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# Mercury-Photosensitized Decomposition of 2-Azetidinone and 4,4-Dimethyl-2-azetidinone

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The mercury-photosensitized decompositions of 2-azetidinone(AZ) and 4,4-dimethyl-2-azetidinone(DMAZ) have been studied at 453 and 423 K and at pressures from 750 to 18000 Pa and from 640 to 5000 Pa, respectively. The major products from AZ were carbon monoxide and ethylene, while ammonia was a minor product. The yields of carbon monoxide and ethylene increased linearly with increasing reaction time and light intensity; they were independent of the AZ pressure. These results suggest that carbon monoxide and ethylene are the primary products. The major products from DMAZ were carbon monoxide, isobutene, and 2,2-dimethylaziridine; ethane, isobutane, and propylene were the minor products. The yields of carbon monoxide, isobutene, and dimethylaziridine increased linearly with increasing reaction time and light intensity at 3800 Pa, showing that these products are the primary ones. The formation of minor products was not linear with time. The quantum yields of carbon monoxide and isobutene were independent of the DMAZ pressure, while the relative yield of dimethylaziridine to that of carbon monoxide increased and those of the minor products decreased with an increase in pressure. Plausible mechanisms were proposed.

There has been considerable interest in both the photolysis and pyrolysis of simple ring compounds.[1] While the photo and thermal decompositions of alicyclic ketones[2–5] and aliphatic lactones[6–9] have been investigated in some detail, there has been only a brief study[10] concerning the thermal decomposition of lactams in the gas phase.

Recently, Frey and Watts investigated the thermal decompositions of $\beta$-butyrolactone (BL)[8] and $\beta$-propiolactone (PL)[9] and found that carbon dioxide and the corresponding olefin were formed as the only products. They obtained relatively small energies of activation (163.4 and 180.5 kJ mol$^{-1}$); they pointed out that a biradical mechanism could be ruled out and that a concerted pathway must be involved. Paquette et al.[10] investigated the thermal decomposition of 3,4-dialkyl-2-azetidinones, finding that fragmentation to olefins and isocyanic acid proceeds virtually with a total retention of stereochemistry. They concluded that this reaction is a concerted-type process. Unlike thermal decomposition, excitation in a mercury-photosensitized reaction can provide sufficient energy to produce biradicals. In fact, it has been found that the mercury-photosensitized reactions of lactones give products different from those from thermal decomposition.[11,12] Although the photolysis of $\alpha$-lactams[13] and $\beta$-lactams[14] were investigated in the liquid phase, the direct photolysis and photosensitized decomposition of lactams in the gas phase had not been reported before.

The present paper describes a study concerning the mercury-photosensitized decompositions of 2-azetidinone (AZ) and 4,4-dimethyl-2-azetidinone (DMAZ). We attempted to establish the reaction mechanism through a determination of the quantum yields and a survey of effects of pressure, reaction time, and intensity of the exciting light.

## Experimental

The apparatus and techniques were similar to those used previously.[11,12] Product analysis was performed by simple fractionations at 77, 185, and 273 K, as well as through measurements with a gas burette and gas chromatography. The light intensity absorbed by mercury atoms at 253.7 nm was determined by means of *cis*-2-butene actinometry[15] ($I_{abs}=7.4\times10^{-9}$ Einstein s$^{-1}$).

AZ(Aldrich, 99%) was used after being recrystallized from diethyl ether. DMAZ was synthesized according to the method of Graf,[16] and was used after drying by calcium hydride, followed by repeated trap-to-trap distillations; *cis*-2-butene (Nihon Tokushu Gasu K.K., pure grade) was used as supplied.

Known amounts of AZ or DMAZ were injected into the reaction cell ($V$=110 cm$^3$) and were degassed after several freeze-pump cycles. The pressures of the reactants in the cell were estimated using the perfect-gas equation.

## Results and Discussion

In order to obtain sufficient vapor pressures of AZ and DMAZ, mercury-photosensitzed reactions were studied at 453 and 423 K, respectively. It was confirmed that neither thermal decomposition at these temperatures nor direct photolysis at 253.7 nm occurred appreciably.

