length is similar and the reactions corresponding to reactions 8, 9 and 11 are 13, 14 and 15, respectively.

$$CH_2CO + h\nu \longrightarrow CH_2CO^* \qquad (12)$$

$$CH_2CO + CH_2CO^* \longrightarrow 2CH_2CO \qquad (13)$$

$$CH_2CO^* \longrightarrow CH_2 + CO \qquad (14)$$

$$CH_2CO^* \longrightarrow CH_2CO \qquad (15)$$

The ratio k_{13}/k_{14} for ketene is 4.7×10^4 liters/mole.[6] The close agreement of the two ratios: k_{13}/k_{14} and k_8/k_9, is indicative of the similarity of the primary processes in ketene and dimethyl ketene. An internal conversion of CH_2CO^* to the ground state is important in ketene[15] and appears to be important in dimethyl ketene. The value of k_{11}/k_9 compares well with the value of k_{15}/k_{14} which is of the order of 26 at room temperature.

A calculation of the mean life of $(CH_3)_2{=}C{=}C{=}O^*$ from the integrated absorption coefficient gives $\tau = 2 \times 10^{-6}$ second, which is longer than the mean life for CH_2CO^* which is 0.3×10^{-6} second.[6] However, a longer lifetime would be expected for $(CH_3)_2{=}C{=}C{=}O^*$ because of the extra degrees of freedom in this molecule.

Conclusion

The results reported in this paper indicate a similarity in the photochemical behavior of the three ketenes investigated so far. The primary process is wave length dependent and similar in ketene and dimethyl ketene, but secondary reactions are different. Ketene, itself, is unique in that methylene cannot isomerize to a stable molecule as can ethylidene and isopropylidene. The rate of isomerization of isopropylidene is probably faster than the rate of isomerization of ethylidene since six hydrogens are available to shift; however, there is no evidence to verify this hypothesis.

Acknowledgment.—The authors are indebted to Mr. R. Vanselow for his assistance and helpful suggestions.

LOS ANGELES, CALIF.

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(15) G. B. Porter, THIS JOURNAL, **79**, 827 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

The Photolysis of Trimethylamine[1]

BY H. GESSER, J. T. MULLHAUPT AND J. E. GRIFFITHS

RECEIVED APRIL 10, 1957

The photochemical decomposition of trimethylamine was investigated over the temperature range of −78 to 175°. The products were hydrogen, methane, ethane and a "liquid." At high temperatures the methane and ethane are primarily formed by the abstraction and recombination reactions of methyl radicals and the hydrogen is formed by a molecular reaction. At low temperatures both methane and hydrogen are probably formed by molecular elimination reactions.

Introduction

The photochemical decomposition of the amines have not been investigated in great detail. The photolysis of methylamine[2] seems complicated by the possibility of more than one primary process. The mechanism of the photolytic decomposition of dimethylamine and trimethylamine is even more uncertain. Bamford[3] had shown that the products of the photolysis of trimethylamine at 100° were hydrogen, methane, ethane and polymer. The mechanism he proposed to account for these products is

$$(CH_3)_3N + h\nu \longrightarrow (CH_3)_2N + CH_3 \qquad (1)$$

$$2(CH_3)_2N \longrightarrow (CH_3)_2NH + CH_3\dot{N}CH_2 \qquad (2)$$

$$(CH_3)_2NH + h\nu \longrightarrow (CH_3)_2N + H \qquad (3)$$

$$(CH_3)_2NH + H \longrightarrow (CH_3)_2N + H_2 \qquad (4)$$

$$(CH_3)_2NH + CH_3 \longrightarrow (CH_3)_2N + CH_4 \qquad (5)$$

$$H + CH_3 \longrightarrow CH_4 \qquad (6)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (7)$$

$$CH_3\dot{N}CH_2 \longrightarrow CH_3{-}N{=}CH_2 \longrightarrow \text{Polymer} \qquad (8)$$

This mechanism must be revised in view of the comparatively low value of 8.8 kcal.[4] for the activation

$$CH_3 + (CH_3)_3N \longrightarrow CH_4 + (CH_3)_2NCH_2 \qquad (9)$$

energy of the abstraction reaction in comparison to 7.2 kcal.[4] for reaction 5.

TABLE I

System A; Reaction time, 4.5 hr.

