[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Photolysis of Azomethane

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Measurements of quantum yields provide a valuable check upon hypotheses regarding energy chains in the corresponding thermal reactions. Carried out in monochromatic light, and at temperatures where a wholly negligible fraction of molecules present can be activated in unit time by collisions, the energy available after reaction can be calculated, and then apportioned among various combinations of molecules presumably involved in subsequent collisions. The temperature coefficients, also, of such photolyses have an obvious bearing upon the interpretation of the data for the thermal reactions.

Ramsperger[1] reported a quantum yield somewhat over two for the photolysis of azomethane, using the treacherous method of light-filters. Under his experimental conditions the non-actinic light was from one-third to five times the light absorbed, and he apparently overestimated the necessary corrections. The initial reaction he wrote $CH_3—N{=}N—CH_3 + h\nu \longrightarrow C_2H_6 + N_2$. The energy of the photon at 366 mμ, 83,000 cal./mole and the heat of reaction, 20,000 cal./mole add up to 103,000 cal./mole of which the ethane would be expected to retain the greater part. Ramsperger has argued that each newly formed ethane molecule might provide energy of activation (51,000 cal./mole) for one new azomethane molecule, and thus bring the total decomposition up to the value observed.

We found it hard to understand why the quantum yield, if two, should be independent of both temperature and pressure as stated by Ramsperger. We were convinced that measurements at additional wave lengths (Ramsperger made use of λ 366 mμ only) would afford additional information.

We carried out four series of measurements, at initial pressures of 664, 377, 184 and 181 mm., respectively. Six wave lengths of monochromatic light were employed. We found that the quantum yield, ϕ, approaches unity as its upper limit for initial decomposition at low pressures. The photochemical temperature coefficient if $t \ngtr 226°$ was found to be zero, in agreement with Ramsperger, as became reasonable in the light of the revised quantum yield. But at 260° this coefficient was no longer negligible.

Experimental

The monochromator, spark source, uranyl oxalate actinometer and trapezoidal gas reaction cell, as well as details of operation and the necessary corrections, were essentially the same as in recent work on ozone in this Laboratory.[2,3] At $\lambda\lambda$ 366 and 313 mμ a constricted mercury arc[4] replaced the spark; its oscillations were controlled by thin annular films of mercury within ground joints.[5] The monochromatic intensities back of the exit slit ranged from 3.8×10^{16} to 7.4×10^{17} quanta per minute.

The actinometer cell used at $\lambda\lambda$ 366 and 335 mμ was trapezoidal in form, 3 cm. deep, and held 11 cc. of a solution containing 0.003 mole of washed uranyl oxalate and 0.003 mole of oxalic acid per liter. At λ 313 mμ the same solution was used in a rectangular cell 5 mm. thick, and holding 5 cc. The quantum yields have been shown by Forbes and Heidt[6] to be identical with those previously established by W. G. Leighton and Forbes.[7] At $\lambda\lambda$ 254 and 208 mμ the rectangular cell was used with a solution 0.001 M in uranyl sulfate and 0.005 molal in oxalic acid, standardized in this wave length range by Brackett and Forbes.[8] Since the gas cell and the actinometer cell were exposed alternately as described below, the fluctuations in intensity of the light source were not followed radiometrically.

The reaction cell was fused into the wall of a quartz beaker which served as a thermostat. A ring of felt surrounding the space between the front window and the exit slit tended to hold the temperature of the former at the temperature inside the cell. Two immersion heaters regulated automatically, or by hand, held temperatures constant within 0.05°. A layer of thermostating liquid over the meniscus of the mercury in the regulator in each case was found to increase greatly the sensitivity of the make-and-break to temperature changes. Water was used in the thermostat from 0 to 70°, diethylene glycol 70 to 125°, n-butyl phthalate 125 to 200° and castor oil 200 to 300°. Temperatures were recorded with a set of Anschütz thermometers. The monochromator was pivoted under the light source[9] so that its exit slit could swing into line with reaction cell or actinometer cell as desired.

