

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## THE PHOTOCHEMICAL DECOMPOSITION OF AMINES AND THE PHOTOCHEMICAL INTERACTION OF AMINES AND ETHYLENE

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In an earlier communication<sup>2</sup> the photochemical interaction of ethylene and ammonia was shown to cause the polymerization of the ethylene at room temperatures to form a liquid product. The evidence presented indicated that atomic hydrogen produced by the photodecomposition of the ammonia might be responsible for a sequence of reactions from which the liquid product resulted. One possible step in such a sequence would be the formation of ethyl radicals from atomic hydrogen and ethylene. The present work had for its object the investigation of the interaction of amines undergoing photodecomposition with ethylene. Since some of the amines have been shown to exhibit the phenomenon of predissociation and since alkyl and  $\text{NH}_2$  radicals are the probable primary products of such light absorption, it was of interest to see how far the results obtained with the ethylene-ammonia systems could be paralleled by corresponding experiments with ethylene-amine systems. The following record of this work is divided into two parts, in the first of which the products of decomposition of methyl- and ethylamine are studied and, in the second section, the nature of the reaction occurring with ethylene present is ascertained.

### Experimental Details

Ethylene and ammonia were prepared as already described. The amines were made by the action of concentrated sodium hydroxide solution on the hydrochlorides of the bases, and were purified by fractional distillation at  $-60^\circ$ , the most volatile and the least volatile fractions being rejected. The reaction vessel was a quartz bulb (12 cm. long, 3.2 cm. diameter), connected with a constant volume mercury manometer by a graded seal, reaction mixtures being prepared by admitting the gases separately up to the required pressure. All pressure measurements were made with the bulb in a water-bath at a definite temperature. Illumination was carried out with the unfiltered light of a mercury arc of the vertical type, taking a current of 2.3–2.6 amps., and with a voltage drop of 55–65 volts across it, the arc being placed either at a definite distance from the side of the reaction vessel, or opposite the quartz window ( $6 \times 2$  cm.) of the heating furnace. After the reaction, the pressure change was measured, and the pressure of gas not condensable in liquid air was determined by pumping off through a liquid air trap. Any condensable gas from the dead space was frozen out and returned to the reaction bulb before measuring the residual pressure. The unchanged amine was estimated by distilling in vacuum into a bulb containing 5% sulfuric acid, allowing absorption to occur, distilling back and measuring the final pressure, which was due to hydrocarbons (originally present or formed in the reaction) and water vapor.

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<sup>2</sup> Taylor and Emeleus, *THIS JOURNAL*, **53**, 562 (1931).

### Experimental Results

**The Photodecomposition of Methylamine and Ethylamine.**—Both methyl- and ethylamines were found to decompose slowly, the reaction being accompanied by an increase in pressure. A small deposit of a non-volatile liquid formed on the walls of the bulb, causing a slowing of the reaction as the liquid accumulated. Hydrogen, methane and nitrogen were produced, together with a small amount of condensable hydrocarbon. Tables I and II summarize the analytical data. All of the gas quantities are expressed in terms of the pressure exerted in the reaction system. For example, under the heading  $\Delta p_{\text{CH}_3\text{NH}_2}$ , the quantity measured is the difference between the pressure of amine taken originally and that of the amine present at the end of the reaction, as determined by acid absorption.

TABLE I

## PRODUCTS OF THE PHOTODECOMPOSITION OF METHYLAMINE

	$p_{\text{CH}_3\text{NH}_2}$ , cm.	Condi- tions	Time, hours	$\Delta p$ in reactn., cm.	$\Delta p_{\text{CH}_3\text{NH}_2}$ , cm.	$p_1$ , cm.	$p_2$ , cm.	H <sub>2</sub> , %	CH <sub>4</sub> , %	N <sub>2</sub> , %
1	19.61	125°	22	+1.40	-2.44	3.84	0.28	81	7	12
2	21.12	125°	15.75	+1.29	-2.35	3.64	.21	79	9	12
3	14.81	155°	15	+1.37	-1.85	2.93	.28	80	11	9
4	24.28	260°	18	+2.23	-3.55	5.78	.10	76	23	1

