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A Kinetic Study of the Mechanism of Nitrosomethane Formation and Decay in the Photolysis of Azomethane–Nitric Oxide Mixtures

BY JACK G. CALVERT, SANDRA S. THOMAS AND PHILIP L. HANST

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The rates of formation and decay of nitrosomethane, formed in the photolysis of azomethane–nitric oxide mixtures at 25°, were determined by infrared absorption spectrometry. The nitrosomethane reached a steady-state concentration, $[CH_3NO]_{max}$, after a few minutes irradiation. The function $[CH_3NO]_{max}/P_{Me_2N_2}{}^{1/2}$ was found to be independent of the azomethane pressure. The rate-determining step in the decay of nitrosomethane monomer in the dark was found to be a homogeneous gas phase reaction which was second order in nitrosomethane. The only measurable final product of the methyl radical-nitric oxide reaction at 25° was the dimer of nitrosomethane. These data are in accord with the simple mechanism: $(CH_3)_2N_2 + h\nu \rightarrow 2CH_3 + N_2$ (I); $CH_3 + NO \rightarrow CH_3NO$ (1); $2CH_3NO \rightarrow (CH_3NO)_2$ (2); $(CH_3NO)_2 \rightarrow (CH_3NO)_2$ (solid at the cell wall). From studies of the rate of methanol formation in azomethane–oxygen mixture and observations of the initial rate of nitrosomethane formation in azomethane–nitric oxide mixtures, the molar absorbancy index of CH_3NO at 6.32 μ, $a_M = 77$ (l./mole-cm.), and the rate constant at 25°, $k_2 = 87$ (l./mole-sec.), were derived.

The fast reaction between nitric oxide and methyl radical has been studied repeatedly over the years. However, some uncertainty still exists in the nature of the products formed under different conditions and the detailed reaction mechanism which describes the transformations between the different possible products. Probably there would be general agreement that the initial product of the interaction of methyl radical and nitric oxide is nitrosomethane

$$CH_3 + NO \longrightarrow CH_3NO \qquad (1)$$

but a quantitative description of the fate of this species is impossible at present.

In explanation of nitric oxide inhibition of acetaldehyde photolyses, Mitchell and Hinshelwood[1] suggested that the over-all chemical changes which occur when methyl radicals and nitric oxide react may be: $CH_3 + NO \rightarrow CH_3NO \rightarrow CH_2{=}NOH \rightarrow HCN + H_2O$, and/or $2CH_3NO \rightarrow CH_4 + CO + H_2O + N_2$. Taylor and Bender[2] followed the course of the thermal decomposition of formaldoxime and concluded that the methyl–nitric oxide reaction was explained adequately on the basis of the formation and subsequent decomposition of formaldoxime. Raley, Rust and Vaughan[3] first proved that formaldoxime is a major product of the reaction under certain conditions; they identified formaldoxime among the products of the thermal decomposition of di-*t*-butyl peroxide in nitric oxide (225°). More recently Bryce and Ingold[4] have successfully followed the methyl–nitric oxide reaction and determined the rate constant for the reaction 1 through mass spectrometric studies of the thermal decomposition of dimethylmercury in nitric oxide. In short reaction times at high temperatures (480–900°) the major product of the methyl–nitric oxide interaction was a compound of parent mass 45, presumed to be CH_3NO. With long reaction times, NH_3, H_2O, HCN, CO, N_2, CO_2 and CH_3CN were also detected; neither $(CH_3NO)_2$ nor $(CH_2{=}NOH)_3$ was found.

Sleppy and Calvert[5] could not find nitrosomethane or its reaction products in the flash photolysis of azomethane–nitric oxide–neopentane mixtures. However, their analysis procedure required repeated condensation and vaporization of the products and excess reactants. Dimerization and/or isomerization to non-volatile products probably resulted under these conditions, and CH_3NO,

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[1] J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A159**, 32 (1937).

[2] H. A. Taylor and H. Bender, *J. Chem. Phys.*, **9**, 761 (1941).

[3] J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 88 (1948).