The products obtained in the mercury-photosensitized decomposition of AZ were carbon monoxide, ethylene, and ammonia. The yields of carbon monoxide and ethylene increased linearly with increasing reaction time and light intensity. The production of ammonia showed an induction period, and its yield showed a nonlinear dependence on the light intensity. These findings indicate that carbon monoxide and ethylene are primary products; ammonia is a secondary one. The quantum yields of carbon monoxide and ethylene were independent of the AZ pressure ($\Phi_{CO}=0.87\pm0.05$ and $\Phi_{ethylene}=0.05\pm0.01$).

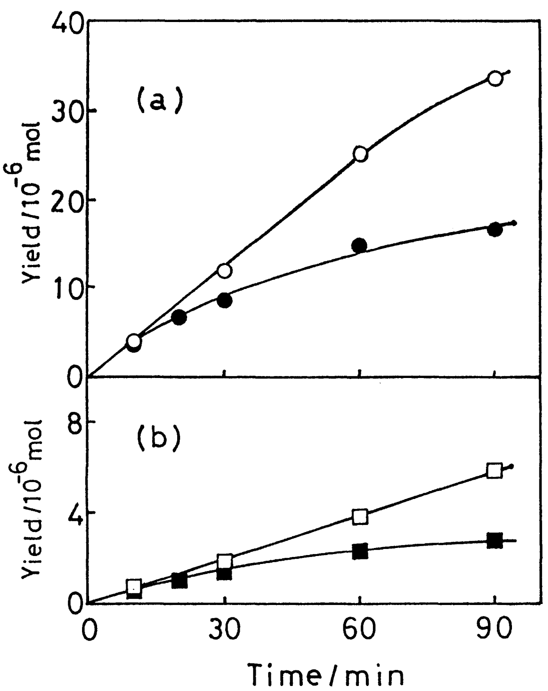


Fig. 1. Time dependence of yields of carbon monoxide (a) and isobutene (b) in the mercury-photosensitized reaction of DMAZ at 3800 (○) and 640 Pa(●).

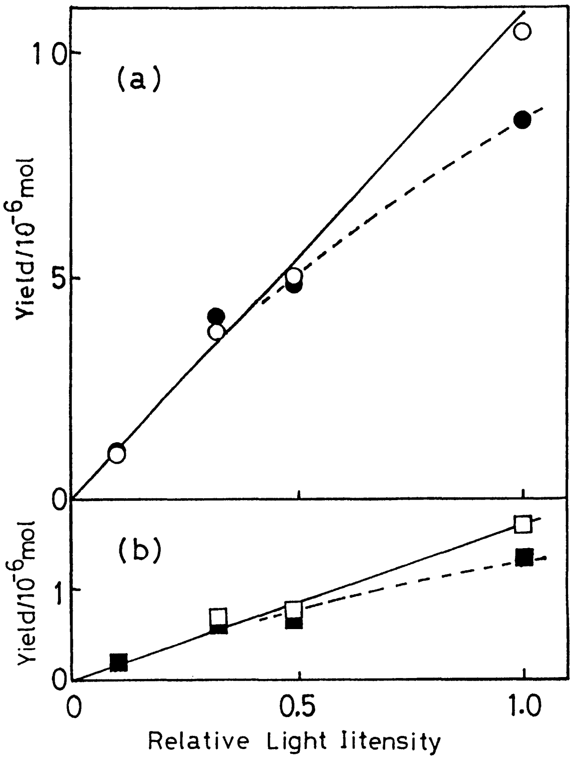


Fig. 2. Dependence of yields of (a) carbon monoxide and (b) isobutene on light intensity in the mercury-photosensitized decomposition of 3800 (○) and 640 Pa (●) of DMAZ. (Reaction time is 20 min and relative light intensity of 1.0 corresponds to $I_{abs}$=7.4×10$^{-9}$ Einstein s$^{-1}$).

