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Arrhenius Curvature in the Gas-phase Photolysis of Azomethane

BY S. TOBY

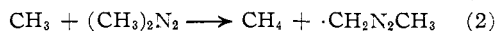
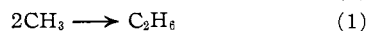
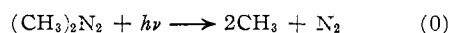
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The photolysis of gaseous azomethane has been investigated from -47 to $+50^\circ$, and the effects of wave length, inert gas concentration and surface have been studied. Arrhenius curvature was found below approximately -10° . The curvature increased when a photolysis cell of greater surface to volume ratio was used and decreased when the light beam was passed through the center of the cell only. The factors which could cause the curvature are discussed and it is shown that the results can be accounted for by a competing heterogeneous reaction between methyl radicals and azomethane adsorbed on the cell wall.

Introduction

The gas-phase photolysis of azomethane in the range 25 to 190° has been quantitatively investigated by Jones and Steacie¹ and azomethane has been used to study the reactions of methyl radicals with isobutane,² aldehydes³⁻⁵ and ketones.⁶

From the reactions



it follows that

$$R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}[\text{A}] = k_2/k_1^{1/2}$$

where A = azomethane.

Jones and Steacie¹ obtained curvature below 80° in an Arrhenius plot of $\log(k_2/k_1^{1/2})$ against $1/T$. Later investigations by Ausloos and Steacie⁶ revealed no curvature for the photolysis of pure azomethane, presumably because an improved preparative method⁷ yielding purer azomethane was used. However Ausloos and Steacie^{3,6} found curvature for $\log(k_5/k_1^{1/2})$ below 80° where k_5 is the rate constant for the abstraction reaction between methyl radicals and a substrate. In the case of the $\text{CH}_3 + \text{acetone}$ reaction, Ausloos and Steacie^{6c} attributed the Arrhenius curvature to a reaction between methyl radicals and acetone adsorbed on the wall. All of this work^{1-6d} was done at or above room temperature.

The purpose of the present investigation was to study the photolysis of pure azomethane at lower temperatures and to account for any curvature.

Experimental

Apparatus.—The reaction vessel consisted of a cylindrical quartz cell mounted with its axis vertical and isolated from the rest of the system by a mercury cutoff. Dead-space was less than 1% of the cell volume. Three photolysis cells A, B, C of volumes 316, 252 and 102 cm.³, respectively, and all with surface to volume ratios of approximately 1 cm.⁻¹ were used. A cell D, volume 89 cm.³, containing two inner concentric quartz tubes and of $S/V = 4.5$ cm.⁻¹ was also used. A slightly larger evacuated Pyrex tube with a cemented quartz window was cemented to the top of the cell to allow an uninterrupted light beam when the cell was submerged in a constant-temperature bath. All runs, except

as noted, were performed with the bottom of the cell silvered to increase light intensity and uniformity.⁸

Before a series of runs the cells were pretreated by photolyzing some azomethane for several hours after which the cell was evacuated overnight. Occasional flaming of the cell had no measurable effect on the products.

For low-temperature runs the cell was immersed in a large Dewar flask containing slushes of organic liquids with convenient melting-points. During longer runs of several hours duration, Dry Ice was occasionally stirred into the Dewar. Temperature control as shown by thermocouples at the ends of the cell was usually within 1° . For higher temperatures water was placed in the Dewar with ice for 0° or a heating spiral for 50° .

After photolysis the products were passed through liquid nitrogen and solid nitrogen traps. Methane and nitrogen were pumped *via* a diffusion pump backed by a Toepler pump into a gas buret connected to a copper oxide furnace. At low temperatures the small amount of methane formed ($\sim 10^{-7}$ mole) necessitated a modification of the standard combustion technique. The method used⁹ had estimated maximum errors of $\pm 1\%$ for 10^{-6} mole methane and $\pm 3\%$ for 10^{-7} mole methane. After combustion the nitrogen and carbon dioxide were measured individually and the balance with the initial total volume was always within the experimental error. Ethane was removed from the condensable products *via* a Ward still set at -175° and its purity occasionally checked by combustion.