[4] W. A. Bryce and K. U. Ingold, *J. Chem. Phys.*, **23**, 1968 (1955).

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

TABLE I

RATE DATA ON THE FORMATION AND DECAY OF CH_3NO (MEASURED AT 6.32 μ) IN THE PHOTOLYSIS OF AZOMETHANE–NITRIC OXIDE MIXTURES AT ROOM TEMPERATURE

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
	Reactant press., mm.		CH_3NO rate[a] $\times 10^4$							
Run no.	$(CH_3)_2N_2$	NO	Formation initial	Decay at time t[b]	$[CH_3NO]$ at time t[b]	$[CH_3NO]$ at maximum	$(4)/(5) \times 10^4$	$(4)/(5)^2$	$(6)/(1) \times 10^3$	$(6)/(1)^{1/2} \times 10^2$
1	5.0	5	0.57	0.60	0.0232	0.0255	25.9	0.112	5.10	1.14
2	11.0	11	1.52	1.54	.0362	.0381	42.5	.118	3.46	1.15
3	20.0	19	(2.05)[c]	2.52	.0487	.0525	51.7	.106	2.63	1.17
4	40.0	42	3.45	3.25	.0519	.0666	62.6	.120	1.67	1.05
5	80.0	52	5.06	4.36	.0594	.0897	73.4	.123	1.12	1.00
6[d]	0.26	0.68	..	0.00566	.00241	...	2.3	.097	..	..

[a] The rates are represented as d(log I_0/I)/dt with the time in sec. The $[CH_3NO]$ values are the quantities log (I_0/I) which are proportional to the actual concentration. Since the extinction coefficient of CH_3NO which we derive in this work is of very limited accuracy, we have chosen this method of presentation. [b] t is the time at which the arc was turned off. [c] This value has considerable uncertainty since an error in the timing at the start of the run was likely. [d] This run was made in the long-path cell using 20 m. of path. The mixture was prepared with nitrogen carrier gas which was present during the run at 744 mm. pressure. The measured quantity, log (I_0/I) was divided by 200 in this case to represent correctly the rates and concentrations based on the 10 cm. cell experiments.

$CH_2{=}NOH$, and possibly other products, would not be detected by infrared spectrophotometric measurements on the volatilized fraction of the condensate.

Coe and Doumani[6] have observed that acetone and a stable dimer of nitrosomethane are the major products of the photodecomposition of *t*-butyl nitrite at 25°. It was suggested that dimer formation from nitrosomethane monomer follows the primary process

$$(CH_3)_3CONO + h\nu \longrightarrow CH_3COCH_3 + CH_3NO$$

Chilton, Gowenlock and Trotman[7,8] have prepared and characterized clearly two forms of the nitrosomethane dimer which appear to be *cis*- and *trans*-isomers. They have described the experimental conditions which favor the formation of each of the dimers and the rearrangement into the isomeric formaldoxime. Recently Lüttke[9] has prepared the monomeric nitrosomethane by heating the dimer. He observed that the characteristic infrared band of the monomer (1564 cm.$^{-1}$) formed in experiments at 160° but quickly disappeared as the absorption bands due to formaldoxime appeared.

In this work we have utilized the analytical method of infrared spectroscopy, incorporating signal amplification and long path techniques, to follow directly the concentration of nitrosomethane formed in the photolysis of azomethane in nitric oxide. Some interesting new details of the methyl radical–nitric oxide reaction mechanism at room temperature have been established.

Experimental

Materials.—Azomethane was prepared and purified by the method of Renaud and Leitch.[10] Nitric oxide tank gas (99% NO) from Matheson was purified by passing the gas in succession through four gas scrubbers, two containing concentrated sulfuric acid, one containing a saturated solution of potassium hydroxide, one containing mercury and finally through a cold trap at −78°. Nitrous oxide was the only impurity which could be detected by infrared absorption. This impurity was inert and remained unchanged during the course of an experiment so that no attempt was made to remove it.