The major products from DMAZ were carbon monoxide, isobutene, and 2,2-dimethylaziridine(DMA); ethane, propylene, and isobutane were the minor products. The production of carbon monoxide and isobutene was approximately linear with time and light intensity at 3600 Pa (with perhaps some downward curvature at longer reaction time and higher light intensity), and depended on the time and light intensity at low pressure (Figs. 1 and 2). The decrease in carbon monoxide and isobutene production with increasing time is thought to be caused by either the reduction of DMAZ or the accumulation of products. As is shown in Fig. 1, the deviations from linear relationships between the yields and the reaction time began at 60 and 10 min for runs at DMAZ pressures of 3800 and 640 Pa, respectively. At these reaction times, the extent of decomposition (measured by the ratio of total yields of carbon monoxide and isobutene/initial amount of DMAZ) were about 0.24 and 0.22. The deviation did not begin at a similar amount of remaining DMAZ, but at a similar conversion. This shows that the decrease in product formation was due to competition between the products and DMAZ for quenching excited mercury atoms. This will be discussed later.

The yields of minor products increased non-linearly with time, with the yield increasing more sharply at lower pressure (Fig. 3). This suggests that these minor producs are secondary ones.

It was found that the quantum yields of carbon monoxide and isobutene obtained at an irradiation time of 20 min are independent of the DMAZ pressure at pressures from 900 to 5000 Pa ($\Phi_{CO}$=0.79±0.15 and

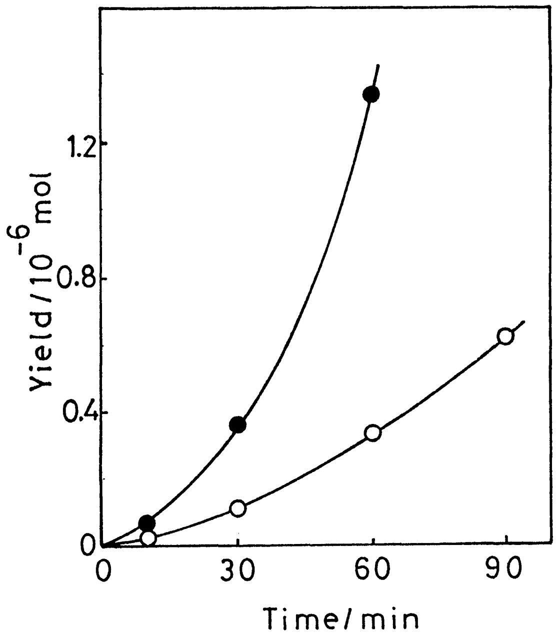


Fig. 3. Time dependence of total yield of ethane, isobutane, and propylene at DMAZ pressures of 3800 (○) and 640 Pa (●).

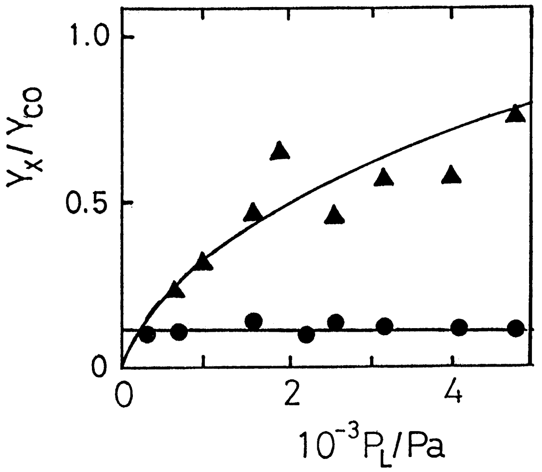


Fig. 4. Pressure dependence of relative yields of products obtained at reaction time of 20 min. ●: isobutene/CO, ▲: 2,2-dimethylaziridine/CO.

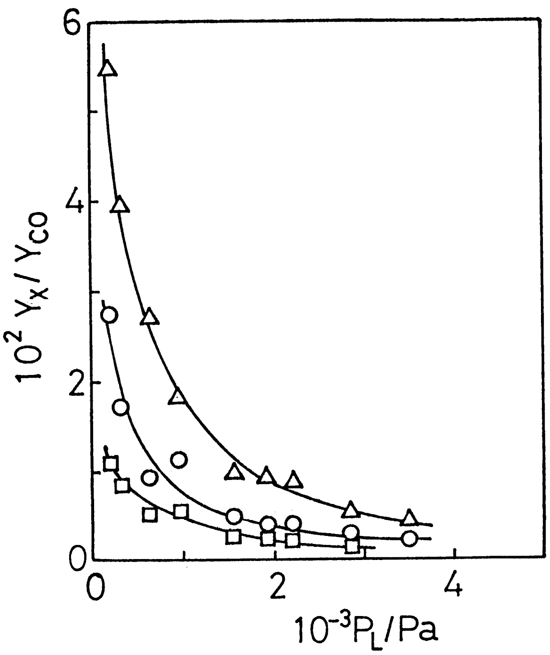
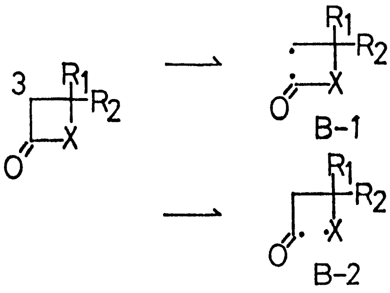