Optical System.—The beam from an Osram HBO-74 high-pressure mercury arc was made approximately parallel using a quartz lens. For the runs at 3130, 3340 and 3660 Å. (Series W, Table I) combination glass-solution filters were used.¹⁰ For these runs light absorption was measured by interposing a semi-silvered quartz plate at 45° to the light beam and measuring the light reflected from the bottom of the cell and the semi-silvered quartz plate with an RCA 935 phototube. All other runs were carried out with a Corning 7-37 (No. 5860) filter which gave approximately monochromatic light at 3660 Å. with an intensity of 2×10^{13} quanta cm.⁻² sec.⁻¹ using azomethane at 25° as an actinometer.¹

Materials.—Azomethane was prepared by the method of Renaud and Leitch,⁷ dried with degassed Drierite and repeatedly fractionally distilled, the last distillation being from -105 to -155° with liberal rejection of head and tail fractions. A gas chromatogram showed no impurity. The azomethane was stored in a blackened flask at room temperature and was degassed before being photolyzed.

Carbon dioxide was prepared by twice distilling commercial Dry Ice.

Results

Runs carried out with up to 6% of azomethane decomposed showed no change in the values of the rates of product formation. Results are given in Table I. Series W runs show that $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}[\text{A}]$ (for simplicity this expression will now be written α , units $1^{1/2}$ mole^{-1/2} sec.^{-1/2}) was independent of wave length at 3130, 3340 and 3660 Å. Quantum yields of approximately unity were

(1) M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953).

(2) M. H. Jones and E. W. R. Steacie, *Can. J. Chem.*, **31**, 505 (1953).

(3) P. Ausloos and E. W. R. Steacie, *ibid.*, **33**, 31 (1955).

(4) J. G. Calvert and J. T. Gruver, *THIS JOURNAL*, **80**, 1313 (1958).

(5) S. Toby and K. O. Kutschke, *Can. J. Chem.*, **37**, 672 (1959).

(6) (a) P. Ausloos and E. W. R. Steacie, *ibid.*, **32**, 593 (1954); (b) **33**, 39 (1955); (c) **33**, 47 (1955); (d) **33**, 1062 (1955).

(7) R. Renaud and L. C. Leitch, *ibid.*, **32**, 545 (1954).

(8) J. A. Davies and P. P. Manning, *THIS JOURNAL*, **79**, 5148 (1957).

(9) S. Toby, *Anal. Chem.*, **31**, 1444 (1959).

