

Quenching of the Triplet State of Acetone and Biacetyl by Azoalkanes

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It is shown that small concentrations of azoalkanes quench the phosphorescence emitted by acetone and biacetyl, but they do not affect their fluorescence. In the case of acetone the relative quenching efficiencies of nitric oxide, azomethane, and oxygen are 2.8:2.2:1.0 and for biacetyl the efficiencies of azoethane, azomethane, nitric oxide, and oxygen are 19:15:6.7:1.0. It is suggested that the ketone molecule can transfer its triplet state energy to form a triplet excited azoalkane molecule. The photochemistry of the energy-transfer reaction was studied in order to obtain additional information about the fate of the triplet excited azoalkane molecule. A fraction of these triplet excited molecules, formed by the energy transfer from acetone- d_6 , decomposes into a nitrogen molecule and two alkyl radicals. The remainder of the triplet azoalkane is collisionally deactivated to the ground state. At 30° and an acetone- d_6 concentration of 8×10^{-3} mole l^{-1} , the quantum yield of nitrogen formation is 0.31, independent of the concentration of azomethane from 0.4×10^{-4} to 8.8×10^{-4} mole l^{-1} . The substitution of azomethane- d_6 or azoethane for azomethane under comparable conditions results in a decrease in the quantum yield of nitrogen while the quantum yield of carbon monoxide is essentially constant. This indicates a longer dissociative lifetime for the triplet azomethane- d_6 or azoethane compared to azomethane.

Introduction

In a recent study it was shown¹ that the phosphorescence emitted by acetone can be readily quenched by aldehydes. It was also demonstrated that the aldehyde molecules, which are presumably formed in the triplet state as a result of this energy-transfer process, decompose in much the same way as the excited molecules produced in the direct photolysis.

In the present investigation which was carried out along lines similar to the previous study, acetone and biacetyl are used as triplet donors while azomethane and azoethane are the acceptors. For comparative purposes, the quenching effects of oxygen and nitric oxide have also been investigated briefly. It should be noted that the azoalkanes have an advantage that they do not phosphoresce or fluoresce when irradiated at any wave length at which these compounds absorb. Thus, the efficiency with which the azoalkanes quench the excited acetone and biacetyl can be simply determined from the variation in the total emission of the system.

A determination of the quantum yield of decomposition of the azoalkanes resulting from the energy-transfer process was also considered to be of interest in view of the recent gas and liquid phase studies²⁻⁸

of the direct photolysis of azoalkanes which showed that the excited molecule can be collisionally deactivated. It may thus be expected that an excited azoalkane molecule, formed in the energy-transfer mechanism, will undergo decomposition with a probability which may be less than unity and which will yield information on the amount of energy transferred.

Experimental

Azomethane, azomethane- d_6 , azoethane, and acetone- d_6 were obtained from Merck Sharp and Dohme of Canada. Both azomethane- d_6 and acetone- d_6 were better than 99 atom % deuterium. Spectrograde acetone and research grade biacetyl were obtained from the Eastman Organic Chemical Co. All compounds were thoroughly degassed at -160° or higher and subsequently distilled at low temperatures into storage flasks which were protected from light. Nitric oxide from the Matheson Co. was purified by low-temperature distillation from silica gel.

In order to prevent any decomposition of the azoalkane by room light, the photochemical experiments were carried out in a darkened room. The cylindrical quartz reaction vessel (5-cm. diameter, 10 cm. long, and approximately 180 cc. in volume) was enclosed in a heavy aluminum furnace, in which the temperature could be controlled to within 1° . The light source was a Hanovia SH-100 lamp which was used in combination with a Baird-Atomic third-order interference filter with a peak wave length located at 3130 Å. After photolysis the reaction products were separated by low-temperature distillation. The different fractions were further analyzed by mass spectrometry. In all experiments the conversions were kept low enough so that not more than 5% of the azomethane or azoethane, added to the acetone, was decomposed.

Quantum yields were based on the production of carbon monoxide in the photolysis of pure acetone at 140° . At this temperature and at the intensities used in this study ($I_{\text{abs}} = 10^{12}$ quanta/cc.-sec.) the quantum yield of carbon monoxide may be taken as unity.⁹

The emission measurements were carried out in a separate system which has been described previously.¹ The light emitted by the acetone passed through a Corning 0-51 filter (transmitting mainly above 3600 Å.) to a 1 P 28 photomultiplier tube. A Corning 3-69 filter (transmitting above 5200 Å.) was used for the biacetyl experiments. The entrance and exit slits of

(2) R. E. Rebbert and P. Ausloos, *J. Phys. Chem.*, **66**, 2253 (1962).