[TMA] molecules/cm.$^3 \times 10^{-18}$	[C_5H_{10}]	Temp., °K.	R_{CH_4} molecules/cm.^{3}/sec. $\times 10^{-12}$	$R_{C_2H_6}$	R_{H_2}	$k_4/k_7^{1/2}$ (mol./cm.^{3}/sec.)$^{1/2} \times 10^{13}$
1.61		299	0.58	1.51	0.96	3.9
1.62	1.44	298	0.50	1.46	0.72	
1.40		347	1.21	1.52	1.05	7.4
1.39	1.28	349	1.04	1.56	0.98	
1.22		398	1.99	1.79	1.55	12.2
1.22	1.22	400	2.45	1.43	1.20	
1.09		448	3.42	0.88	1.50	33.4
1.09	1.09	445	3.62	0.29	1.21	

It was believed that the mechanism could be tested by a study of the product yields in the presence of a hydrocarbon and at low temperatures where reactions requiring high activation energies would become unimportant. Cyclopentane was chosen as the hydrocarbon because its vapors did not interfere with the analysis of the products and because it has a low value for the activation energies of abstraction by hydrogen atoms, 7.7 kcal.[5] and methyl radicals, 8.5 kcal.[4]

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(1) This work was supported in part by a Naval Research Contract of the U. S. Navy and by the National Research Council of Canada.

(2) For review see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941.

(3) C. H. Bamford, *J. Chem. Soc.*, 17 (1939).

(4) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

(5) H. I. Schiff and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1 (1951).

Experimental

The experiments were performed on two different apparatuses. System A (Rochester) consisted of a reaction system similar to that used previously[6] and was free of stopcocks, mercury cut-offs being used to isolate parts of the vacuum apparatus. The light source was a Hanovia S-100 Alpine Burner. The parallel beam was collimated by one quartz lens and a stop, and was made to fill the quartz cell. The cell (volume, 50 cm.^{3}) was 2.5 cm. in diameter and 10 cm. long and was enclosed in a brass block. System B (Manitoba) was similar to that of McElcheran and Steacie[7] and consisted of a mercury-free vacuum line in which reactants were stored and the photolysis done; and an analysis line free of stopcocks utilizing mercury float valves. The two units were separated by two stopcocks and a small oil diffusion pump. The light source was a Hanovia S-500 medium pressure mercury arc. The light beam was collimated as above. The cell (volume, 130 cm.^{3}) was 2.6 cm. in diameter and 25 cm. long. The cell was designed for low temperature studies and is shown in Fig. 1. The volume of the cell and connecting tubing was 260 cm.^{3}. The low temperatures were obtained in all cases by acetone–Dry Ice mixtures. The pressures of reactants were measured by a silicon oil manometer in conjunction with a bourdon gage which was used as a null point indicator.

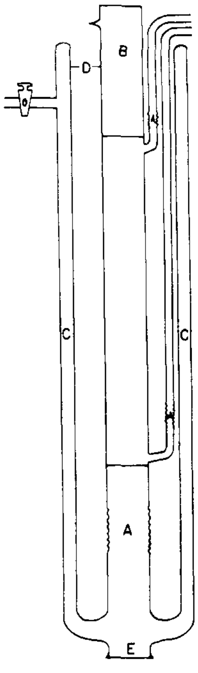

Fig. 1. Low temperature cell: A, quartz-Pyrex seals; B, vacuum jacket; C, silvered sides; D, coolant level; E, cemented quartz window.

The analyses were performed by utilizing a trap for solid nitrogen to separate the methane and hydrogen from the ethane, and a Le Roy still for fractionations. A copper–copper oxide furnace maintained at 215° was used to analyze the hydrogen. The trimethylamine was obtained from Eastman white label 25% aqueous solution. It was dried by passage through potassium hydroxide pellets and by repeated distillations from −78° and degassed at −140°. The cyclopentane was Phillips reagent grade and was used after bulb-to-bulb fractionation and degassing. The intensity of incident light was varied by means of neutral density filters of aluminum evaporated on quartz.

Degassed trimethylamine was distilled into the cell through a trap maintained at −80°. After an experiment it was observed that some gases were produced which were not volatile at −75°. These "liquid" products could not be identified but were estimated in System A to be from 10% to 50% of the hydrogen formed.

Results and Discussion

Preliminary experiments on the photolysis of trimethylamine, in which decomposition was carried to less than 1%, showed that the products were methane, hydrogen and ethane and no trace of polymer. Thus, unless dimethylamine shows very strong mercury line absorption, the reaction sequence postulated by Bamford[3] for hydrogen production must be erroneous.