Previous experience with the photolysis of ozone[2,3] had convinced us of the fundamental importance of rigorous purification of reactants and the elimination of stopcocks. The purifying train as well as the reaction cell was thoroughly flamed, and degassed by means of a diffu-

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[1] Ramsperger, This Journal, **50**, 123 (1928).

[2] Forbes and Heidt, *ibid.*, **56**, 1671 (1934).

[3] Heidt and Forbes, *ibid.*, **56**, 2365 (1934).

[4] Forbes and Harrison, *J. Opt. Soc. Am.*, **11**, 99 (1925).

[5] Forbes and Heidt, This Journal, **53**, 4349 (1931).

[6] Forbes and Heidt, *ibid.*, **56**, 2363 (1934).

[7] W. G. Leighton and Forbes, *ibid.*, **52**, 3139 (1930).

[8] Brackett and Forbes, *ibid.*, **55**, 4459 (1933).

[9] Forbes, Kistiakowsky and Heidt, *ibid.*, **54**, 3246 (1932).

TABLE I

Serial number	λ in mμ	$\bar{P}$	$\bar{p}$	t	Q	A	B	Time	ΔP	ϕ	k
1-1 a	208-4 Zn	181.8	(181)	20.5	7.5	100	7.5	25.0	1.18	0.96	
b		183.0	(180)	20.2	6.8	100	6.8	44.5	1.76	.90	
1-2 a	335-1 Zn	184.4	(179)	22.4	9.9	45	4.4	46.0	1.15	.87	4.5
b		185.5	(178)	22.2	9.1	45	4.1	50.0	1.20	.89	
c		186.8	(176)	22.4	8.8	45	4.0	53.5	1.32	.94	
1-3 a	208-4 Zn	188.4	(175)	22.7	10.0	100	10.0	53.0	2.34	.68	
b		190.6	(172)	23.0	6.8	100	6.8	48.5	1.55	.72	
c		192.1	(171)	23.2	6.7	100	6.6	51.5	1.35	.61	
d		193.2	(170)	22.2	9.2	100	9.2	51.0	1.53	.50	
e		194.9	(168)	22.5	8.2	100	8.2	59.0	1.51	.48	
f		196.1	(167)	21.5	8.1	100	8.1	50.0	1.29	.49	
g		197.2	(166)	22.1	6.5	100	6.5	51.0	0.98	.46	
1-4	335-1 Zn	198.1	(165)	21.2	12.2	44	5.4	57.0	1.54	.77	4.5
1-5		199.4	(164)	21.2	11.5	43	5.1	50.0	1.22	.73	
1-6	208-4 Zn	200.9	(162)	22.6	13.1	100	13.0	55.0	1.56	.33	
1-7 a		201.8	(161)	21.9	11.8	100	12.0	55.0	2.16	.50	
b		203.3	(160)	22.1	6.8	100	6.8	54.0	0.83	.35	
c		203.9	(159)	21.5	5.5	100	5.5	56.5	.65	.32	
1-8	335-1 Zn	204.6	(158)	22.3	10.3	42	4.3	52.0	.86	.59	4.5
1-9		205.4	(157)	21.3	10.3	41	4.2	54.5	.85	.57	

TABLE II

Serial number	λ in mμ	$\bar{P}$	$\bar{p}$	t	Q	A	B	Time	ΔP	ϕ	k
2-1 a	208-4 Zn	377.8	(376)	23.9	6.2	100	6.2	52.0	1.62	0.77	
b		378.9	(375)	23.1	7.0	100	7.0	58.5	1.43	(.54)	
2 a	254-2 Zn	379.8	(374)	23.6	5.1	20	1.0	58.5	0.1	.26	0.8
b		379.9	(374)	23.8	6.8	20	1.4	65.5	.15	.25	
3	208-4 Zn	380.0	(374)	22.1	5.7	100	5.7	58.5	0.93	.43	complete
4 a	335-1 Zn	381.3	(373)	22.7	8.3	70	5.8	54.5	1.80	.87	4.5
b		382.7	(371)	21.6	11.3	70	7.9	52.0	2.25	.84	
5 a	366 Hg	384.9	(369)	21.2	6.2	56	3.5	207.0	1.42	.30	3.0
b		386.0	(368)	21.5	3.3	56	1.9	225.0	0.89	.32	
6 a	313 Hg	386.9	(367)	21.8	9.1	48	4.4	307.0	.3	.041	3.0
b		387.2	(366)	22.0	4.0	47	1.9	271.0	.2	.06	