(3) H. Cerfontain and K. O. Kutschke, *Can. J. Chem.*, **36**, 344 (1958).

(4) J. L. Weininger and O. K. Rice, *J. Am. Chem. Soc.*, **74**, 6216 (1952); P. Ausloos and E. W. R. Steacie, *Bull. soc. chim. Belges*, **63**, 87 (1954).

(5) R. H. Riem and K. O. Kutschke, *Can. J. Chem.*, **38**, 2332 (1960).

(6) R. W. Durham and E. W. R. Steacie, *ibid.*, **31**, 377 (1953).

(7) J. A. Kerr and J. G. Calvert, *J. Am. Chem. Soc.*, **83**, 3391 (1961).

(8) S. S. Thomas and J. G. Calvert, *ibid.*, **84**, 4207 (1962).

(9) D. S. Herr and W. A. Noyes, Jr., *ibid.*, **62**, 2052 (1940).

(1) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **86**, 4803 (1964).

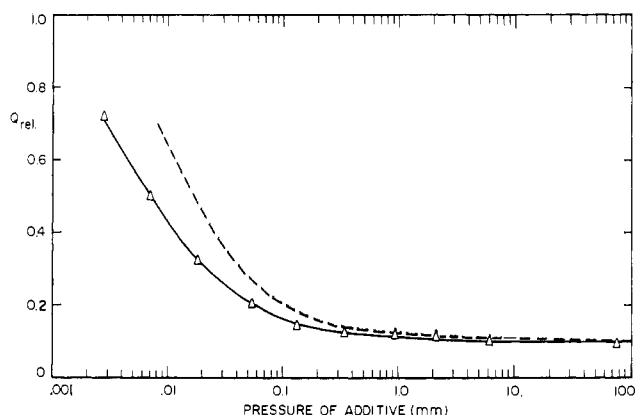


Figure 1. The relative emission from acetone vs. pressure of additive at 32°: Δ , azomethane; -----, oxygen. Pressure of acetone, 103 mm.

the 250-mm. focal length Bausch and Lomb monochromometer were 1.0 and 0.5 mm., respectively. The relatively small quantities of azoalkanes that were added to acetone or biacetyl were measured in a small calibrated volume and subsequently condensed with the ketone into the fluorescence section which is provided with a glass circulating pump. The actual measurement of the light emitted by the gas mixture was done only after sufficient time was allowed (about 5 min.) to ensure complete mixing of the different components.

Results

Phosphorescence and Fluorescence. When azomethane or azoethane are irradiated at wave lengths varying from 3130 to 4000 Å., no emission above 4400 Å. (a Corning 3-73 filter was used) was observed in our apparatus. This indicates that the quantum yield of any light emitted by the excited molecules in the visible region must be less than 5×10^{-5} . This is in agreement with the results of other investigators^{8, 5, 10} who also failed to find any fluorescence from azoalkanes.

Figure 1 shows a typical plot of the relative intensity of the light emitted by acetone above 3600 Å. as a function of the azomethane pressure which was varied from 0.003 to 75 mm. The constant value of Q_{rel} reached at high pressures of azomethane, is within experimental error the same as that obtained when oxygen is added to acetone. Moreover, the emission spectrum taken by means of an Aminco-Keirs spectrophosphorimeter was the same for the acetone-azomethane mixture as for the acetone-oxygen mixture. These measurements were made at high pressures of additives where the relative intensity of the light emitted by acetone has reached a limiting value.

The light emission from acetone at high pressures of azomethane may thus be designated as fluorescence, just as in the case of oxygen-containing mixtures where the emission comes from the upper singlet state of acetone.¹¹ The emission which is quenched by azomethane or oxygen apparently originates only from the triplet state of acetone and consequently may be called phosphorescence.

(10) R. F. Hutton and C. Steel, *J. Am. Chem. Soc.*, **86**, 745 (1964).

(11) W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956).