TABLE II

## PRODUCTS OF THE PHOTODECOMPOSITION OF ETHYLAMINE

	$p_{\text{C}_2\text{H}_5\text{NH}_2}$ , cm.	Condi- tions	Time, hours	$\Delta p$ in reactn., cm.	$\Delta p_{\text{C}_2\text{H}_5\text{NH}_2}$ , cm.	$p_1$ , cm.	$p_2$ , cm.	H <sub>2</sub> , %	CH <sub>4</sub> , %	N <sub>2</sub> , %
1	24.69	Arc at 1.5 cm.	16	+4.85	-4.72	9.57	1.40	88	7	5
2	19.42	140-145°	22	+2.79	-2.64	4.30	1.13	80	14	6
3	10.87	200°	3	+1.66	-1.18	2.46	0.30	72	16	12

In Tables I and II,  $p_1$  is the pressure of the non-condensable gas formed in the decomposition, and its composition is given in the last columns;  $p_2$  is the pressure of condensable hydrocarbon remaining after absorbing unchanged amine in acid. The method used to determine the amount of amine decomposed would give correct results only if no ammonia or volatile amine were produced in the reaction. It was found by fractionally distilling the product obtained by decomposing methylamine photochemically at 250° that 90% of the residual gas absorbable in dilute acid could be distilled at -80°. Besides methylamine, only ammonia, ethylamine and dimethylamine would be volatile at this temperature. These three substances would themselves undergo photochemical decomposition if present, and it is probable, also, that the decomposition of dimethylamine would cause the polymerization of ethylene, just as that of ammonia and the two other amines does. These facts appear to justify the method used in determining the amount of amine decomposed in the reaction.

In the decomposition of both amines the condensable hydrocarbon formed (recorded under  $p_2$  in the tables) was found by combustion and by absorp-

tion in bromine water to consist of more than 90% ethane. The quantity in the decomposition of methylamine is of the order of 10% of the amount of amine decomposed, while for ethylamine the amount is higher (30–40%). The liquid decomposition product is formed only in very small amounts, and no attempt was made to determine its composition directly. From the analytical data given one may calculate the following formulas for the residues: for methylamine, Expt. 1,  $C_{1.6}H_{3.2}N_{2.0}$ ; Expt. 4,  $C_{2.0}H_{3.0}N_{3.5}$ ; for ethylamine, Expt. 1,  $C_{6.0}H_{5.1}N_{4.2}$ ; Expt. 3,  $C_{3.9}H_{10.3}N_{2.2}$ . These formulas, beyond showing the very high nitrogen content of the liquid product, do not have any special significance, as there is no reason to suppose that the liquid is a simple substance. It is of interest to record that the rate at which methylamine decomposes in a static system in the presence of excited mercury is considerably greater than when the hot arc is used for illumination. This probably represents the best method of obtaining the liquid product in sufficient quantity for further investigation.

Mention may also be made of the influence of oxygen on the photochemical decomposition of the two amines. On illuminating a mixture of methylamine or ethylamine with oxygen there is a rapid reaction, the pressure decreasing at the rate of 8–12 cm. per hour with the arc at 1.5 cm. from the wall of the reaction vessel. These reactions with oxygen are probably similar to the photo-oxidation of methyl iodide.<sup>3</sup>

On heating methylamine or ethylamine alone at 250° under the conditions used in the photochemical experiments, neither underwent any appreciable thermal decomposition.<sup>4</sup> The amines were also found not to react thermally with ethylene at 250°.

**Photochemical Reaction of Methylamine and Ethylamine with Ethylene.**—The pressure of mixtures of methylamine and ethylene decreased on illumination, and the amount of non-condensable gas formed was very much less than in the decomposition of the amine alone. From this it was evident that the decomposition of the amine does not follow its normal course in the presence of the unsaturated hydrocarbon. When ethylene was illuminated alone under the same conditions (*i. e.*, with the mercury arc placed at 1–2 cm. from the surface of the reaction vessel) it polymerized, the rate of decrease of pressure being about one-third that in the presence of methylamine. It has already been shown<sup>2</sup> that this direct polymerization, due probably to light of wave length near the limit of transmission of quartz, may be eliminated by using a reaction vessel immersed in water. Since the reaction between methylamine and ethylene was still observed under these conditions, it follows that absorption of light by the ethylene is not an essential factor for its reaction with methylamine.

<sup>3</sup> Bates and Spence, *THIS JOURNAL*, **53**, 1689 (1931).

<sup>4</sup> This is confirmed by the results for ethylamine of H. A. Taylor, *J. Phys. Chem.*, **34**, 2761 (1930).

The following series of experiments was made to determine the relation between the amount of methylamine decomposed photochemically and the decrease in the pressure of the amine-ethylene mixture. In Expts. 1-6 the arc was placed at a distance of 1-4 cm. from the reaction vessel. The temperatures recorded are approximate values indicated by a thermometer placed at an equal distance with the same conditions of cooling. The remaining runs were made with the bulb in the heating furnace, and illuminated through the quartz window. Experiments in which ethylene or methylamine were illuminated alone are included for comparison.