(10) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

TABLE I
 RATE DATA FROM PHOTOLYSIS OF AZOMETHANE^a

Series	Temp., °C.	[Azomethane] mole/l. × 10 ⁶	Rate of product formation mole/l. sec. × 10 ¹⁰			$R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2} [A]$ 1, 1/2 mole ^{-1/2} sec. ^{-1/2} × 10 ⁴		
			R _{N₂}	R _{CH₄}	R _{C₂H₆}			
Series W								
3130A	Φ _{N₂} = 0.9	-38.8 ± 0.3	4.81	36.9	0.28	36.2	0.97	B
3340A	Φ _{N₂} = 1.1	-38.9 ± .7	4.82	56.0	.35	55.2	.98	B
3660A	Φ _{N₂} = 1.1	-40.1 ± .4	6.04	205	.84	202	.98	C
Series A								
		-47.2 ± .6	2.87	144	.42	142	1.2	A
		-47.0 ± .2	3.46	176	.51	175	1.1	A
		-47.0 ± .3	3.59	170	.53	168	1.1	A
		-40.0 ± .6	3.20	156	.5 ₂	155	1.3	A
		-40.2 ± .3	3.98	173	.59	171	1.14	A
		-40.0 ± .5	4.02	182	.60	181	1.11	A ^b
		-38.6 ± .9	6.55	247	1.08	246	1.06	A
		-27.1 ± .8	3.98	192	0.90	186	1.66	A
		-26.1 ± .5	5.32	248	1.37	243	1.65	A
		-13.2 ± .1	6.25	252	2.40	245	2.45	A ^c
		0.0 ± .2	1.79	112	0.98	109	5.26	A
		.5 ± .2	3.01	176	1.99	170	5.09	A
		.2 ± .1	4.18	227	3.07	218	4.98	A
		24.5 ± .1	2.14	141	3.48	131	14.2	A
		24.6 ± .1	3.74	202	7.46	178	14.9	A
		49.5 ± .1	2.35	140	8.16	111	32.9	A
		49.4 ± .2	3.58	198	13.6	151	31.0	A
Series C								
	CO ₂ /A = 0.16	-40.8 ± .5	4.18	191	0.66	190	1.15	A
	CO ₂ /A = 0.86	-40.3 ± .3	6.20	314	1.12	313	1.02	C
	CO ₂ /A = 1.67	-39.6 ± .4	6.25	311	1.17	306	1.07	C
Series S								
		-46.6 ± .3	3.33	74.3	0.48	73.7	1.7	D
		-40.0 ± .9	2.58	75.7	.48	74.8	2.1	D
		-39.9 ± .8	3.22	80.9	.52	79.9	1.8	D
		-40.5 ± .8	5.58	70.4	.75	64.3	1.7	D ^d
		-40.6 ± .9	6.07	107	1.3 ₀	105	2.0	D
		-28.0 ± .7	9.42	171	2.52	161	2.10	D
		-13.2 ± .1	7.58	158	2.67	151	2.86	D
		0.0 ± .1	6.12	148	3.74	133	5.31	D
		24.4 ± .2	5.08	110	6.65	103	12.9	D

^a A, B, C, D refer to cells: see "Apparatus." ^b 6.9% azomethane decomposed. ^c Poorly silvered mirror. ^d No mirror.

obtained. Experiments below -50° were not feasible with the present apparatus. The data in Series A show that a plot of $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$ against [A] is linear over the somewhat limited range of [A] employed. A graph of the mean values of $\log \alpha$ against the reciprocal of the absolute temperature is given in Fig. 1 together with data at higher temperatures. The linear portion of the present data gives a least mean squares line of $k_2/k_1^{1/2} = 160 \pm 50 \exp \{(-6860 \pm 180)/RT\} 1.1/2 \text{ mole}^{-1/2} \text{ sec.}^{-1/2}$

There is rather poor agreement for reported values of $E_2 - 1/2 E_1$. They are 6.9 ± 0.2 (present work), 7.3 (Ausloos and Steacie⁶), 7.6 ± 0.2 (Jones and Steacie¹) and 8.4 ± 0.3 (Toby and Kutschke⁵) kcal./mole. Since these values increase with the average temperature over which the experiments were performed, it appears that the "straight" portion of the Arrhenius plot is slightly curved, although the curvature is far less than that encountered below -10° in this investigation.

Series C shows the effect of added inert gas. A ten-fold range of carbon dioxide concentration has no effect on α at -40° .

Series S was carried out in a cell of higher S/V to test the effect of surface. The values of $\log \alpha$ are shown as the upper series of experimental points in Fig. 2. The lower points are taken from Series A.

The final two series of experiments were carried out to study the effect of passing light through the center of the cell only. This was expected to decrease the effect of surface reactions and give information on the diffusion of radicals out of the light beam. Masks over the cell window reduced the light to a cylindrical beam 12 and 29% of the cell volume. The cell used had a volume of 252 cm.³ and was not silvered. The results are given as an Arrhenius plot in the lower portion of Fig. 3.

Discussion

There are many effects which might cause or contribute to the observed Arrhenius curvature. It will be convenient to discuss these effects under separate headings.