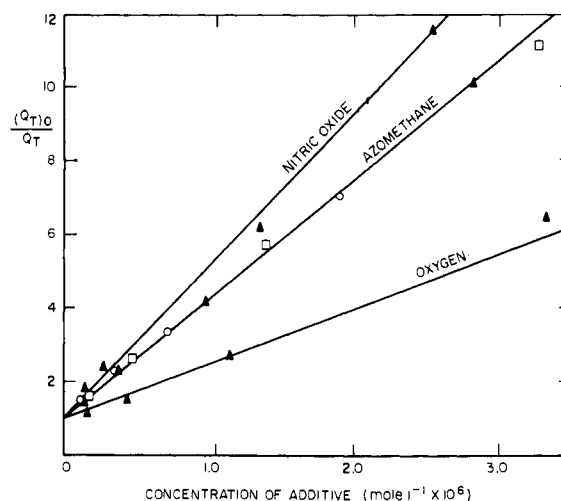


Figure 2. $(Q_T)_0/Q_T$ for acetone at 3130 Å. vs. concentration of additive at 32°. Concentration of acetone: \blacktriangle , 8.0×10^{-3} ; \square , 2.65×10^{-3} ; \circ , 0.84×10^{-3} mole l^{-1} .

Analogous plots have also been obtained for biacetyl-azomethane and biacetyl-oxygen mixtures using the exciting light of 4358 Å. In these cases the relative intensity of the light emitted by biacetyl above 5200 Å. was plotted against the pressure of azomethane or of oxygen. Again, the same constant value of Q_{rel} was obtained at high pressures of either azomethane or oxygen. Thus, it may be concluded that, as in the case of acetone, the light emission from biacetyl at high pressures of oxygen or azomethane comes from the excited singlet state (fluorescence), while the emission which is quenched by oxygen or azomethane originates from the triplet state of biacetyl (phosphorescence). At 32° fluorescence is only about 1% of the total light emitted from biacetyl while, for acetone, fluorescence accounts for 10% of the total light emitted. These results are to be expected, and they agree with the published data.¹²

In Figure 2, $(Q_T)_0/Q_T$ has been plotted against the concentration of azomethane, nitric oxide, or oxygen. Q_T was obtained by subtracting the constant emission observed at high azomethane or oxygen concentration (Figure 1) from the total emission observed for the gas mixture in the low concentration region. $(Q_T)_0$ is the emission calculated in the same way but for pure acetone. In Figure 3, similar plots have been presented but with biacetyl instead of acetone as the donor. A change of wave length from 4358 to 3660 Å. for the exciting light for biacetyl produced no change within experimental error in the quenching efficiency of azomethane.

Acetone-Photosensitized Decomposition of Azoalkanes.

In Table I are presented a few typical results for the isotopic distributions for methane and ethane from the acetone- d_6 -photosensitized decomposition of azomethane. No corrections to these isotopic distributions have been made even though the parent compounds were incompletely deuterated. Such corrections would only be minor, and certainly they would not affect any of the conclusions drawn in this paper. The ratios N_2/CO , CH_4/CD_3H , and $CH_3CD_3/2C_2D_6$, which at 133° are within experimental error

(12) J. Hecklen, *J. Am. Chem. Soc.*, **81**, 3863 (1959).

Table I. Acetone- d_6 -Sensitized Photolysis of Azomethane

Temp., °C.	CD ₃ -COCD ₃ press., mm.	CH ₃ -N ₂ CH ₃ press., mm.	R _{N₂}	R _{CO}	R _{CH₄}	R _{CH₃D}	R _{CD₃H}	R _{CD₄}	R _{C₂H₆}	R _{CH₃CD₃}	R _{C₂D₆}	N ₂ /CO	CH ₄ /CD ₃ H	CH ₃ CD ₃ /2C ₂ D ₆
30	154	1.65	3.12	0.10	0.032	0.019	0.0033	0.0023	2.51	0.44	0.018	31.2	9.7	12.2
133	202	7.6	3.94	2.48	0.58	0.62	0.375	0.49	1.08	1.53	0.485	1.59	1.55	1.58
133	201	2.25	3.35	3.50	0.26	0.58	0.29	0.87	0.87	2.25	1.30	0.96	0.90	0.87
133	202	1.1	2.81	4.79	0.15	0.50	0.23	1.15	0.67	2.56	2.28	0.59	0.65	0.56
133	196	9.28	0.15	2.09	7.21

equal to one another, increase with an increase in azomethane concentration.