Equipment.—Most of the reactions were carried out in a 10 cm. infrared absorption cell which was placed in the sample beam of the Perkin–Elmer Model 21 infrared spectrophotometer. Fixed in position about twelve inches from the side of the cell was an AH-6 high pressure mercury arc (General Electric). The incident light intensity was essentially constant in experiments 1–5 of Table I. The Pyrex jacket on the arc and the Pyrex cell body limited the light entering the reaction cell to wave lengths greater than 3000 Å.

In run 6 of Table I, the experiment was carried out using the Perkin–Elmer dual multiple reflections cells which were adjusted to provide a 20 m. path length. The photolysis was effected by the 3600 Å. region of radiation from a G.E. black-light fluorescent tube mounted inside the long path reaction cell. The original optical black finish of the cell interior supplied by the company proved to be highly reactive and absorbent. The inner surface of the cells was removed and the wall covered with aluminum-grey baked enamel, similar to that used on the exterior of the Perkin–Elmer equipment. It proved to be very inert to reactive gases such as NO, NO_2 and O_3, and there was no noticeable effect on the infrared signals due to scattered light.

Procedures and Results

Products of the Reaction.—The usual products of azomethane photolysis, ethane and methane, are not formed in azomethane–nitric oxide mixture photolyses under our conditions. In the homogeneous gas phase reaction which occurs under most conditions only one product (other than nitrogen), nitrosomethane, was observed. When azomethane was photolyzed in mixtures with nitric oxide, the characteristic band of CH_3NO at 6.3–6.4μ appeared.[9] Figure 1 shows the spectrum of the products of an extensive photolysis (15 min.) in a preliminary run made with 4 mm. of azomethane and 8 mm. of nitric oxide in one atmosphere of nitrogen gas. The spectrum was determined in a 1-m. Perkin–Elmer metal cell with untreated walls as furnished by the manufacturer. Under these conditions the CH_3NO band (6.3–6.4μ) decreased as the $CH_2{=}NOH$ bands near 11μ and at the OH region increased. However, the appearance of formaldoxime in the products was peculiar to the use of the 1-m. cell. In all of the rate studies made in the 10 cm. glass–NaCl cell and the long path cells with inert walls, no trace (less than 0.5% of the total product) of the possible product, formaldoxime could be found by infrared analysis. However, a small number of

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(6) C. S. Coe and T. F. Doumani, THIS JOURNAL, **70**, 1516 (1948).

(7) H. T. J. Chilton, B. G. Gowenlock and J. Trotman, *Chemistry and Industry*, 538 (1955).

(8) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 4190 (1955).

(9) W. Lüttke, *Z. Elektrochem.*, **61**, 302 (1957).

(10) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

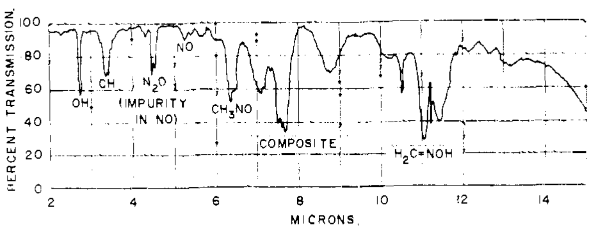

Fig. 1.—The infrared spectrum of the products of the extensive photolysis of azomethane (4 mm.) and nitric oxide (8 mm.) in nitrogen (740 mm.); the spectrum was determined in a 1-m. path length metal cell with the original untreated interior surface provided by manufacturer; the characteristic band at 6.3–6.4 μ is due to monomeric nitrosomethane.[9]

small white crystals of a solid product built up on the cell walls as a run progressed. These crystals had all of the characteristics of the dimers $(CH_3NO)_2$, described by Coe and Doumani[6] and Gowenlock, *et al.*[7,8] A positive nitroso test (blue color) was observed using diphenylamine in concentrated sulfuric acid. The impure sample of the solid taken directly from the cell wall after a run had a melting range (94–97°) in the vicinity of the *cis*-isomer of $(CH_3NO)_2$ reported by Gowenlock (97.5°). The *cis*-isomer might be formed under these conditions since Gowenlock reports the *trans* to *cis* transformation is promoted by ultraviolet irradiation. Some small needle-like crystals, similar in appearance to those pictured by Coe and Doumani,[6] were observed in samples which had been aged before investigation. These melted sharply at about 120°; the *trans*-isomer of $(CH_3NO)_2$ is reported to melt at 122°.[6–8]