Purity of Azomethane.—Since the curvature Jones and Steacie¹ observed at higher temperatures can be accounted for by an impurity with a low activation energy of abstraction, azomethane purity was checked carefully in the present in-

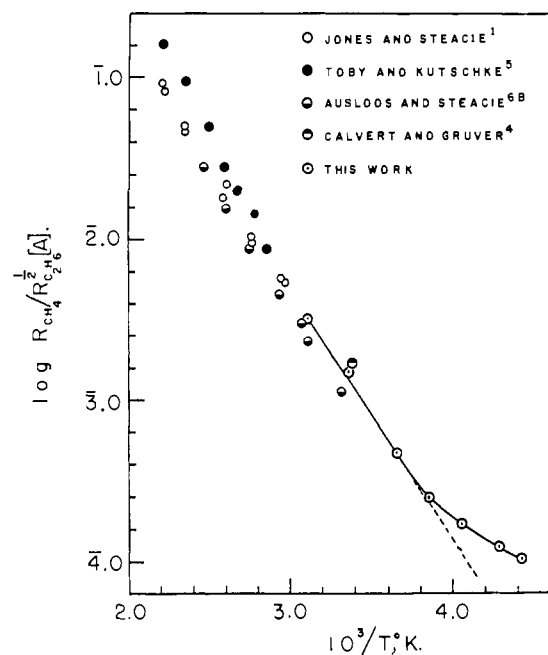


Fig. 1.—Arrhenius plot of abstraction of hydrogen from azomethane by methyl radicals. Units of $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$ [A] are $l^{1/2}$ mole $^{-1/2}$ sec. $^{-1/2}$ throughout.

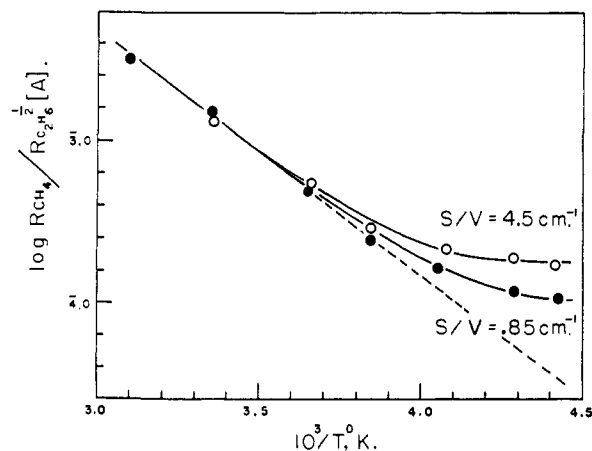


Fig. 2.—Effect of surface on photolysis of azomethane. Solid curves are $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$ [A] = $k_2/k_1^{1/2} + 1.0 \times 10^{-7} (S/V)^{1/2} e^{2900/RT}$. Points are experimental values.

vestigation. Runs at -40° gave the same rate constants regardless of whether the azomethane was used without being degassed for a week, was degassed immediately before using or was triple distilled immediately before using. No values of α less than those of Series W ever were obtained. It will therefore be assumed that the curvature is not due to impurity.

Errors in Measurements.—The azomethane concentration was calculated from its pressure assuming ideality. It was found that deviations from ideality under the experimental conditions employed were negligible.

Temperature control as shown in Table I was satisfactory. Benson¹¹ has shown that thermal

(11) S. W. Benson, *J. Chem. Phys.*, **22**, 46 (1954).

