

water, extracted with ether and the ether evaporated at room temperature. The residue was dissolved in 10 cc. of benzene. To this solution was added a solution of 500 mg. of chromic anhydride in 15 cc. of 80% acetic acid, and the mixture stirred for five hours at room temperature. The benzene layer was washed with water and the solvent evaporated. The residue was dissolved in 20 cc. of glacial acetic acid and the solution heated on the steam-bath for thirty minutes with 2 g. of zinc dust. The solution was decanted into water and the precipitated solid extracted with ether. After washing with dilute sodium carbonate solution the ether was evaporated and the residue crystallized from acetone to give white needles, m. p. 125–126°.

*Anal.* Calcd. for  $C_{27}H_{44}O$ : C, 84.3; H, 11.5. Found: C, 84.3; H, 11.7.

**3-Acetyl-4-hydroxy-cholesterol.**—A mixture of 50 g. of cholesteryl acetate in 250 cc. of benzene was oxidized with a solution of 20 g. of selenium dioxide in 500 cc. of 98% acetic acid as described in a previous paper for sitosteryl acetate. The product was crystallized from acetic acid and after treatment with Norite it was crystallized from methanol to give white needles, m. p. 163–165°.

*Anal.* Calcd. for  $C_{29}H_{48}O_3$ : C, 78.3; H, 11.1. Found: C, 78.2; H, 10.9.

The acetic acid filtrate from the above initial crystallization upon standing deposited pale tan plates. After

treatment with Norite and crystallization from methanol-ether the product formed white plates, m. p. 189–191°. The mixture with the product of m. p. 163–165° melted over an intermediate range of 163 to 184°.

*Anal.* Calcd. for  $C_{29}H_{48}O_3$ : C, 78.3; H, 11.1. Found: C, 78.3; H, 11.0.

Both polymorphic forms yielded the diacetate of 4-hydroxycholesterol, m. p. 162–163°, on refluxing with acetic anhydride. Hydrolysis of both forms with ethanolic potassium hydroxide yielded 4-hydroxycholesterol, m. p. 174–175°.

### Summary

Reduction of 7-ketocholesterol derivatives with hydrogen and Adams catalyst in neutral medium tends to reduce the ethylenic linkage, yielding a saturated 7-keto compound.

$\Delta^{5,6}$ -Cholestenol-7 has been prepared by the reduction of 7-hydroxycholesteryl chloride with sodium and amyl alcohol.

The preparation of 4-hydroxycholesteryl acetate by the oxidation of cholesteryl acetate with selenium dioxide is reported.

STATE COLLEGE, PENNA.

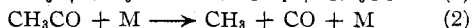
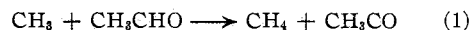
RECEIVED JULY 7, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

## The Photolysis of Azomethane and of Azomethane-Acetaldehyde Mixtures

BY FRANCIS E. BLACET AND ALVIN TAUROG

Several investigators are in agreement that at elevated temperatures the thermal<sup>1,2</sup> and photochemical<sup>3,4</sup> decomposition of acetaldehyde involves the reactions



However, the evidence for these reactions in room temperature photolysis is indirect,<sup>5</sup> being based upon analyses of decomposition products, and is opposed by the experimental proof that  $CH_3CO$  is fairly stable<sup>6</sup> below 60°, as well as by a rather high calculated minimum value of 17 kcal. for the energy of activation of reaction 2.<sup>7</sup> By mixing azomethane and acetaldehyde vapors at room temperature, and irradiating the mixture with  $\lambda$  3660 Å., which is not absorbed by the aldehyde but which dissociates azomethane to give free methyl

radicals,<sup>8</sup> the present authors have obtained additional information which pertains to this mechanism. A brief study has been made also of the gaseous decomposition products and the quantum yield of azomethane photolysis.

### Experimental Method

Azomethane was obtained by preparing dimethylhydrazine dihydrochloride after the manner of Hatt<sup>9</sup> and oxidizing this with cupric chloride by the method suggested by Jahn.<sup>10</sup> This oxidation process was found to be definitely superior to the potassium chromate method of Thiele.<sup>11</sup> Ramsperger's procedure<sup>12</sup> was followed in purifying the azomethane.

Radiant energy was obtained from a high pressure mercury arc and a quartz monochromator. The gas train was similar to that which has been described<sup>13</sup> except that a second storage reservoir and mercury trap was added to accommodate the azomethane. This reservoir was pro-

(1) Rice and Herzfeld, *THIS JOURNAL*, **56**, 284 (1934).

(2) Allen and Sickman, *ibid.*, **56**, 1251 (1934).

(3) Leermakers, *ibid.*, **56**, 1537 (1934).