Kinetic Studies.—The absorption due to CH_3NO was determined at 6.32μ at regular intervals (15 to 30 sec.) during the build up period of the photolysis. The rate data are summarized in Fig. 2 and Table I for runs at different azomethane–nitric oxide pressures. Throughout this paper we have chosen to represent the values of $[CH_3NO]$ as the quantity log (I_0/I) which is proportional to the actual concentration, since the extinction coefficient of CH_3NO which we derive in this work is of rather limited accuracy. When the absorption due to CH_3NO had reached its maximum or plateau region (see Fig. 2), the arc was turned off (note the breaks in the curves of Fig. 2), and the decay of CH_3NO was followed in a similar fashion. The pressures of CH_3NO were low (1.4 to 0.06 mm. initial pressures in runs 5 and 6, respectively, of Table I),[11] but the small changes in absorption could be followed readily in runs with the 10-cm. cell through the use of the 10-fold or 5-fold scale expansion feature of the Perkin-Elmer instrument, or with no amplification when the long path cells were employed.

In the runs with the long path cells, oxygen-free nitrogen gas was used to purge the cell repeatedly, and then the reactants were flushed into the system with nitrogen gas, so that the reaction cell contained essentially 1 atm. of nitrogen with very small pressures of reactants. Since the incident intensity was greatly different in this experiment and no theoretical significance could be attributed to the initial rate of formation in this case, the rate of build up of nitrosomethane was not determined.

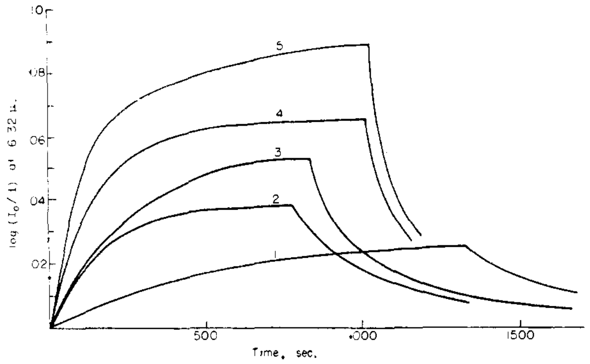

Fig. 2.—The time dependence of the concentration of monomeric CH_3NO in the photolysis of approximately equimolar mixtures of azomethane and nitric oxide; $P_{Me_2N_2}$ = 5, 11, 20, 40 and 80 mm. for runs 1–5, respectively; the break in each curve indicates the point at which the arc was turned off in that experiment.

Figure 3 shows the concentration–time plot for the determination of the initial rates of decay of CH_3NO. The time scale is much too small to show the decrease in concentration of CH_3NO found in run 6. Through similar plots the initial rates of formation of CH_3NO were determined. These are summarized in Table I.

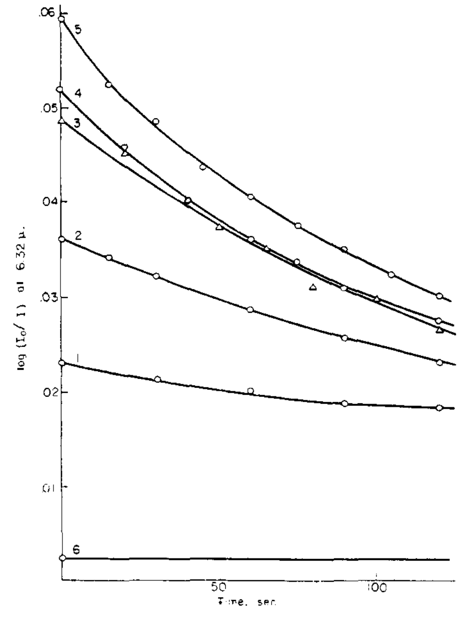

Fig. 3.—A plot of the initial CH_3NO concentration–time dependence in the experiments at varied initial concentrations; the numbers refer to the runs of Table I; initial rates of decomposition (column 4 of Table I) were determined from the initial slopes of these curves.