TABLE III  
PHOTOCHEMICAL REACTION OF METHYLAMINE WITH ETHYLENE

Expt.	$p_{\text{CH}_3\text{NH}_2}$ , cm.	$p_{\text{C}_2\text{H}_4}$ , cm.	Time, hours	Temp., °C.	Total $\Delta p$ , cm.	$\Delta p_{\text{CH}_3\text{NH}_2}$ , cm.	$R$	$p_{\text{n.c.g.}}$ , cm.
1	10.65	27.16	2.2	25	- 0.92	- 1.06	0.87	0.30
2	...	29.66	2	25	- .26	...	..	..
3	9.78	29.10	8.5	100	-12.60	-5.25	2.3	2.04
4	11.58	...	6	100	+ 2.79	-4.77	..	7.13
5	...	29.34	9	100	- 4.45	...	..	1.62
6	12.89	27.56	21	150	-11.47	-2.51	4.6	0.30
7	10.42	32.66	5	165	- 8.46	-1.47	5.8	0.15
8	10.36	...	3.7	165	+ 0.78	-1.20	..	1.91
9	...	32.73	4.2	165	- 2.30	...	..	0.22
10	14.27	30.73	18.5	250	-18.28	-2.82	6.5	.71

The groups of Expts. 1, 2; 4, 5, 6; and 8, 9, 10 were made under approximately identical conditions. The figures in the last column ( $p_{\text{n.c.g.}}$ ) (*cf.* Expts. 4, 5, 6 and 8, 10) show that, in the presence of ethylene, the decomposition of the amine gave less than 10% of the amount of non-condensable gas which would normally have been formed in decomposing the amine alone. This offers a close parallel with the behavior of ammonia-ethylene mixtures, from which an equally small proportion of nitrogen and hydrogen is formed on illumination. The table shows that the amount of methylamine decomposed is approximately the same whether or not ethylene is present (*cf.* Expts. 3, 4 and 7, 8). The values tabulated under  $R$  are the ratios of the total pressure decrease in the reaction to the pressure of methylamine decomposed, as determined by absorption in acid. This ratio has a value of almost unity at room temperature, and increases with temperature to a value between 6 and 7 at 200°. In the reaction between ethylene and ammonia the corresponding ratio has a value of 5 at room temperature. Taking the total pressure decrease in the reaction as proportional to the amount of ethylene which has reacted,  $R$  then measures the efficiency of the amine in bringing about the polymerization of ethylene. Regarding the nature of the polymer very little can be said definitely. Little of the nitrogen from the amine decomposed is recovered in the free state, and most of it must be combined in the process of polymerization.

A similar thing happens in the case of ammonia-ethylene mixtures on illumination.

Similar results are obtained for the reaction of ethylamine with ethylene. Instead of the pressure increase normally observed on illuminating the amine alone, the pressure of the mixture decreases on illumination, and the amount of permanent gas formed is greatly reduced. The following table summarizes the results of these experiments.

TABLE IV  
PHOTOCHEMICAL REACTION OF ETHYLAMINE WITH ETHYLENE

Expt.	$p_{C_2H_5NH_2}$ , cm.	$p_{C_2H_4}$ , cm.	Time, hours	Temp., °C.	Total $\Delta p$ , cm.	$\Delta p_{C_2H_5NH_2}$ , cm.	$R$	$p_{n.o.g.}$
1	10.17	20.57	16	40-50	- 2.79	-1.19	2.3	0.23
2	10.28	...	15.5	40-50	+ 1.45	-0.59	...	1.27
3	10.25	21.69	6	125	- 7.19	-1.84	3.9	0.53
4	10.19	21.87	3.8	200	-10.34	-1.20	8.6	.42
5	10.87	...	2.8	200	+ 1.66	-1.18	...	2.46

All of these runs were made using the furnace. The figures in the last column again show the amount of non-condensable gas formed in the presence of ethylene to be less than 20% of the amount formed in the simple decomposition of the amine.  $R$  exhibits the same increase with increasing temperature, the value at 200° being somewhat greater than that for methylamine. The interpretation to be given to the increase of  $R$  with temperature is discussed later.