The rates of formation of the products are given in Tables I and II. The results at high temperature show that in all cases the rate of hydrogen formation decreases when cyclopentane is added and would seem to indicate the absence of hydrogen atoms in the reaction system. Another possible explanation for this observed decrease in R_{H_2} (where R represents "rate of formation") is the possible quenching effect of cyclopentane on an excited trimethylamine molecule. This would seem to be important at all temperatures.

TABLE II

System B

[TMA] mole/cc. × 10^{-18}	Temp., °K.	Time, sec.	Relative incident intensity	R_{CH_4}	$R_{C_2H_6}$	R_{H_2}	$\frac{R_{C_2H_6}}{R_{H_2}+R_{CH_4}}$	$\frac{R_{H_2}}{R_{CH_4}}$
				molecules/cc./sec. × 10^{-12}				
0.20	193	1800	100	1.19	3.45	2.27	1.00	1.9
1.5	213	1800	100	1.78	3.96	1.88	1.08	1.2
0.69	210	1800	100	1.77	4.27	2.63	0.97	1.5
0.27	212	1800	100	1.67	4.15	2.99	0.89	1.8
0.11	211	900	100	1.72	4.00	2.99	0.85	1.8
1.4	213	1800	100	1.67	3.69	1.85	1.04	1.1
0.77	213	1560	100	1.48	3.65	2.37	0.95	1.6
0.92	211	1800	48	0.81	1.84	0.98	1.03	1.2
0.84	211	3600	26	0.74	1.86	1.20	0.96	1.6
0.83	212	5400	4.3	0.20	0.41	0.26	0.89	1.3

If it is assumed that methane and ethane are formed only by reactions 9 and 7, respectively, then it is possible to evaluate $E_9 - {}^1/_2E_7$ by an Arrhenius plot of the relation

$$\frac{R_{CH_4}}{(R_{C_2H_6})^{1/2}[\text{TMA}]} = k_9/k_7^{1/2}$$

(where [TMA] represents the concentration of trimethylamine). Such a plot is shown in Fig. 2 where comparison is made with the results of Trotman-Dickenson and Steacie.[4] The value of E_9 (E_7 is assumed to be zero) for the two highest temperatures is 7.1 kcal., as compared to Steacie's value of 8.8 kcal. This discrepancy is probably due to an additional step for methane formation at the lower temperature. The change in slope of the Arrhenius line rules out the alternate explanation,

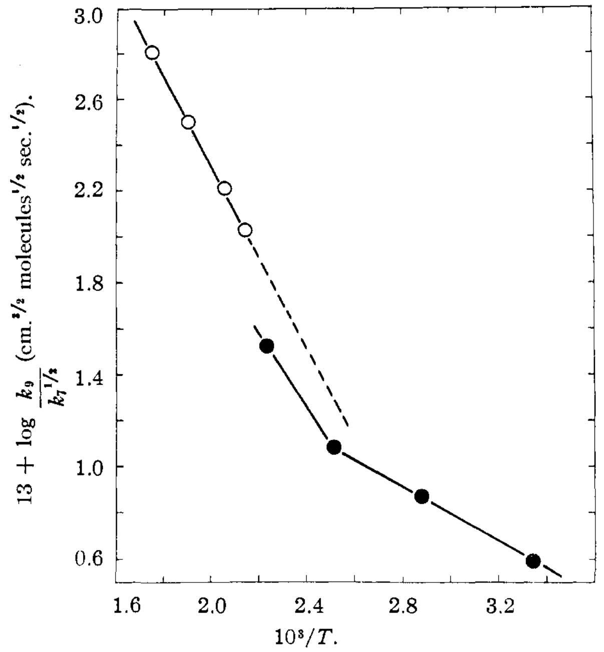

Fig. 2.—Arrhenius plot of $k_9/k_7^{1/2}$. Open circles are from the work of Trotman-Dickenson and Steacie. Filled circles represent the present work.

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(6) H. Gesser, THIS JOURNAL, **77**, 2626 (1955).

(7) D. E. McElcheran and E. W. R. Steacie, *Can. J. Chem.*, in press.

namely, an additional step for ethane formation at the high temperature. The disagreement between the intercept values may be due to strong absorption for trimethylamine (in comparison to acetone) and the consequent smaller effective volume. This also accounts for the small effects observed at low temperatures when the concentration of trimethylamine and the incident intensity were varied. Trimethylamine begins to absorb at about 2570 Å.[8] with an extinction coefficient of about 0.15×10^6 cm.^{2}/mole at 2500 Å. which increases to 1×10^6 cm.^{2}/mole at 2330 Å. and 4×10^6 at 2000 Å. These high extinction coefficients imply transmittancy values much less than 0.05% in agreement with the above conclusion.