Table II and Figure 4 give the variations of the quantum yields of nitrogen and carbon monoxide with changes in concentrations. The quantum yields of nitrogen which are given in Tables II, III, and IV

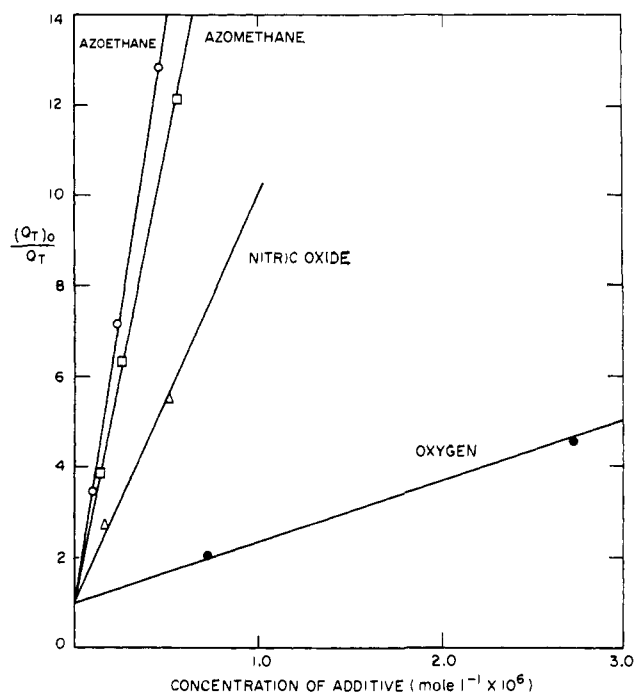


Figure 3. $(Q_T)_0/Q_T$ for biacetyl at 4358 Å. vs. concentration of additive at 32°. Concentration of biacetyl is 0.85×10^{-3} mole l.⁻¹.

and in Figures 4 and 5 have been corrected for the photochemical production of nitrogen which results from the direct absorption of the 3130-Å. light by azomethane and azoethane. At 133°, this correction is only about 2.3% of the nitrogen when the azomethane concentration is 0.4×10^{-4} mole l.⁻¹ and is about 24% of the nitrogen at a concentration of 8.5×10^{-4} mole l.⁻¹ of azomethane. At 30° and constant acetone concentration the quantum yields of nitrogen and carbon monoxide remain constant with a change in azomethane concentration from 0.4 to 8.8×10^{-4} mole l.⁻¹. At 133° over the same concentration range there is a gradual decrease of carbon monoxide and an increase in the nitrogen quantum yield with an increase in azomethane concentration. Moreover, with a decrease in acetone concentration there is a corresponding increase in the quantum yield of nitrogen, and at 133° the sum ($\Phi_{N_2} + \Phi_{CO}$) approaches unity at the lower pressure.

In Figure 5 are given the variations in the quantum yields of nitrogen and carbon monoxide with temperature from 30 to 196°. The quantum yield of carbon monoxide increases with temperature and approaches

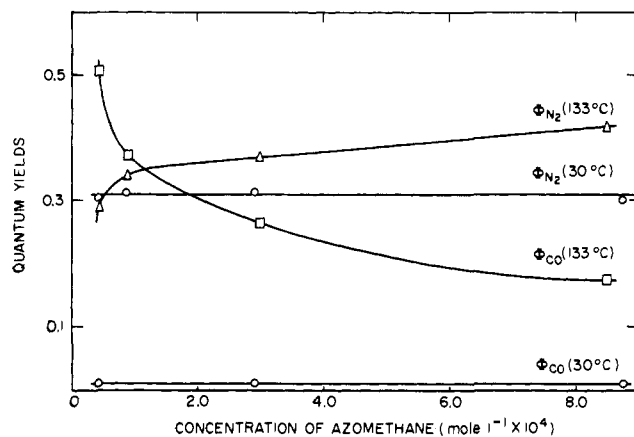


Figure 4. Quantum yields at 3130 Å. vs. concentration of azomethane. Concentration of acetone- d_6 is 8×10^{-3} mole l.⁻¹.