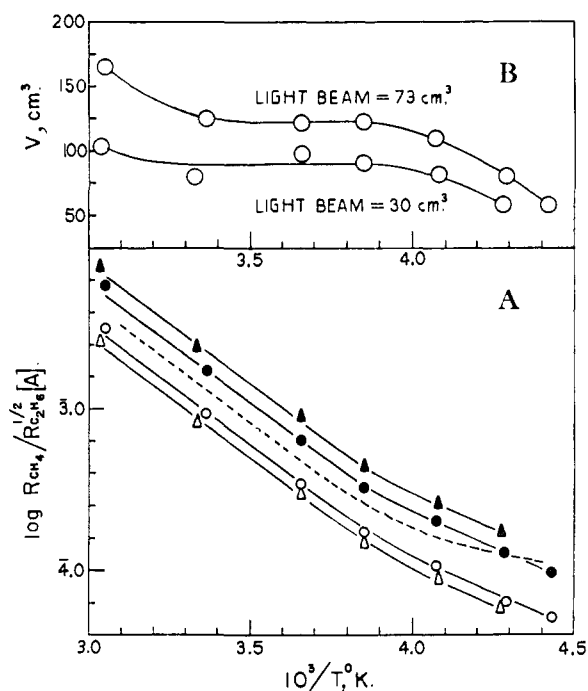


Fig. 3.—(A) Effect of reduced light beam in photolysis of azomethane; \blacktriangle , 30 cm^3 light beam, reaction volume taken as light volume; \bullet , 73 cm^3 light beam, reaction volume taken as light volume; \circ , 73 cm^3 light beam, reaction volume taken as cell volume; \triangle , 30 cm^3 light beam, reaction volume taken as cell volume; - - -, no reduction in light beam; (B) variation of effective reaction volume with temperature.

gradients due to exothermic reactions within a reaction vessel can cause appreciable errors in kinetic measurements. Any thermal gradients would be considerably reduced in the narrow, high S/V cell used in Series S. The curvature from this series was markedly increased (Fig. 2). This implies that any curvature due to increase of temperature within the cell was considerably less than that due to surface effects.

Homogeneous Reactions.—The constancy of α at a given temperature over a range of wave lengths, azomethane concentrations and inert gas concentrations is strong evidence against an excited molecule mechanism, at least over the ranges employed. This agrees with Jones and Steacie's findings at higher temperatures. In Series W the value of α is very slightly less than for other runs at the same temperature. This could mean that the 7-37 filter transmitted a very small amount of short-wave ultraviolet light.

Curvature would result if k_1 decreased sharply at low temperatures. Available evidence from work of Ingold and Lossing¹² and Stepukhovich¹³ shows that k_1 changes little from 25 to 825° and has a small negative temperature coefficient.

The pressure dependence of k_1 in the photolysis of acetone has been investigated extensively by Kistiakowsky and Roberts¹⁴ and Dodd and

(12) K. U. Ingold and F. P. Lossing, *ibid.*, **21**, 1135 (1953).

(13) A. D. Stepukhovich, *Zhur. Fiz. Khim.*, **32**, 2415 (1958).

(14) G. B. Kistiakowsky and E. K. Roberts, *J. Chem. Phys.*, **21**, 1637 (1953).

Steacie.¹⁵ They found a marked increase of $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}[\text{Acetone}]$ at 250° at pressures of less than 10 mm. of acetone consistent with a third body restriction on the recombination of methyl radicals. No corresponding trend was noted in the present investigation as the azomethane concentration was reduced from 95 to 47 mm. at -40° and it is concluded that this work was done in the "high-pressure" region.

In the photolysis of acetone Ausloos and Steacie^{6c} found an increase of $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}[\text{Acetone}]$ with light intensities above 10^{13} quanta cm^{-2} sec^{-1} which they attributed to reactions of the acetyl radical. In the case of azomethane, the corresponding $\text{CH}_3\text{N}_2\cdot$ radical, although isoelectronic with acetyl, is too short-lived to react, even under the conditions of flash photolysis, as Sleppy and Calvert¹⁶ found.

Surface Reactions.¹⁷—If azomethane is adsorbed on the wall of the cell the heterogeneous reaction



may occur. In this case

$$\alpha = k_2/k_1^{1/2} + k_3[\text{A-wall}]/k_1^{1/2}[\text{A}][\text{CH}_3] \quad (4)$$

From simple collision theory

$$k_3 = [\text{CH}_3](RT/2\pi M)^{1/2} \text{ collisions with wall/cm}^2 \text{ sec.}$$

Taking 500 ± 500 cal. mole^{-1} for E_1 we have

$$k_1 = 4Pd^2(\pi RT/M)^{1/2} e^{-500/RT} \text{ collisions/cm}^2 \text{ sec.}$$

where the symbols have their usual collision-theory significance.