Fig. 5. Pressure dependence of relative yields of minor products obtained at reaction time of 20 min. △: ethane/CO, ○: isobutane/CO, □: propylene/CO.

$\Phi_{\mathrm{isobutene}}=0.12\pm0.03$). In Figs. 4 and 5 the yields of products relative to that of carbon monoxide are shown as a function of the DMAZ pressure. The relative DMA yield increased, while the relative yields of the minor products decreased with an increase in the DMAZ pressure.

The relative quenching efficiencies of Hg($^3P_1$) by AZ and DMAZ to that by *cis*-2-butene were estimated to be 0.69±0.03 and 0.63±0.02 from the effect of AZ and DMAZ on the yield of *trans*-2-butene. These values are similar to those reported for PL (0.62) and BL (0.61).

It has been concluded in previous studies[11,12] that the triplet lactones formed in the mercury-photosensitized reaction undergo a Norrish type-I cleavage. If the triplet lactams are also formed (the similar quenching efficiencies for lactones and lactams mentioned above suggest a similarity regarding their initial processes) and undergo similar cleavages, the following biradicals may be formed:



(1)

(2)

| | X | R1 | R2 |
|---|---|---|---|
| AZ | NH | H | H |
| DMAZ | NH | $CH_3$ | $CH_3$ |
| PL | O | H | H |
| BL | O | $CH_3$ | H |

Scheme 1.

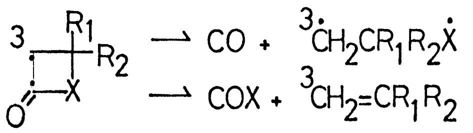
In the case of lactones,[11,12] Reaction (1) is followed by an elimination of carbon dioxide by breakage of the $C_4$–O bond, producing equimolar olefins ($C_2H_4/CO_2=1$ for PL and $C_3H_6/CO_2=1$ for BL); Reaction (2) is followed mainly by the production of carbon monoxide. It has been pointed out[12] that the ratio of Reaction(2)/Reaction(1), which is approximately equal to the ratio of $\Phi_{CO}/\Phi_{CO_2}$, decreases in the order PL, BL, and γ-butyrolactone; this order agrees with the order for the increase in the difference in bond-dissociation energies between OC–O and OC–C bonds ($\Delta E_b=E_b(\mathrm{OC{-}O})-E_b(\mathrm{OC{-}C})$).

In the case of lactams, ethylene and isobutene were the primary products. Isocyanic acid (HNCO) may be produced by the decomposition of the biradical, B-1, though it was not detected. HNCO could be lost in product traps, perhaps by polymerization and by a reaction with the lactams.

The ratios of $\Phi_{CO}/\Phi_{\mathrm{ethylene}}$ for AZ and $\Phi_{CO}/\Phi_{\mathrm{isobutene}}$ for DMAZ are 17.4±1.8 and 6.2±1.5, respectively. They are quite different from the ratios of $\Phi_{CO}/\Phi_{\mathrm{ethylene}}$ for PL (0.38)[11] and $\Phi_{CO}/\Phi_{\mathrm{propylene}}$ for BL (0.089).[12] The differences ($\Delta E_b'=E_b(\mathrm{OC{-}N})-E_b(\mathrm{OC{-}C})$) in the bond dissociation energy between the OC–C and OC–N bonds in AZ and DMAZ were estimated to be 51.9 and 58.2 kJ mol$^{-1}$ (the heats of formation of biradicals were estimated according to a method of McGee and Shleifer[17] using available thermochemical data[18,19]). These values are not very different from those for PL ($\Delta E_b=46.4$ kJ mol$^{-1}$) and BL ($\Delta E_b=54.8$ kJ mol$^{-1}$).