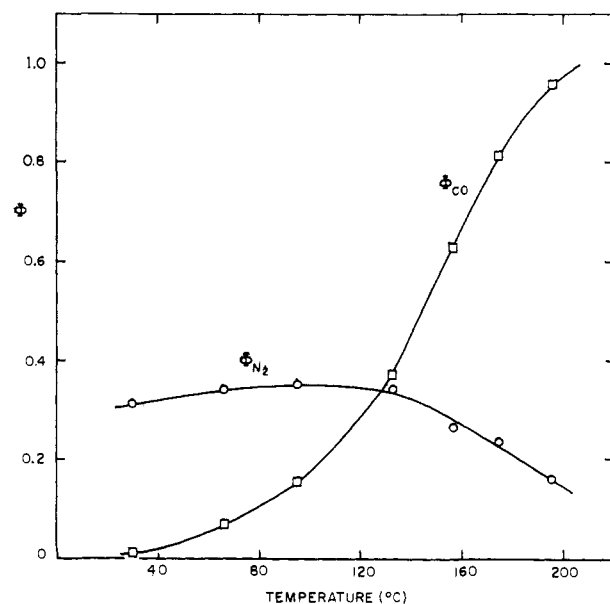


Figure 5. Quantum yields of nitrogen and carbon monoxide at 3130 Å. vs. temperature. Concentration of acetone- d_6 is 8×10^{-3} mole l.⁻¹; concentration of azomethane is 8.9×10^{-6} mole l.⁻¹.

unity while the quantum yield of nitrogen goes through a maximum and then decreases apparently approaching zero at very high temperature. It should be mentioned that the quantum yield of nitrogen is probably too

Table II. Effect of Pressure on the Quantum Yields

Temp., °C.	CD ₃ - COCD ₃ press., mm.	CH ₃ - N ₂ CH ₃ press., mm.	Φ _{N₂}	Φ _{CO}
30	12.4	0.4	0.52	0.034
30	25.6	0.85	0.44	0.024
30	49.6	1.8	0.40	0.023
28	149	5.45	0.31	0.011
133	65.3	1.25	0.39	0.52
134	202	1.1	0.29	0.51

Table III. Effect of Deuterium Labeling on the Quantum Yields

Temp., °C.	Azometh- ane ^a	Φ _{N₂}	Φ _{CO}
26	CD ₃ N ₂ CD ₃	0.16	0.0084
26	CH ₃ N ₂ CH ₃	0.37	0.0098
133	CD ₃ N ₂ CD ₃	0.14	0.33
133	CH ₃ N ₂ CH ₃	0.25	0.32

^a The concentration of acetone is 8×10^{-3} mole l.⁻¹, and the concentration of azomethane is 8.9×10^{-3} mole l.⁻¹.

Table IV. Acetone-*d*₆-Sensitized Photolysis of Azoethane

Temp., °C.	CD ₃ COCD ₃ press., mm.	C ₂ H ₅ N ₂ - C ₂ H ₅ press., mm.	Φ _{N₂}	Φ _{CO}
130	200	1.05	0.042	0.48
129	202	2.3	0.051	0.42
129	202	7.5	0.059	0.26
129	66	2.0	0.079	0.70

high at the upper temperatures owing to a thermal reaction for which no correction has been made. This is also at least partially responsible for the fact that the sum of the two quantum yields (Φ_{N₂} + Φ_{CO}) is slightly above unity at the highest temperature.

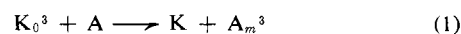
Table III shows the effect on the quantum yields of nitrogen and carbon monoxide at 26 and 133° when azomethane-*d*₆ is used in place of azomethane. The quantum yield of nitrogen decreases when mixtures of acetone-azomethane-*d*₆ are photolyzed in place of acetone-azomethane while the carbon monoxide quantum yield remains almost constant.

The results for the photolysis of acetone-*d*₆ in the presence of azoethane are presented in Table IV. Again, the quantum yield of carbon monoxide decreases with an increase in azoethane pressure at 129°. The quantum yield of nitrogen increases over the same interval but always remains very low.

Discussion

Phosphorescence and Fluorescence. The high efficiency of azoalkanes in quenching the phosphorescence from triplet ketones was unexpected. For instance, in the case of biacetyl, the quenching efficiency of either azoalkane is about an order of magnitude larger than that of oxygen. The fact that the fluorescent emission is not affected by these compounds shows that energy transfer occurs only from an excited triplet ketone to an azoalkane molecule. If the Wigner spin conservation rule may be applied to such systems, then a triplet excited azoalkane molecule will result from

this energy-transfer process. Thus, the energy-transfer reaction



can be added to the generally accepted mechanism that accounts for most observations on the phosphorescence and fluorescence from pure acetone or biacetyl.¹² K₀³ is the ketone molecule in a low vibrational level of the triplet state from which level phosphorescence is generally assumed to occur, while A_{*m*}³ is an azoalkane molecule excited to the *m*th vibrational level of the triplet state. Evidence which indicates that the results cannot be explained by a chemical reaction between an azoalkane and an excited ketone molecule will be presented later in the Discussion.