(4) P. A. Leighton, *J. Phys. Chem.*, **43**, 749 (1938).

(5) Blacet and Volman, *THIS JOURNAL*, **60**, 1243 (1938).

(6) Spence and Wild, *J. Chem. Soc.*, 352 (1937).

(7) E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

(8) Burton, Davis and Taylor, *THIS JOURNAL*, **59**, 1038 (1937).

(9) Hatt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Vol. XVI, 1936, p. 18.

(10) Jahn, *THIS JOURNAL*, **59**, 1761 (1937).

(11) Thiele, *Ber.*, **42**, 2575 (1909).

(12) Ramsperger, *THIS JOURNAL*, **49**, 912 (1927).

(13) Leighton and Blacet, *ibid.*, **54**, 3165 (1932).

tected from the light of the room, and was kept at  $-80^{\circ}$  to diminish photodecomposition of the vapor by stray light and to reduce the vapor pressure enough to allow mercury traps of moderate length to be used.

The gaseous decomposition products were determined by the Blacet-Leighton method of microanalysis. Residual azomethane vapor in the gas was removed with a sintered glass bead containing 12 *N* hydrochloric acid, followed by solid potassium hydroxide. The alkali also removed residual acetaldehyde. Fuming sulfuric acid was used to test for unsaturated hydrocarbons, silver oxide for carbon monoxide, copper oxide and potassium hydroxide at approximately  $300^{\circ}$  for hydrogen, and saturated hydrocarbons were removed by combustion with a hot platinum coil.<sup>14</sup> The percentage nitrogen was calculated from the difference in volume of a sample taken for analysis and the sum of the volumes of the other gases found present.

Quantum yields for pure azomethane decomposition were determined in essentially the same manner as previously described for aldehyde photolysis<sup>13</sup> except that calculations were made in two different ways, one based on the pressure change in the system and the other based on the free nitrogen produced in the reaction. Special care was taken to exclude atmospheric nitrogen from the reaction system and the storage reservoirs by flushing them with carbon dioxide several times and evacuating by means of a Toepler pump. Possible residual carbon dioxide was removed from the gaseous decomposition products in the same operations which took out the excess azomethane. All photochemical experiments were performed at  $30^{\circ}$  and with the wave length 3660 Å.

The absorption spectrum of azomethane vapor was taken using a model E-316 Hilger spectrograph and a hydrogen discharge as the radiation source.

### Experimental Results

The azomethane made by the cupric chloride method was water white in the liquid state. A column of the vapor 40 cm. in length, having a pressure of 300 mm. at  $22.5^{\circ}$ , gave continuous absorption between  $\lambda$  3020 and 3850, with a maximum at 3380 Å. A second region of continuous absorption began at  $\lambda$  2570 and extended to shorter wave lengths. In agreement with Ramsperger,<sup>15</sup> no discontinuous absorption was observed at lower pressures.

In a Paneth type experiment azomethane was found to remove tellurium mirrors readily when irradiated with  $\lambda$  3660.<sup>16</sup>

**Azomethane.**—The apparatus used in this work was equipped with thermopile and galvanometer for energy measurements and although the primary object of the investigation

(14) Blacet and Volman, *Ind. Eng. Chem., Anal. Ed.*, **9**, 44 (1937).

(15) Ramsperger, *THIS JOURNAL*, **50**, 123 (1928).

(16) The authors are indebted to Professor P. A. Leighton and the Chemistry Department of Stanford University for the Paneth apparatus and to Mr. D. H. Volman for performing the experiments with it.

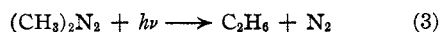
was to study azomethane-acetaldehyde mixtures, a few quantum yield determinations of pure azomethane photolysis were made. This seemed especially worth while since the two previous quantum yield studies are in disagreement: Ramsperger<sup>15</sup> having reported a value of approximately 2 while Forbes, Heidt and Sickman<sup>17</sup> have given yields approaching unity as a maximum. In both of these cases quantum yields were based upon the experimental fact that the pressure after the complete thermal decomposition of azomethane was 2.04 times the original pressure.

In Table I are the results of analyses of the non-condensable gas produced in several runs on azomethane which differed from one another only in initial pressure. The percentages given represent the average of 2 or 3 separate analyses which differed in most cases by 5–10% from the mean value. Tests for unsaturated hydrocarbons with fuming sulfuric acid gave an average reduction in volume of less than 0.3%. No evidence for propane was found.

