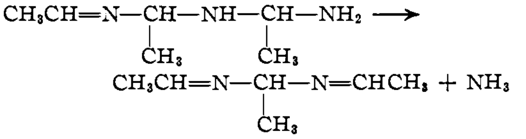
Reaction intermediates homologous to ethylidineimine produced in (2) have been proposed in decomposition reactions of methyl[6] and *t*-butylamines.[7] This molecule must play an important role in the production of ammonia by some rearrangement or polymerization reaction and, in fact, evidence for existence of small amounts of the monomeric form was obtained in the −80° (b) fractions. Many of these spectra contained a substance whose parent mass was apparently 43 but whose spectrum did not agree with that of ethylenimine, the stable isomer of this mass.

A possible polymerization reaction of ethylidine monomer is illustrated by the following mechanism in which M represents the monomer molecule



$$CH_3CH{=}NH \xrightarrow{+M} CH_3CH{=}N{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}NH_2 \xrightarrow{M+} CH_3CH{=}N{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}NH{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}NH_2 \xrightarrow{+M} \quad (9)$$

Such a mechanism leading to a linear trimer of ethylidineimine is favored because of evidence obtained by Aschan[8] on the structure of the dehydrated form of the acetaldehyde–ammonia complex salt which indicated that this trimer lost NH_3



$$CH_3CH{=}N{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}NH{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}NH_2 \longrightarrow CH_3CH{=}N{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}N{=}CHCH_3 + NH_3 \quad (10)$$

under rather mild conditions to form hydacetamide. Although the actual mechanism for formation of ammonia has not been investigated in detail, its production is consistent with a mechanism whereby ethylidine is formed by (2), polymerized by a reaction similar to (9), and ammonia subsequently liberated by (10). Compounds containing at least four to six monomer units probably make up the majority of the polymerized product inasmuch as reaction 10 allows the liberation of one molecule of ammonia per chain. A substantial fraction of the ammonia obtained as a final product may not have been present as such in the photolysis cell, but rather may have been liberated by decomposition of various linear polymers of ethylidine imine at the low pressures obtained by the toepler pumping used to separate the product fractions. Evidence that the polymer had not been decomposed to ammonia in the reaction system at 30° and 3020–3130 Å. can be obtained from the data of Photolyses 1 and 5 which were carried to more than 50% completion. The pressure change in the cell during the irradiation was essentially zero for both of these trials although the production of ammonia and small amounts of other gases shown in Tables I and II would require a pressure increase of 15 to 20%.

The quantum yield of ethane production is very low in all photolyses except those at 30° in the short wave length region. In consideration of the nature of the acetaldazine system it is reasonable to assume that ethane is formed by combination of methyl radicals. These methyl radicals may combine, add to azine by reaction 8, or produce methane by abstraction

$$CH_3 + CH_3CH{=}N{-}N{=}CHCH_3 \longrightarrow CH_4 + CH_2CH{=}N{-}N{=}CHCH_3 \quad (11)$$

The behavior of the ethane and methane quantum yields shown in Fig. 3 is indicative that such a mechanism is responsible for the majority of the methane formed. In view of the increase in both methane and ethane and the decrease in acetonitrile at the short wave lengths, reaction 3 must be replacing process (2) to a considerable extent. The effect of this replacement is evident in the pressure changes occurring in the photolyses at

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[5] L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 474 (1954); D. H. Volman and W. M. Graven, THIS JOURNAL, **75**, 3111 (1953).

[6] O. C. Wetmore and H. A. Taylor, *J. Chem. Phys.*, **12**, 61 (1944).

[7] H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 546 (1954).

[8] O. Aschan, *Ber.*, **48**, 875 (1915).

TABLE III

VARIATION OF $R_{CH_4}R_{C_2H_6}^{-1/2}(Az)^{-1}$ WITH WAVE LENGTH AT 30°

Photolysis no.	13	14	16	10	11	12	4	2	15
Wave length, Å.	2380	2537	3020	3020 3130	3020 3130	3020 3130	3130	3130	3340
R_{CH_4} (mole sec.$^{-1}$ × 10^{11})	1.03	3.29	1.32	4.46	7.67	4.83	2.83	1.31	.061
$R_{C_2H_6}$ (mole sec.$^{-1}$ × 10^{11})	1.09	1.68	0.093	0.433	0.313	0.334	0.020	0.026	0.006
$R_{CH_4 \cdot C_2H_6}R^{-1/2}(Az)^{-1}$ (cc. mole$^{-1/2}$sec.$^{-1/2}$)	1.41	3.53	6.6	7.3	15.6	9.4	42	11	1