The following equation can be derived by using the generally accepted mechanism¹² for phosphorescence and fluorescence plus reaction 1

$$\frac{(Q_T)_0}{Q_T} = 1 + \frac{k_1}{C}[A]$$

C represents the summation of the rates of the reactions which K³ can undergo other than reaction 1. In Figure 2 it can be seen that a plot of (Q_T)₀/Q_T vs. the concentration of azomethane gives a good straight line independent of the concentration of acetone which was varied from 0.8 to 8×10^{-3} mole l.⁻¹ (16 to 153 mm). Moreover, similar plots for nitric oxide and oxygen give the following variation for the probability of energy transfer from acetone: nitric oxide > azomethane > oxygen. From the slopes of these straight lines, the following relative efficiencies for energy transfer, *k*₁, can be calculated, taking a value of 1.0 for oxygen: 2.8:2.2:1.0.

Likewise, for the biacetyl-azoalkane system, plots of (Q_T)₀/Q_T vs. concentration of additive (Figure 3) give good straight lines for both azomethane and azoethane. The relative probabilities for the energy-transfer mechanism from biacetyl to azoethane, azomethane, nitric oxide, and oxygen are 19:15:6.7:1.0, respectively.

It is interesting to note that nitric oxide is more efficient than oxygen for both systems. This result agrees rather well with that reported by Bäckström, *et al.*,¹³ who found nitric oxide 2.7 times more effective than oxygen in quenching the triplet benzophenone molecule in the liquid phase. Likewise of interest is the fact that oxygen has about the same efficiency in quenching the triplet states of both acetone and biacetyl even though there is a difference in lifetime between the two of almost a factor of 10 (acetone, 2×10^{-4} sec.¹⁴; biacetyl, 1.8×10^{-3} sec.¹⁵). However, all of the available evidence seems to indicate that the quenching efficiencies of oxygen and nitric oxide are a result of their free-radical properties which lead to chemical reactions with the triplet excited molecules.¹⁶ Thus, as Bäckström, *et al.*,¹³

(13) H. L. J. Bäckström, A. Steneryr, and P. Perlmann, *Acta Chem. Scand.*, **12**, 8 (1958).

(14) W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, **16**, 223 (1948).

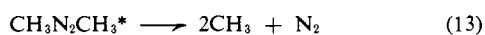
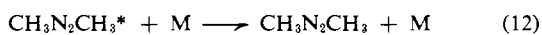
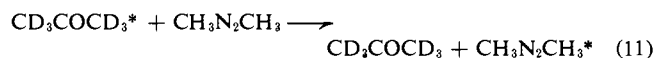
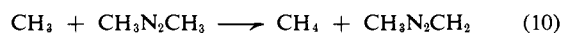
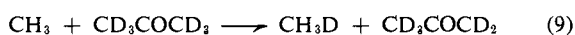
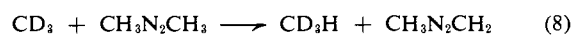
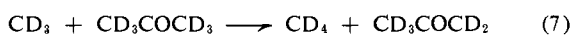
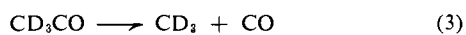
(15) W. E. Kaskan and A. B. F. Duncan, *ibid.*, **18**, 427 (1950).

(16) See, for instance: W. A. Noyes, Jr., *Radiation Res. Suppl.*, **1**, 164 (1959); R. Srinivasan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **82**, 5591 (1960); G. M. Almy, H. Q. Fuller, and G. D. Kinzer, *Phys. Rev.*, **55**, 238 (1955); G. B. Porter, *J. Chem. Phys.*, **32**, 1587 (1960); and ref. 13.

suggested, these differences in deactivating efficiency of nitric oxide and oxygen may be due to a difference in activation energy for the two systems. In contrast, the difference in efficiency for azomethane in quenching triplet acetone and biacetyl is very nearly equal to the difference in lifetime of these two triplet states. This suggests a physical type of quenching as given in reaction 1 instead of a chemical reaction. This view will be corroborated later in the Discussion.

The pressure for half-quenching of biacetyl by oxygen at 32° is 0.014 mm. This is in very good agreement with the value of 0.013 mm. reported by Almy, *et al.*¹⁷ If a collisional cross section of 20×10^{-16} cm.² is assumed in the biacetyl-oxygen system and the lifetime of triplet biacetyl of 1.8×10^{-3} sec. is accepted, then about 250 collisions between triplet biacetyl and oxygen are necessary before a quenching collision takes place. In like manner, if a collisional cross section of 36×10^{-16} cm.² is assumed for the biacetyl-azoethane system, then about 20 collisions are necessary before a quenching collision takes place. For the acetone-azomethane system using the collisional cross section of 36×10^{-16} cm.² and a lifetime of 2×10^{-4} sec., about 20 collisions are necessary to quench the triplet state.