**Photochemical Reaction of Ammonia, Methylamine and Ethylamine with Ethane.**—It is of interest to record the results of some preliminary experiments in which ethane was used instead of ethylene in a series of experiments. The ethane was prepared from a cylinder of the commercial gas by washing with fuming sulfuric acid, bromine water and alkali, and fractionating. The product contained 2% of unsaturated hydrocarbon. The experiments were carried out in the same way as those with ethylene, the results being summarized in Table V.

TABLE V  
PHOTOCHEMICAL REACTION OF AMMONIA WITH ETHANE

Expt.	$p_{NH_3}$ , cm.	$p_{C_2H_6}$ , cm.	Conditions of illumination		Total $\Delta p$ , cm.	$\Delta p_{NH_3}$ , cm.	$\Delta p_{C_2H_6}$ , cm.	$p_{n.o.g.}$ , cm.
1	11.71	15.39	18 hrs.	Arc at 1.0 cm.	-0.13	-0.27	-4.23	4.37
2	11.70	...	18 hrs.	Arc at 1.0 cm.	+8.56	-8.56	...	..
3	12.50	12.67	24 hrs.	Arc at 1.3 cm.	-0.10	-0.64	-4.40	5.00
4	12.86	...	22.5	Arc at 1.3 cm.	+5.98	-5.98	...	..
5	...	12.59	24	Arc at 1.3 cm.	-0.05	...	-2.01	1.96
6	11.30	12.70	13	Arc at 1.3 cm.	+ .01	-0.53	-3.52	4.06
7	12.48	10.72	14 hrs.	Furnace 155°	+ .07	- .17	-2.39	2.58

The two following experiments were made using methylamine and ethylamine instead of ammonia.

1.  $p_{\text{C}_2\text{H}_5\text{NH}_2} = 16.03$  cm.  $p_{\text{C}_2\text{H}_6} = 12.83$  cm. Time of illumination = 16.5 hrs. with arc at 1.5 cm.  $\Delta p$  in reaction = +3.67 cm. Pressure of non-condensable gas = 11.49 cm.  $\Delta p_{\text{C}_2\text{H}_6} = -2.16$  cm.  $\Delta p_{\text{C}_2\text{H}_5\text{NH}_2} = -5.66$  cm.

2.  $p_{\text{C}_2\text{H}_5\text{NH}_2} = 10.05$  cm.  $p_{\text{C}_2\text{H}_6} = 17.43$  cm. Time of illumination = 16 hrs. with arc at 1.5 cm.  $\Delta p$  in reaction = +2.89 cm. Pressure of non-condensable gas = 8.67 cm.  $\Delta p_{\text{C}_2\text{H}_6} = 1.44$  cm.  $\Delta p_{\text{C}_2\text{H}_5\text{NH}_2} = 4.34$  cm.

From these results certain differences between the behaviors of ethane and ethylene are at once apparent. Ethane itself absorbs light (Expt. 5), giving as product a liquid of low volatility, and a small amount of gas not condensed in liquid air (probably hydrogen and methane). When ethane and ammonia are illuminated there is only a very slight change in the total pressure of the mixture, and a small amount of permanent gas, of the same order as that to be expected from the ethane decomposition, is formed. Instead of a normal decomposition of the ammonia, which is found in the reaction with ethylene, the apparent amount of ammonia decomposed is much less than that which would be observed in the absence of the hydrocarbon (of the order of 10%). This may be due to one of two causes. The ethane may absorb the light which would otherwise have decomposed ammonia, or the ammonia may have formed a volatile amine (e. g., ethylamine), which would then be estimated as unchanged ammonia on absorption in acid.

In the case of the reaction of ethylamine, and ethylamine with ethane, the same general behavior is observed. The experiments were made under conditions for which 3-4 molecules of ethylene would have polymerized per molecule of amine decomposed. Instead of this we find that the pressure of the reaction mixture actually increases. The polymerization reaction is no longer the main process when the saturated hydrocarbon replaces the unsaturated. The experiments have not been carried far enough to determine what reactions occur between the fragments formed from the primary decomposition of the two reactants.

**The Influence of Ethylene and Methylamine Pressure on the Rate of the Photochemical Reaction.**—As already pointed out, the liquid reaction products retard the reaction, so that it is impossible to measure rates over a period of time with a constant light intensity. The measurements recorded below were made in exactly the same way as those for the reaction between ethylene and ammonia,<sup>2</sup> the pressure decrease in thirty minutes after successive additions of either reactant being observed.