30° since a decrease in the pressure of the system may be associated with the radical induced polymerization of acetaldazine. At higher intensities and longer wave lengths the photolyses occurred at essentially constant pressure. A decrease in either the radiation intensity or wave length caused small pressure decreases (*ca.* 10% in the extreme cases) to take place during the course of the photolyses (4–8% conversion). The smaller reaction pressure differentials and lower methane quantum yields (Fig. 2) which occurred at higher light intensities are characteristic of a chain mechanism terminated by a second-order radical combination.

One additional confirmation of the existence of the methyl radical mechanism is furnished by the increase in methane quantum yield and the apparent disappearance of ethane as a product at 100 and 170° as is shown in Fig. 4 and Table I. It seems reasonable that reaction 11 would have an activation energy of 7 to 8 kcal./mole similar to other olefinic reactions.[9] The relatively greater role played by the abstraction mechanism at higher temperatures as compared to that of the low activation addition reaction and the methyl radical combination reaction of about zero activation energy[10] is to be expected.

Although the preceding discussion has shown that methane and ethane formation is in qualitative agreement with a methyl radical reaction scheme, another mechanism, probably intramolecular, must produce at least a small part of the methane. If all the ethane were formed by methyl radical combination and (11) represents the only mode of methane production, the ratio,[11] $R_{CH_4} \cdot R_{C_2H_6}^{-1/2}(Az)^{-1}$ should be constant at a single temperature. R_{CH4} and R_{C2H6} represent the respective rates of methane and ethane formation and (Az) the acetaldazine concentration. The values of this ratio for photolyses at 30° with wave length variation from 3340 to 2380 Å. are shown in Table III.

The value of the ratio shows a marked increase in going from 2380 to 3020 Å. At still longer wave lengths the values are erratic and probably not significant because the small quantity of ethane determined in the mass spectrometric analyses in these cases was of the same order of magnitude that might be associated with the background and contamination spectra. In any event some other process such as (4) for methane production in addition to abstraction by methyl radical must be active at least in the long wave length region and perhaps to a smaller extent with the shorter radiations.

Two reactions, (5) and (6), offer possible although not altogether satisfactory explanations of the formation of 2-butene and nitrogen. The small yields of 2-butene given in Table I and Figs. 2, 3 and 4 are constant to within experimental error for all photolyses at 30 and 100° but a somewhat higher value was obtained in photolysis 32 at 170°. This increase is apparently real since it was duplicated in two trials not shown in Table I. It is difficult to explain uniform yields unless a primary process such as (5) acts to produce the 2-butene and a corresponding amount of nitrogen. The increased yield at 170° could well occur as a consequence of the shifting in the relative probabilities of the primary reactions by the increased internal energy of the azine molecule at higher temperatures. In contrast to the behavior of 2-butene, nitrogen yields decrease with increase in intensity, have a minimum at about 2800 Å., and increase strikingly at 170° to an extent which approaches the product distribution of the 250° dark reaction. In addition the ratio of the nitrogen to 2-butene quantum yields is always above two at 30°, about five at 100°, and greater than ten at 170°. These characteristics point to a radical type mechanism for the formation of nitrogen in addition to process (5) but it is doubtful whether reaction (6), the ethylidine radical source originally sought, plays any important role in the over-all photolysis.

Acknowledgments.—The author wishes to express his indebtedness to Dr. Amos Newton and Mr. Herbert Di Grazia of the Radiation Laboratory, University of California, Berkeley, for their assistance in conducting mass spectrometric analyses. He also expresses his appreciation to the Research Corporation for financial aid to the investigation.

DAVIS, CALIFORNIA

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[9] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 169 (1951).

[10] R. Gomer and G. B. Kistiakowsky, *ibid.*, **19**, 85 (1951).

[11] This test was used by (a) L. M. Dorfman and W. A. Noyes, Jr., *ibid.*, **16**, 557 (1948), on acetone photolysis. For subsequent application see (b) A. F. Trotman-Dickenson, *Quart. Rev.* (*London*), **7**, 198 (1953).