TABLE III

Serial number	λ in mμ	$\bar{P}$	$\bar{p}$	t	Q	A	B	Time	ΔP	ϕ	k
3-1 a	208-4 Zn	666	(664)	25.0	16.7	100	16.7	26.0	2.2	0.77	
b		668	(662)	25.0	14.5	100	14.5	28.5	2.1	.77	
c		670	(660)	25.0	16.0	100	16.0	21.5	1.5	.67	
2 a	335-1 Zn	672	(658)	25.0	18.5	88	16.3	26.5	1.95	.69	4.5
b		674	(656)	25.0	16.2	88	14.2	24.5	1.5	.66	
c		675	(655)	25.0	15.5	88	13.6	22.5	1.15	.58	
3 a	366 Hg	678	(652)	24.9	74.0	75	56.0	52.0	3.60	.19	3.0
b		680	(650)	25.2	58.0	75	44.0	38.0	2.25	.21	
c		688	(647)	25.3	56.0	75	42.0	46.3	2.40	.19	
d		691	(644)	26.1	56.0	74	41.0	54.0	2.45	.17	
4 a		693	(642)	99.8	67.0	75	50.0	42.5	1.85	.13	
b		696	(639)	100.0	67.0	74	50.0	32.5	1.3	.12	
c		697	(638)	100.0	67.0	74	50.0	43.0	1.80	.13	
5		725	(610)	226.0	55.5	74	41.0	120.0	3.1	.097	
6		727	(608)	25.0	34.4	73	25.0	57.5	0.50	.077	

sion pump backed by an oil pump. The supply of azomethane (two samples separately prepared) was fractionated before each filling of the cell with rectification in a tower packed with glass beads and held at −80°. The distillate, entirely free from color in the liquid state, was outgassed at −80° until about a third of it had evaporated.

TABLE IV

TEMPERATURE COEFFICIENT OF ϕ FOR AZOMETHANE

$\lambda = 366$ mμ, $k = 3.0$

$\bar{P}$	$\bar{p}$	t	Q	A	B	Time	ΔP	ϕ
184.2	184.2					0		
185	(183)	26.6	23	0.33	7.6	34.5	1.90	1.1
187	(181)	26.3	26	.33	8.6	52.0	2.75	0.94
190	(178)	26.3	31	.32	10.0	37.5	1.95	.79
209	(159)	260.0	32	.30	9.5	38.0	(4.4–1.3)	1.3
213	(151)	260.0	29	.29	8.5	20.0	(2.05–0.75)	1.2
219	(149)	260.0	29	.29	8.5	33.5	(3.15–1.2)	1.1
227	(141)	28.2	27	.27	7.2	60.5	2.1	0.73
230	(138)	28.2	27	.26	7.0	95.5	3.0	0.69

and then stored in a liter bulb. In view of these precautions it appeared proper to assume that initial pressures in the reaction cell represented azomethane exclusively. After introduction of gas, this cell, together with the spiral quartz manometer, was sealed off from the rest of the apparatus. The mercury manometer to which the zero readings of the quartz manometer were referred reproduced pressure changes within 0.05 mm.