The Rate of Methyl Radical Formation in Azomethane Photolysis.—The rate of photolysis of azomethane was determined in two experiments in which azomethane and oxygen were mixed in the

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[11] Calculated using the approximate extinction coefficient for CH_3NO which is derived in this work.

photolysis cell. The initial rates of formation of the product methanol were determined. Under the conditions used the only important products of the methyl radical–oxygen reaction have been shown to be methanol and formic acid in approximately equal amounts, and $2(d[CH_3OH]/dt)$ = the rate of methyl radical formation from azomethane photolysis.[12] The incident light intensity in our present azomethane–oxygen experiments was the same as that in runs 1–5 of Table I. The pertinent rate data of methanol formation found in the azomethane–oxygen photolyses are given herewith: 0.00335 mm. CH_3OH/sec., $P_{Me_2N_2}$ = 22.5 mm., P_{O_2} = 720 mm.; 0.0161_5 mm. CH_3OH/sec., $P_{Me_2N_2}$ = 102 mm., P_{O_2} = 640 mm. From these data it can be seen that the rate of methyl radical formation in mm./sec.-mm. azomethane is a constant within the experimental error independent of the pressure of azomethane (0.00029_8 and 0.00031_7 for runs at 22.5 and 102 mm. of azomethane, respectively). Thus for our conditions the rate of methyl radical formation (mm. CH_3 radicals/sec.) in experiments 1–5 of Table I is given by $(0.00030_8)(P_{Me_2N_2}$ in mm.), or the equivalent rate in moles/l.-sec. = $(1.66 \times 10^{-8}$ mole CH_3 radicals/l.-sec.-mm. $Me_2N_2)(P_{Me_2N_2}$ in mm.).

Discussion

The Kinetics of the Decay of Nitrosomethane.—Nitrosomethane was prepared through the photolysis of mixtures of azomethane and nitric oxide. Nitrosomethane monomer is not a stable final product but decays rapidly as it is formed so that a steady-state concentration of nitrosomethane is established after a few minutes irradiation (see Fig. 2). When the steady state had been reached, the light was turned off (at the break in the curves of Fig. 2), and the decay of the monomeric nitrosomethane was followed by absorption measurements at 6.32μ in the characteristic band for CH_3NO.[9] The initial portion of the decay curves is shown in Fig. 3. The rates of decay determined from these data are given in column 4 of Table I. These instantaneous rates correspond to times near the start of the dark period when the concentrations were those shown in column 5. The quantities, $(-d(\log I_0)/dt)/(\log I_0/I)$ and $(-d(\log I_0/I)/dt)/(\log I_0/I)^2$, are shown in columns 7 and 8, respectively, of Table I. The figures of column 7 are far from a constant value which is required for a first-order process. However, the figures of column 8 of Table I are essentially a constant over the 10-fold initial concentration range that the reaction was studied; this is the requirement for second-order kinetics. The minor variations from constancy are not surprising in view of the several uncertainties associated with the determination of the small quantities of CH_3NO: (a) the deposition of dimeric nitrosomethane with subsequent scattering of the infrared beam was noticeable particularly in the runs 4 and 5 at the highest nitrosomethane concentrations; some uncertainty as to the correct value of the transmission at infinite time resulted in these cases; (b) deviations from the assumed Beer's law dependence of absorption on concentration may occur for CH_3NO at 6.32μ. In view of these probable sources of the observed scatter of the data we consider the agreement of the values of column 8 as reasonable proof of the second-order kinetics for the rate of decay of nitrosomethane.