TABLE I  
ANALYSES OF NON-CONDENSABLE PRODUCTS FROM AZOMETHANE

Pressure, mm.	% hydrogen	% methane	% ethane	% nitrogen
13	1.5	9	40	49
31	2.5	4	39	54
32	0.5	3	40	56
49	2.0	7	33	57
57	2.0	7	38	53
80	3.0	9	32	56
Average %	1.9	6.5	37	54

Quantum yields,  $\Phi$ , were determined in the four cases listed in Table II. The run at 13 mm. should be discounted with respect to the others since at very low pressures experimental errors may be very large. The third column in this table gives the yield calculated from the pressure change in the reaction system assuming the overall reaction



The yield in the fourth column was calculated from the nitrogen produced, the assumption be-

TABLE II  
QUANTUM YIELDS OF AZOMETHANE PHOTOLYSIS

Pressure, mm.	$\Delta P$ , mm.	$\Phi$ calcd. from $\Delta P$	from $\text{N}_2$
13	0.67	0.37	0.59
49	1.01	.70	0.97
57	1.01	.71	1.1
80	0.93	.85	1.1

(17) Forbes, Heidt and Sickman, *THIS JOURNAL*, **57**, 1935 (1935).

ing that one molecule of nitrogen was formed per decomposition process irrespective of secondary reactions.

**Azomethane-Acetaldehyde Mixtures.**—The first few runs in which the azomethane pressure was about one-half to one-third the acetaldehyde pressure gave no carbon monoxide in the photolysis products. However, by going to lower ratios appreciable amounts of carbon monoxide were found as shown in Table III. The percentages given are of the non-condensable gas in each case. Complete analyses of the gas were not made in these experiments.

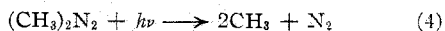
TABLE III  
CARBON MONOXIDE AND HYDROGEN FROM PHOTOLYSIS  
OF AZOMETHANE-ACETALDEHYDE MIXTURES

Azomethane pressure, mm.	Acetaldehyde pressure, mm.	% CO	% H <sub>2</sub>
139	501	0.7	4.6
98	500	.9	4.7
66	505	.2	8.1
48	501	2.5	3.6
25	427	4.0	2.5
14	501	6.8	1.0
7.5	487	11.6	3.0
3.0	503	14.3	2.2

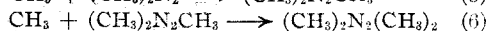
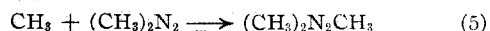
### Discussion of Results

**Azomethane Photolysis.**—The removal of tellurium mirrors in the Paneth experiment indicates that some free radicals are produced at room temperature when azomethane is irradiated with  $\lambda 3660$ ; however, the experiments were qualitative and do not exclude the possibility of partial dissociation directly into stable molecules. The formation of radicals in the thermal dissociation had previously been demonstrated.<sup>18,19</sup>

The average of 54% nitrogen in the non-condensable gases formed in the photolysis of azomethane is in excellent agreement with 54.7% reported by Burton, Davis and Taylor.<sup>8</sup> These authors have explained this high percentage by assuming that methyl radicals produced thus



may react with additional azomethane to give condensable products in some such manner as the following

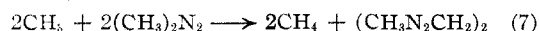


The methane percentage is also in qualitative agreement with that reported by these authors.

(18) Leermakers, *THIS JOURNAL*, **55**, 3499 (1933).

(19) Rice and Evering, *ibid.*, **55**, 3898 (1933).

Although no completely satisfactory mechanism has been given for the formation of this hydrocarbon, the over-all reaction



should be mentioned as a type of process which might occur in competition with reactions 5 and 6. Davis, Jahn and Burton<sup>20</sup> have found that nitric oxide greatly diminishes the amount of hydrocarbons produced in azomethane photolysis. They interpret this to mean that reaction 3 does not occur to an appreciable extent and have suggested that the large amount of ethane production in the absence of nitric oxide is the result of some process which follows reaction 5. If such a mechanism were to occur, one would expect the free methyl to attack the azomethane itself giving  $\text{C}_2\text{H}_6$  and  $\text{CH}_3\text{N}_2$ . Since  $\text{CH}_3\text{N}_2$  is unstable<sup>8</sup> and dissociates immediately after formation to give  $\text{CH}_3$  and  $\text{N}_2$  the net result would be a chain process for which there is no photochemical evidence at room temperature.

The possibility that reaction 3 would occur in the absence of, but not in the presence of, nitric oxide should not be ignored. If azomethane remains activated for an appreciable length of time before dissociating, as indicated by the work of Forbes, Heidt and Sickman,<sup>17</sup> it is conceivable that it would react directly with nitric oxide, thus partially suppressing both reactions 3 and 4. The initial nitric oxide pressures in the above-mentioned experiments varied from 9.9 to 20.5 mm. The small but definite percentage of hydrogen found is difficult to account for without postulating the formation of an equivalent amount of unsaturated hydrocarbons. It is possible that these were formed but escaped detection by dissolving in the 12 *N* hydrochloric acid used to remove the excess azomethane.