1. Temperature = 12°. Initial methylamine pressure = 10.96 cm.

$p_{\text{C}_2\text{H}_4}$ , cm.	2.22	5.00	12.35	25.16
$p$ in 30 min., cm.	0.44	0.35	0.35	0.35

2. Temperature = 12°. Initial ethylene pressure = 12.51 cm.

$p_{\text{CH}_3\text{NH}_2}$ , cm.	0.65	1.92	5.28	14.97
$p$ in 30 min., cm.	..10	0.14	0.31	0.29

These results show that the reaction rate is independent of the ethylene concentration over a ten-fold pressure range. At still lower ethylene pressures there must come a point at which the rate falls off. As the pressure of amine falls below a certain limit, the reaction rate falls off, due presumably to incomplete absorption of the light. These results are completely parallel with those obtained for the reaction of ethylene with ammonia.

### Discussion of Results

The small absolute amounts of reaction, over periods of hours, in the photochemical decomposition process, as contrasted with the rapid reaction when oxygen is present, indicates definitely that the photodecomposition is a process of low quantum yield. In this respect the amines parallel the case of methyl iodide recently studied by Bates and Spence,<sup>3</sup> who found quantum yields of 0.02 and 2 for the decomposition and oxidation processes, respectively. The nature of the reaction products indicates that the decomposition process is very complex. It is striking that hydrogen is formed in considerable excess of the elementary nitrogen produced. At the lower temperatures methane is a subordinate product, but elevation of temperature increases the amount received. This is to be expected, since it is now known<sup>5</sup> that the reaction  $\text{CH}_3 + \text{H}_2 = \text{CH}_4 + \text{H}$  although exothermic has an activation energy of about 8 kg. cal. The smaller yield of condensable hydrocarbons ( $\text{C}_2\text{H}_x$  and higher) with methylamine as compared with ethylamine is also in agreement with experience in the case of the corresponding iodides. With both amines the high percentage of hydrogen and methane is remarkable, indicating that even ethyl radicals break down to simpler units.

While there is a parallelism between the amines and ammonia in their capacity to induce polymerization of added ethylene, the outstanding divergence between them is that the efficiency of ammonia is marked even at room temperatures whereas that of the amines only becomes equal to that of ammonia at temperatures of 200° and upward. Two possible interpretations of these observations have been suggested. On the one hand it may be that a reaction between alkyl and ethylene requires an activation energy that is supplied thermally in the case of amines and by the exothermic interaction of hydrogen atom and ethylene to yield an activated ethyl radical in the case of ammonia as the sensitizing agent. On the other hand, it may be that, at higher temperatures, in the case of amines the increasing frequency of the reaction  $\text{CH}_3 + \text{H}_2 = \text{CH}_4 + \text{H}$  and corresponding reactions supplies atomic hydrogen to induce the polymerization process obtainable at ordinary temperatures with ammonia.

<sup>5</sup> Hartel and Polanyi, *Z. physik. Chem.*, [B] 11, 97 (1930).

### Summary

1. The photochemical decompositions of methylamine and ethylamine have been studied. Gaseous products, mainly hydrogen, methane, ethane and nitrogen and a non-volatile liquid of uncertain composition are obtained.

2. A relatively fast photoreaction between methylamine and oxygen has been observed.

3. The photodecomposition of amines is a process of low quantum yield.

4. The photodecomposition of amines induces the polymerization of ethylene. The ratio of polymerized ethylene to amine decomposed is 6-8 at temperatures of 200° and upward in contrast to ammonia, with which this ratio obtains at room temperatures.

5. The reaction rates are independent of the ethylene concentration over a range of 2-25 cm. and also independent of the amine concentration for complete light absorption.

6. Ethane appears to inhibit the normal photodecomposition of ammonia. At the same time some polymerization of the hydrocarbon occurs.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]  
**THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN  
ALUMINUM CHLORIDE SOLUTIONS**

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The cells



containing hydrochloric acid at 0.05 *M* concentration and varying amounts of aluminum chloride, and hydrochloric acid and aluminum chloride mixtures at both constant total molality and constant total ionic strength have been measured at 25°. These results supplement previous work with similar cells containing the acid in univalent and bivalent halide solutions.<sup>1</sup>

### Experimental Results

The measurements were obtained with the usual type of cell without the employment of vacuum technique. At the concentrations of acid employed, any hydrolysis of the aluminum chloride solutions was sufficiently suppressed as to have no noticeable effect. The concentrated solution of aluminum chloride was prepared from the repurified salt, and its strength determined by analysis of the chlorine content. All other

<sup>1</sup> A bibliography of the earlier results may be found in Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, 1930, 2d ed., Vol. I, p. 801.