That the rate determining step in this reaction is a purely homogeneous second-order gas phase reaction is suggested by the following facts: (a) the second-order rate constant (or its equivalent in column 8 of Table I) was the same in experiments with a "clean" cell wall and with cell walls containing a deposit of dimer; (b) the second-order rate constant was independent of a sevenfold change in surface to volume ratio (long path cell to 10 cm. cell); (c) there was no effect of a third body on the reaction rate as evidenced by the fact that the rate constant was essentially unchanged in experiments from 10 to 760 mm. pressure.

The Mechanism of Nitrosomethane Formation and Decay.—The following simple mechanism adequately describes our results of nitrosomethane formation and decay in the photolysis of azomethane in nitric oxide.

$$(CH_3)_2N_2 + h\nu \longrightarrow 2CH_3 + N_2 \qquad (I)$$

$$CH_3 + NO \longrightarrow CH_3NO \qquad (1)$$

$$2CH_3NO \longrightarrow (CH_3NO)_2 \text{ (gas)} \qquad (2)$$

$$(CH_3NO)_2 \text{ (gas)} \longrightarrow (CH_3NO)_2 \text{ (solid at wall)} \qquad (3)$$

Under our conditions of equal pressures of nitric oxide and azomethane, reactions of the methyl radical other than (1) are unimportant. It has been shown in a preceding section that the rate of formation of methyl radicals in (I), which is equal to the rate of formation of CH_3NO monomer, is directly proportional to the pressure of azomethane used under our conditions. Incorporating this information with the above mechanism we expect the rate law 4 to describe CH_3NO formation

$$\frac{d[CH_3NO]}{dt} = 2I_a\phi_1 - [CH_3NO]^2k_2 = aP_{Me_2N_2} - [CH_3NO]^2k_2 \qquad (4)$$

I_a is the intensity of the absorbed light; ϕ_I is the primary quantum efficiency of photodecomposition of azomethane; and a is a proportionality constant (0.00030_8 mm. of CH_3NO/sec.-mm. azomethane for experiments 1–5 of Table I). There are two simple tests which show the compatibility of the data with rate law 4.

(a) The initial rate of formation of nitrosomethane is determined by the first term of the rate law 4, $2I_a\phi_I$ or $aP_{Me_2N_2}$, since $[CH_3NO] = 0$ at zero time. After the steady-state concentration of nitrosomethane has been established in a given experiment (the plateau region of Fig. 2), then $d[CH_3NO]/dt = 0$, and $2I_a\phi_I = [CH^7NO]^2k_2$. Now when the light is turned off the initial rate of decay of CH_3NO should equal $2I_a\phi_I$; that is, the initial rate of decay should equal the initial rates of formation of nitrosomethane. Compare the initial rates of formation and decay of CH_3NO in columns 3 and 4, respectively, of Table I. The near identity of these two independent rate measurements for the experiments 1–4 lends credence to the interpretation given. In run 5 the greater

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(12) P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 71 (1959).

uncertainty in the [CH_3NO] values as a result of the more extensive deposition of dimer in this run at the higher concentration, may account for the significant difference between the two rates for this experiment.

(b) According to the mechanism I, 1, 2 and 3, the concentration of nitrosomethane at the maximum or plateau region should be related to the absorbed light intensity or azomethane pressure according to (5).

$$[CH_3NO]_{max} = (2I_a\phi_I/k_2)^{1/2} = (aP_{Me_2N_2}/k_2)^{1/2} \quad (5)$$

The near constancy of the ratio $[CH_3NO]_{max}/P_{Me_2N_2}{}^{1/2}$ of column 10 of Table I is consistent with the relation 5. If the destruction of nitrosomethane were first order the function $[CH_3NO]_{max}/P_{Me_2N_2}$, column 9 of Table I, would have been a constant.