Acetone-Photosensitized Decomposition of Azoalkanes. In order to obtain additional information about the fate of the triplet excited azoalkane molecule, presumably formed in energy-transfer process 1, the quantum yields of the gaseous products which are formed in the photolysis of acetone-*d*₆ at 3130 Å. in the presence of relatively small concentrations of azoalkanes have been determined. The following simplified reaction mechanism can be proposed to account for most observations



In this reaction mechanism $\text{CD}_3\text{COCD}_3^*$ represents the acetone molecule in the triplet state since this is the most important excited state for our discussion and the only excited state which participates in energy-transfer reaction 11. It has also been stated that at 3130 Å. the yield from the singlet state of acetone is a small fraction of the total primary quantum yield even at 25°. Other radical-radical combination and disproportionation reactions have been omitted from

(17) G. M. Almy, H. A. Fuller, and G. D. Kinzer, *J. Chem. Phys.*, **8**, 37 (1940).

(18) J. Hecklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 3858 (1959).

the above mechanism since they are irrelevant to the following discussion.

All our observations are consistent with the above mechanism. In particular, it is concluded from the fact that at 133° the ratio N_2/CO is equal to the ratios $\text{CH}_4/\text{CD}_3\text{H}$ and $\text{CH}_3\text{CD}_3/2\text{C}_2\text{D}_6$ (see Table I) that two methyl radicals are initially formed for each nitrogen molecule produced by the decomposition of the excited azomethane molecule formed in energy-transfer reaction 11. This conclusion is important because, if the nitrogen resulted from a chemical quenching reaction instead of a physical quenching reaction, it is unlikely that this material balance (that is $R_{\text{N}_2} = 2R_{\text{CH}_3}$) would hold. A direct test of this material balance could not be made since some of the methyl radicals initially formed do not produce methane and ethane by reactions 4-10. Some either add to the azomethane or combine with larger radicals as $\text{CD}_3\text{-COCD}_2$ or $\text{CH}_3\text{N}_2\text{CH}_2$, forming products which were not determined in our investigation. However, if both acetone-*d*₆ and azomethane decompose into two CD_3 or CH_3 radicals, then the ratio of N_2/CO will be equal to the ratio of the steady-state concentrations of CH_3 and CD_3 . Furthermore, it can be shown that $[\text{CH}_3]/[\text{CD}_3]$ is equal to $\text{CH}_4/\text{CD}_3\text{H}$ or $\text{CH}_3\text{CD}_3/2\text{C}_2\text{D}_6$. At 30° the ratio N_2/CO is approximately three times the ratio $\text{CH}_4/\text{CD}_3\text{H}$ or $\text{CH}_3\text{CD}_3/2\text{C}_2\text{D}_6$. This is so because not all of the acetyl radicals formed in reaction 2 decompose at this temperature by reaction 3. Thus, less carbon monoxide is produced than indicated by the ratios $\text{CH}_4/\text{CD}_3\text{H}$ or $\text{CH}_3\text{CD}_3/2\text{C}_2\text{D}_6$.

The constant quantum yields of nitrogen and carbon monoxide at 30° with a change in concentration of azomethane from 0.4 to 8.8×10^{-4} mole l.⁻¹ is consistent with the effective quenching of azomethane seen in Figure 1 and also demonstrates the occurrence of quenching reaction 11, followed by decomposition reaction 13. The change in quantum yield of nitrogen and carbon monoxide seen at 133° with a change in azomethane concentration is to be expected because of the decrease in lifetime of the triplet acetone molecule with an increase in temperature.¹⁵ This is also seen even in Figure 5 where the quantum yield of carbon monoxide continually increases with temperature while the nitrogen quantum yield first increases and then decreases under the conditions of constant concentration of azomethane and acetone. The increase in the quantum yield of nitrogen with temperature may be explained by an increase in the rate of reaction 13, compared to 12. The decrease in nitrogen quantum yield is due to the decreased lifetime of the triplet acetone molecule and consequently to the decrease in the rate of energy-transfer reaction 11.