Tables I to IV include all our photolytic measurements where Q and B are respectively quanta incident upon, and absorbed by, the gas per minute, with omission of the factor 10^{16}. A is the percentage of incident light absorbed by the gas. The average total pressure during a photolysis is $\bar{P}$ and the average partial pressure of azomethane calculated from Ramsperger's mechanism is $\bar{p}$. The temperature of the cell, t, follows. Time of a given photolysis is in minutes. The manometer and barometer readings in millimeters of mercury have been corrected to 0°, and the gas pressures reduced to 0° by means of the simple gas law. Following Ramsperger, our quantum yields, ϕ, represent the increase in the number of molecules, in the reacting system, per quantum absorbed, and were calculated by use of Ramsperger's absorption coefficients, k, except at 208 mμ, beyond the spectral range covered by him, where the absorption, in our cell, was evidently complete. As he obtained these data by using a spectrograph and calibrated screens, after the method of Ramsperger and Porter,[10] the uncertainties inherent in the filter method could not have vitiated the results. We were, however, obliged to make the undesirable assumption that the variation of extinction coefficients with temperature is unimportant over a range of 240°. Except at 260°, the highest temperature employed by us, the velocity of decomposition in the absence of light was negligible.

Discussion of Results

In order to make the corrections for transmitted light as small as possible the wave lengths 208 and 335 mμ (the latter corresponding to an absorption maximum of azomethane) were first employed. The *initial* value of ϕ is seen to be close to unity at 181 mm., a pressure intermediate between Ramsperger's greatest pressure and his next smaller one. But at 377 and 665 mm. $\phi = 0.77$, indicating clearly the increase in deactivation with pressure. The decrease in ϕ at all pressures, as decomposition increased at room temperature, is very striking. Ramsperger gives four averaged quantum yields only, one for each of four initial pressures, but we calculated relative values of ϕ for each of his twenty separate experiments, and found that his values also decreased with increasing decomposition at room temperature. The decrease of ϕ with increase of initial pressure was less noticeable in Ramsperger's results, because three out of four of his pressures were much smaller than any of ours. He observed that "a very slight deposit was formed on the front window of the reaction chamber" upon raising temperature from 20 to 100°. Such a deposit was evident to us almost immediately after beginning of illumination by λ 208 mμ in the pressure range in which we operated. No deposit was formed at λ 366 mμ. The photolysis of even one millimeter of gas was attended by a decrease in ϕ far greater than experimental error whenever a deposit was formed. As our material was insufficient in amount to permit of refilling the cell after each twenty-minute run, we had to resort to graphical treatment of results to eliminate this complication. In Fig. 1, plots of ϕ against pressure change yield a straight line within the limits of experimental error, which might be expected if the falling off in the light entering the cell, for *small* changes in extinction by the deposit on the window, were roughly proportional to the thickness of this de-

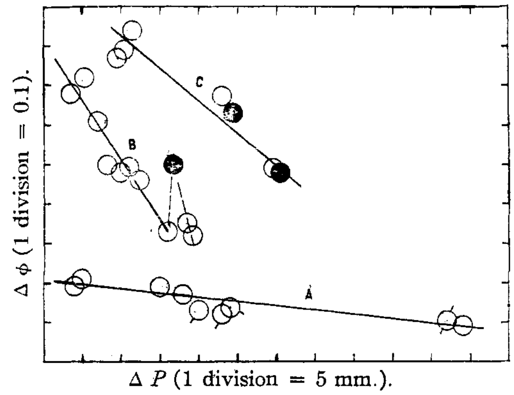

Fig. 1.—$\Delta\phi/\Delta P$ shown as independent of t (if $t \not> 226°$), and dependent on wave length only. Curve A at λ 366 mμ; circles at 25°, single-flag circles at 100°, double-flag circles at 226°. Curve B at λ 208 mμ; all experiments at 21°. The solid circle resulted just after heating the front window to 100° for twelve hours. Curve C at λ 335 mμ; all experiments at 21°. No break resulted (solid circles) upon heating the front window to 100° for twelve hours.