The evidence indicates that the quantum yield of azomethane decomposition calculated from the free nitrogen formed in the process is more reliable than the one calculated from a pressure increase in the system. If the low value obtained at 13 mm. pressure may be discounted, the yield is unity within experimental error over the pressure range 49 to 80 mm. at 30°. This is in accord with the conclusions reached by Forbes and his collaborators,<sup>17</sup> in spite of the fact that the two methods of arriving at the value of unity are not entirely consistent with each other.

It is interesting to note that if one assumes both

(20) Davis, Jahn and Burton, *ibid.*, **60**, 10 (1938).

primary processes given above and reactions 5, 6 and 7 as the only secondary reactions which occur, he can show from the percentages of methane, ethane and nitrogen given in Table I that the quantum yield given from pressure increase should be approximately 74% of that calculated from the nitrogen. Experimentally, the last three values of Table II give an average for the pressure method which is 71% of the nitrogen method. The small amount of hydrogen was ignored in this calculation.

**The Photolysis of Azomethane-Acetaldehyde Mixtures.**—Table III shows that under the proper experimental conditions azomethane will photosensitize the decomposition of acetaldehyde. It is probable that this process is initiated by free methyl radicals as indicated in reaction (1). The fact that the percentage of carbon monoxide is not appreciable until the ratio of acetaldehyde to azomethane is of the order of 10 to 1, is an additional indication that free methyls react with azomethane and that the energy of activation of this process is less than that for the aldehyde reaction. Such a conclusion is in accord with the low hydrocarbon to nitrogen ratio discussed above and also explains the failure of Burton, *et al.*,<sup>3</sup> to detect carbon monoxide in a similar experiment with a mixture of azomethane and acetaldehyde since the molecular ratio used by them was approximately 1 to 1. The hydrogen percentages found are somewhat erratic; nevertheless, they lead to the conclusion that this gas comes from the azo-

methane and not from the acetaldehyde. All of these results are consistent with reactions (1) and (2). At the same time it must be recognized that others have presented strong objections to reaction (2) as a room temperature process and it is possible that carbon monoxide was produced by reactions not considered in this discussion.

### Summary

1. The quantum yield of azomethane decomposition by  $\lambda$  3660 Å. at room temperature and in the pressure range 49 to 80 mm., has been found to be unity when calculated on the basis of the number of molecules of free nitrogen formed per quantum absorbed. Quantum yields calculated on the basis of pressure increase in the reaction system averaged 0.75. The nitrogen method is considered more reliable.

2. Analyses of the gaseous photodecomposition products of azomethane gave an average of 1.9% hydrogen, 6.5% methane, 37% ethane and 54% nitrogen. A mechanism is suggested which would account for all gases except the hydrogen.

3. It has been shown by the detection of carbon monoxide that azomethane will photosensitize the decomposition of acetaldehyde when the ratio of acetaldehyde to azomethane is greater than 10 to 1. This is interpreted as meaning that free methyl radicals produced in the photolysis of azomethane will react with either azomethane or acetaldehyde, preferably with the former.

LOS ANGELES, CALIF.

RECEIVED AUGUST 18, 1939

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Contact Potential of an Iodine Film on Tungsten

BY M. J. COPLEY AND R. W. SPENCE<sup>1</sup>

Monomolecular films of oxygen and of hydrogen on metals have been widely investigated, but little information is available about the properties of halogen films. Van Pragh<sup>2</sup> exposed a platinum surface to iodine vapor, noted its effect on the accommodation coefficient of argon on platinum, and concluded that, at a pressure of 0.027 mm., an iodine film is formed below 1565°K. Glockler and Calvin<sup>3</sup> in their determination

of the electron affinity of iodine from thermionic data taken in the presence of iodine vapor, found no evidence of adsorption of iodine on tungsten at temperatures above 2000°K. with pressures as high as  $10^{-4}$  mm. Hendricks, Phipps and Copley<sup>4</sup> measured the degree of surface ionization taking place when molecular rays of the potassium halides impinged upon a hot tungsten filament. The course of the ionization curves showed that, at temperatures below 1600°K., for the specific rate of arrival ( $4.3 \times 10^{13}$  molecules

(1) Present address: University of Illinois College of Pharmacy, Chicago, Illinois.

(2) Van Pragh, *J. Chem. Soc.*, 798 (1933).

(3) Glockler and Calvin, *J. Chem. Phys.*, **3**, 20 (1935).

(4) Hendricks, Phipps and Copley, *ibid.*, **5**, 868 (1937).