Deactivation reaction 12 has been included in the mechanism for the following reasons. First, the quantum yield of nitrogen at 30°, although constant, is not near unity in the region of azomethane concentration where complete quenching of triplet acetone is observed. As mentioned above,¹⁸ the triplet state of acetone accounts for almost all of the primary quantum yield at 3130 Å. and 25°. Second, the sum of the quantum yields of nitrogen and carbon monoxide even at 133° is not unity. At this temperature all the acetyl radicals decompose so that carbon monoxide is a

measure of the number of acetone molecules photolyzed. Thus, with added azomethane a decrease in carbon monoxide should be balanced by an increase in nitrogen quantum yield. Next, a decrease in acetone pressure at either 30 or 133° brings about an increase in the quantum yield of nitrogen, and the sum of quantum yields of nitrogen and carbon monoxide approaches unity. This is to be expected since a lower pressure should cause less deactivation of the azomethane. Finally, the decrease in the quantum yield of nitrogen, when $\text{CD}_3\text{N}_2\text{CD}_3$ is substituted for $\text{CH}_3\text{N}_2\text{CH}_3$, can also be explained by the deactivation of an excited azomethane if the assumption is made that triplet $\text{CD}_3\text{N}_2\text{CD}_3$ has a longer dissociative lifetime and consequently a higher probability of deactivation than triplet $\text{CH}_3\text{N}_2\text{CH}_3$. There is some direct evidence in the literature that deuteration does increase the lifetime of the triplet state.¹⁹

The fact that, in the direct photolysis, the quantum yield of nitrogen is unity at pressures below 1 atm. of azomethane shows that collisional deactivation is not occurring under these conditions. However, recently in this laboratory²⁰ the direct photolysis of gaseous azomethane at pressures above 1 atm. has shown that the quantum yield of nitrogen does in fact decrease with an increase in pressure. This confirms the occurrence of the deactivation of excited azomethane in the gas phase. In addition, when mixtures of $\text{CD}_3\text{N}_2\text{CD}_3$ and $\text{CH}_3\text{N}_2\text{CH}_3$ were photolyzed in this work, $\text{CD}_3\text{N}_2\text{CD}_3$ was deactivated more effectively than $\text{CH}_3\text{N}_2\text{CH}_3$. This is in agreement with the statement made above that deuteration increases the dissociative lifetime of the triplet excited species. Similar results had also been obtained earlier in the study of the photolysis of azomethane in the liquid phase² in which the low quantum yield of nitrogen as well as the difference in the quantum yield of nitrogen for $\text{CH}_3\text{N}_2\text{CH}_3$ ($\Phi_{\text{N}_2} = 0.1$) and $\text{CD}_3\text{N}_2\text{CD}_3$ ($\Phi_{\text{N}_2} = 0.03$) indicated the possibility of a deactivation step. Collisional deactivation had also been proposed for

(19) See, for instance, G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **38**, 1187 (1963), and ref. 30-34 of this paper.

(20) P. Ausloos and E. E. Hatch, unpublished results.

some of the higher azoalkanes, such as azoethane,^{3,4} azoisopropane,^{5,6} azo-*n*-propane,⁷ and 2,2'-azoisobutane.⁸

It is obvious from the results that excited azomethane is more easily deactivated when produced by the acetone-photosensitized reaction than by the direct photolysis at 3660 Å. This difference in collisional deactivation may be due to the difference in energy given to the azomethane molecule. In the direct photolysis, the light used (3660 Å.) is equivalent to 78 kcal. Unfortunately, the triplet-singlet O-O level is not known exactly for acetone, but it may be estimated²¹ to be at ~4000 Å. This is equivalent to ~72 kcal. In addition, some of this energy may be lost to the acetone as translational or vibrational energy. This indicates that the excited azomethane is in a lower vibrational state for the acetone-sensitized reaction than for the direct photolysis. Consequently, it can be more easily deactivated in the sensitized case.

The results presented in Table IV for the acetone-*d*₆-sensitized photolysis of azoethane may also be explained by a mechanism similar to the one given above for azomethane. However, in the case of azoethane, collisional deactivation is much more probable than it was for azomethane. This conclusion is based on the fact that the quantum yield of nitrogen is very low for azoethane even though it is just as efficient as azomethane in quenching triplet excited acetone. This is also in agreement with the results observed for the photolysis of azoethane and azomethane at pressures below 1 atm. in which the quantum yield of nitrogen is unity for azomethane but decreases with a pressure increase for azoethane.^{3,4}

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(21) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).