If the total adsorption is small, the number of moles adsorbed on a given amount of adsorbent will approximately follow Henry's law.

$$x = ap$$

where x moles are adsorbed at pressure p at constant temperature, and a is a function of T . From the integrated Clapeyron-Clausius equation

$$p = be^{-Q/RT} \text{ at constant } x$$

where Q is the isosteric heat of adsorption, and b is a function of x . It follows that

$$a = (x/b)e^{Q/RT} = c_1e^{Q/RT} \text{ where } c_1 \text{ is independent of } x.$$

This gives $x = c_1pe^{Q/RT} = c_2[\text{A}]Te^{Q/RT}$

To account for the results obtained with cells of differing S/V the term $(S/V)^{1/2}$ is empirically

(15) R. E. Dodd and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A223**, 283 (1954).

(16) W. C. Sleppy and J. G. Calvert, *THIS JOURNAL*, **81**, 769 (1959).

(17) P. Ausloos and J. Paulson (*J. Phys. Chem.*, **62**, 501 (1958)) showed that when CD_3COCD_3 was photolyzed in a cell where water was present, CD_3 reacted with the water heterogeneously. When no water was added, no CD_3H was formed. Since azomethane is easier to free from traces of water than is acetone, there is little reason to suppose that $\text{CH}_3 + \text{H}_2\text{O}(\text{wall}) \rightarrow$ is a significant reaction in the present system.

introduced so that

$$[\text{A-wall}] = c_3(S/V)^{1/2}[\text{A}]Te^{Q/RT}$$

where c_3 is a numerical constant

Substituting the values of k_3 , k_1 and $[\text{A-wall}]$ in (4)

$$\alpha = k_2/k_1^{1/2} + c_4(S/V)^{1/2}T^{5/4}e^{(Q+250)/RT}$$

The change of the exponential term with T will be considerably larger than the change of $T^{5/4}$ and the latter term may be considered constant with little increase in error.

Hence

$$\alpha = k_2/k_1^{1/2} + c(S/V)^{1/2}e^{(Q+250)/RT}$$

Taking the value of $k_2/k_1^{1/2}$ from the straight line portion of the Arrhenius plot from Series A data, setting $c = 1.0 \times 10^{-7}$ ($\text{l.cm.}/\text{mole.sec.}$)^{1/2}, $Q = 2750 \pm 500$ cal. mole^{-1} , the curves in Fig. 2 are obtained, in good agreement with the experimental points. The value of Q is a feasible value for the heat of adsorption of azomethane on a quartz surface. No satisfactory explanation for the $(S/V)^{1/2}$ term is apparent to the author.

Confirmation that the curvature was a result of surface reactions was obtained by experiments with the light beam passing the center of the cell. Reduction of surface effects results in a decrease in Arrhenius curvature as shown in the lower portion of Fig. 3. For the results with the reduced light beam to be collinear with the straight portion of the other results, the effective reaction volume would have to be intermediate between the light beam volume and the cell volume. Dodd and Steacie¹⁵ found that in the photolysis of acetone at 250° the effective reaction volume equalled the cell volume. The lower temperatures used in the present work doubtless slowed the rate of radical diffusion out of the light beam to the wall. The question of radical diffusion will be discussed further in a subsequent publication.

If the rates of production of methane and ethane in the reduced light beam experiments are given by r_{CH_4} , $r_{\text{C}_2\text{H}_6}$ mole/sec. and if V is the effective reaction volume, then

$$V = r_{\text{CH}_4}^2 R_{\text{C}_2\text{H}_6} / R_{\text{CH}_4}^2 r_{\text{C}_2\text{H}_6} \text{ liters}$$

where R_{CH_4} , $R_{\text{C}_2\text{H}_6}$ are taken from Series A, assuming no change in mechanism in the reduced light beam runs. The variation of V with temperature is shown in the upper portion of Fig. 3. At the lowest temperatures surface reactions predominate, the assumption breaks down and V apparently becomes smaller than the light beam.

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