In the presence of cyclopentane, methane can also be formed by the reaction

$$CH_3 + \text{cyclo-}C_5H_{10} \longrightarrow CH_4 + \text{cyclo-}C_5H_9 \quad (10)$$

It is possible to calculate[4] a value of E_{10} (positive for the two highest temperatures only) of 14.4 kcal. This value is about 6 kcal. too high and signifies an incomplete mechanism. A reaction sequence utilizing an excited intermediate in the primary process can account for the results

$$(CH_3)_3N + h\nu \longrightarrow (CH_3)_3N^* \quad (11)$$

$$(CH_3)_3N^* + M \longrightarrow (CH_3)_3N + M \quad (12)$$

$$(CH_3)_3N^* \longrightarrow (CH_3)_2N + CH_3 \quad (13)$$

where M is a molecule or the wall. Such a sequence is consistent with the results at low temperature where a decrease in concentration of trimethylamine from 0.27×10^{18} mol./cm.^{3} to 0.11×10^{18} mol./cm.^{3} is accompanied by a slight increase in R_{CH_4}.

At low temperature, the results (Table II) show that $R_{C_2H_6}/(R_{CH_4} + R_{H_2})$ is approximately equal to unity (0.97 ± 0.06), and that R_{H_2}/R_{CH_4} has an average value of 1.5 with a mean deviation of ± 0.24. It is reasonable to assume that reaction 9 does not occur at the low temperature. Hence if all methyl radicals react to form ethane, then the methane and hydrogen are formed by the disproportionation of the dimethylamine radical. It is therefore proposed that at low temperatures, reactions 11, 12, 13 and 7 are followed by the reaction

$$2(CH_3)_2N - \left[\begin{array}{l} \xrightarrow{k_a} H_2 + X \\ \xrightarrow[k_b]{} CH_4 + Y \end{array} \right.$$

where k_a/k_b is 1.5 and X and Y are the liquid products and perhaps dimethylamine. It is hoped that a detailed study of the reactions of the dimethylamine radical will further clarify the mechanism.

Acknowledgment.—The authors are indebted to Mr. George Ensell of the National Research Council of Canada for the construction of the low temperature cell.

WINNIPEG, CANADA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Photoreduction of Methylene Blue by Ethylenediaminetetraacetic Acid[1a,b]

BY GERALD OSTER AND NEIL WOTHERSPOON

RECEIVED APRIL 1, 1957

Methylene blue in the presence of ethylenediaminetetraacetic acid (EDTA) is reduced to the leuco dye on irradiation with red light. The rate of photoreduction depends upon *p*H in the same way as does the base titration of EDTA. EDTA is consumed in the reaction suggesting that it is oxidized although it does not normally function as a reducing agent. A number of nitrogen-containing chelating agents were tested but only those wth secondary or tertiary nitrogens behaved as electron donors in the photochemical reaction. The photoreduction involves a long-lived excited state of the dye (10^5 times that of the first electronically excited state) and is retarded by small amounts of *p*-phenylenediamine. The rate of regeneration of the dye by near ultraviolet irradiation of the leuco form increases with increasing hydrogen ion concentration

Introduction

Early workers in the development of photographic bleach-out processes noted that thiazine dyes are photoreduced readily in the presence of mild reducing agents such as allylthiourea, anethol, glyoxal[2] and ferrous sulfate,[3] etc. When a thiazine dye is photoreduced by ferrous ion to give the leuco dye, the ferric ion thus produced oxidizes the leuco dye in the dark, and for intermediate illumination levels, a steady state is achieved.[4] Stannous chloride and ascorbic acid, on the other hand, do not allow the leuco dye to revert to its colored form, but under excitation with near ultraviolet light the dye is regenerated.[5]

Nickerson and Merkel[6] in their studies on the photochemistry of riboflavine noted that methylene blue is photoreduced with ethylenediaminetetraacetic acid (EDTA). This is an unexpected result since EDTA does not normally function as a reducing agent. It is the purpose of the present paper to investigate the role of EDTA as an elec-

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[1] (a) This paper represents a part of the dissertation to be submitted by Neil Wotherspoon to the faculty of the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600) 1182.

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