The evidence given provides abundant proof of the homogeneity of the reactions of formation and removal of nitrosomethane. The dimer which accumulates on the cell wall is the likely origin of the oxime product which is found under certain conditions. Only in our preliminary experiments with the 1-m. cell (with untreated, chemically reactive walls) was the spectrum of formaldoxime observed as the band of nitrosomethane decayed. Formaldoxime could not be detected in the products from any of the photolyses in the 10-cm. cell or in the long-path cell. It seems well established from our findings and the results of the many previous studies that dimeric nitrosomethane is the major final product of the reaction between methyl radicals and nitric oxide at room temperature under normal experimental conditions. Isomerization of the dimer to the oxime is rapid and the oxime and the products of its decomposition are the dominant products of the reaction when metallic or other reactive surfaces are in contact with the product, when the temperature is above the melting point of the dimers or when water or certain non-aqueous solvents contact the dimer.[8]

Estimate of the Rate Constant for the Homogeneous Dimerization of Nitrosomethane.—Since no direct observation of the pressure of nitrosomethane monomer present in the reaction mixtures is possible, and the extinction coefficient of nitrosomethane is unknown, an indirect method of estimation of these quantities must be made. It has been established through the azomethane–oxygen mixture photolyses (described in the Results section) that the rate of formation of methyl radicals, which is also equal to the initial rate of formation of CH_3NO, is given by

$$(d[CH_3NO]/d)/P_{Me_2N_2} = 1.66 \times 10^{-8} \text{ mole } CH_3NO/\text{l.-sec.-mm. } Me_2N_2 \quad (6)$$

An average of the most accurate rate data (runs 1, 2 and 3 of Table I) gives

$$(d[\log I_0/I]/dt)/P_{Me_2N_2} = 0.128 \times 10^{-4} \text{ (sec.-mm. } Me_2N_2)^{-1} \quad (7)$$

Since log (I_0/I) = a_Mbc (where a_M is the molar absorbancy index, b is the path length (10 cm.), and c is the molar concentration), then relation 8 follows

$$(d[\log I_0/I]/dt)/P_{Me_2N_2} = a_Mb(d[CH_3NO]/dt)/P_{Me_2N_2} \quad (8)$$

From (6), (7) and (8) we estimate a_M = 77 (l./mole-cm.) for the molar absorbancy index of monomeric CH_3NO at 6.32μ (resolution, 927; slit width, 56μ). Using this estimate of a_M and the average value of the rate function given in column 8 of Table I, we derive that k_2 = 87 (l./mole-sec.) at 25°. Suitable equipment for the determination of k_2 at temperatures other than 25° are not now available to us, so that a measurement of E_2 must be delayed.

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COLUMBUS, OHIO

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

Complex Formation in the Flash Photolysis and Combination of Iodine in Benzene[1]

BY S. J. RAND AND R. L. STRONG

RECEIVED MAY 8, 1959

The flash photolysis of iodine in liquid benzene at room temperature produces a transient intermediate that absorbs light in the visible region, although no over-all photochemical reaction occurs. It is proposed that this is a complex formed between an iodine atom and a benzene molecule, and the absorption is a charge-transfer spectrum. The disappearance of the complex is second order, consistent with the combination mechanism: $2C_6H_6\cdot I \xrightarrow{k} C_6H_6\cdot I_2(+C_6H_6)$. Values of k/ϵ_c where ϵ_c is the molar extinction coefficient of the complex, are independent of initial iodine concentration (0.65 to 5.5 × 10^{-5} M). An IBM-650 digital computer has been used to calculate values of k and ϵ_c for various assumed values of the primary quantum yield of dissociation of iodine in benzene.

Introduction

The combination of iodine atoms in several "inert" solvents has been studied by the flash photolysis technique[2-4] and by the allyl iodide and oxygen scavenger technique combined with rotating sector measurements.[5,6] The primary quantum yield of dissociation ϕ, defined for these systems as the quantum yield for producing a pair of atoms that escape from each other and ultimately combine with atoms from other dissociations,[6]

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[1] Presented at the 135th meeting of the American Chemical Society, Boston, Massachusetts, April, 1959.

[2] R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 2086 (1953).

[3] R. L. Strong and J. E. Willard, THIS JOURNAL, **79**, 2098 (1957).

[4] S. Aditya and J. E. Willard, *ibid.*, **79**, 2680 (1957).

[5] F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954).

[6] H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958).