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(10) Ramsperger and Porter, THIS JOURNAL, 48, 1267 (1926).

posit. The opacity of the deposit is greatest at λ 208 mμ due in part to increased scattering. Interference rings were plainly seen after the deposit had become well developed, an observation in harmony with the fact that the light intensity was greatest at the center of the window, and fell off toward the edges. The deposit could be partially dispelled by gentle heating of the front windows over twelve hours, as is evident from Fig. 1 upon comparing experiment 1–6 with 1–7a at 208 mμ. On the other hand, no increase in transmission at λ 335 mμ was observable—compare 1–4 with 1–5, also 1–8 with 1–9. The falling off in ϕ with increase in decomposition was likewise much less rapid at λ 335 mμ than at λ 208 mμ—compare series 1–2, 1–4, 1–5, 1–8, 1–9 all at 335 mμ with 1–1, 1–3, 1–6 and 1–7 all at 208 mμ.

Unfortunately we had material insufficient to trace the relation between ϕ and λ over the entire wave length range. Still, series 2a where $\phi = 0.25$ at λ 254 mμ may properly be compared with the average of series 2–1 and experiment 2–3 at λ 208 mμ, $\phi = 0.54$. This increase in ϕ with size of the quantum indicates that the probability of dissociation before deactivation increases in the same sense. At λ 254 mμ the light energy, 110,000 cal./mole, is more than twice the activation energy, 51,000 cal./mole while at 208 mμ the ratio is nearly three. But even with this great excess of energy there is no evidence that a second azomethane molecule is activated and subsequently decomposed.

In view of the fact that ϕ is halved in going from λ 208 mμ back to λ 254 mμ, the approximate equality in ϕ for initial decomposition at λλ 366, 335 and 208 mμ is at first sight unexpected. However, the maximum in absorption at λ 335 mμ appears to correspond to absorption in the N=N bond, for the N–C bond does not absorb in this region as is evident upon examining for instance the absorption curve of acetamide.[11] Owing to the stability of the N=N bond and the fact that the two N–C linkages are *both* adjacent to it, a smaller quantum might well produce dissociation than in the case where a larger quantum is absorbed beyond the first absorption maximum, presumably by a single N–C bond.

The temperatures represented by the various points in Fig. 1, plot a, are distributed in random fashion along the (approximately) straight line, the slope of which, as pointed out above, is to be referred to the increase in the deposit upon the front window. It therefore seems permissible to draw the conclusion that the effect upon ϕ of an increase in temperature of 206° is incapable of detection. If the photolysis were a chain reaction at 226° the large percentage of molecules in high vibrational states at this temperature might contribute noticeably to the quantum yields.[12,13] At 260°, however, the dark reaction has become equal to one-third of the photochemical reaction, and the contribution of such molecules to the photochemical reaction rate is no longer negligible.

We are indebted to Dr. O. K. Rice for the opportunity to discuss with him various aspects of this research.

A subsequent paper will deal with approximate physical analyses of the reaction products both thermal and photochemical. In the light of these data it would appear that the reaction mechanism is closely similar in both cases.

Summary

Quantum yields, ϕ, for photolysis of azomethane at 181, 184, 377 and 665 mm. were measured by reference to a uranyl oxalate actinometer. Purification and photolysis alike were carried out in a train without stopcocks, following the technique and precautions developed in previous researches. Six monochromatic radiations were employed. By graphical methods allowance was made for deposition of difficultly volatile decomposition products upon the front window.

The quantum yield ϕ approaches unity as its upper limit for initial decomposition at low pressures.

A temperature increase, 20 to 226°, had no effect on ϕ. Evidently reaction chains are absent in this temperature interval. But in the vicinity of 260° the photochemical temperature coefficient became measurable.

With increasing pressure ϕ falls off rapidly, apparently because of collisional deactivation.

In the region 366 to 335 mμ approximately, ϕ passes through a maximum apparently corresponding to a maximum of absorption by the N=N bond. With increasing quanta ϕ next decreases to a minimum, then increases again when the N–C bond begins to absorb.

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[11] "International Critical Tables," Vol. V, p. 364.

[12] Sickman and Allen, THIS JOURNAL, **56**, 1251 (1934).

[13] Leermakers, *ibid.*, **56**, 1537, 1899 (1934).