The results for lactones have been explained in terms of the idea that the ease of cleavage of $\alpha$-bonds in the lactones determines the ratios of $\Phi_{CO}/\Phi_{olefin}$. The large ratios of $\Phi_{CO}/\Phi_{olefin}$ observed for lactams, however, can not be explained only by this idea. A possible explanation for the large fraction of carbon monoxide formation for lactams is that in this case carbon monoxide can also be formed from the biradical, B-I, through OC-N bond breakage.

The biradicals formed in Reactions (1) and (2) must be triplets according to the spin-conservation rule. The estimated enthalpy changes for the following reactions are listed in Table 1.



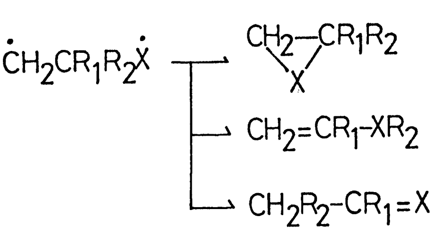
(3)

(4)

The heat of formation of the triplet biradicals involved in Reaction (3) were calculated by the method mentioned above by assuming that the differences in energy between triplet and singlet states can be neglected. The triplet energies of the olefins were cited from the literature.[20]

As shown in Table 1, the enthalpy changes of Reaction (3) for lactams are similar to those for lactones, while the enthalpy changes of Reaction (4) for lactams are much larger than those for the lactones. This large difference in the enthalpy changes of Reaction (4) comes from the large difference in the heats of formation of HNCO (=104.2 kJ mol⁻¹) and CO (=343.7 kJ mol⁻¹). The large endothermicity of Reaction (4) for lactams may show that this reaction is difficult to occur in the case of lactams. This results in the large amount of carbon monoxide compared to that of the corresponding olefins.

The fate of the biradicals, $\dot{C}H_2CR_1R_2\dot{X}$, formed in Reaction (3) requires some comments. We suggest the following three possibilities:



(5)

(6)

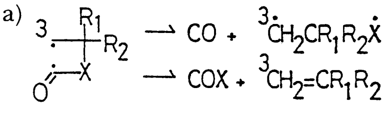
(7)

Reaction (5) shows a ring closure and Reactions (6) and (7) show hydrogen-transfer reactions from the 2-position to the 1- or 3-position, respectively. In the case of the lactones, some products which suggest the presence of Reactions (5) and (7) were observed (ethylene oxide and acetaldehyde for PL,[11] as well as propylene oxide and acetone for BL[12]). In the case of AZ, however, none of them was observed. Ethenamine and ethanimine, which are products in Reactions (6) and (7), are known to be unstable and easily polymerize to cyclic and linear higher compounds.[21,22] In the photolysis of AZ, aziridine (a ring-closure product) also could not be detected (the identification limit of our analytical system was about $5\times10^{-8}$ mol). This suggests that even though a hydrogen transfer in the biradical, $\dot{C}H_2CH_2\dot{N}H$, may occur, a ring closure does not.

Table 1. Enthalpy Change for Reactions (3) and (4)[a]

| Compounds | $\Delta H_3$ kJ mol⁻¹ | $\Delta H_4$ kJ mol⁻¹ |
|---|---|---|
| AZ | 85.9 | 151.9 |
| DMAZ | 92.3 | 149.6 |
| PL | 74.4 | 23.8 |
| BL | 88.3 | 24.6 |

a)



It is interesting to note that DMA was detected in the mercury-photosensitized decomposition of DMAZ. As is shown in Figs. 4 and 5, the relative yield of DMA increased and those of minor products decreased with an increase in pressure. In order to explain these results, the following reactions are proposed in addition to the above-mentioned reactions:

$$CH_2C(CH_3)_2NH \rightarrow DMA^*, \qquad (8)$$

$$DMA^* \rightarrow X_i, \qquad (9)$$

and

$$DMA^* + M \rightarrow DMA, \qquad (10)$$

where DMA* is 2,2-dimethylaziridine with excess energy and $X_i$ denote unknown products. From the large exothermicity of the reaction $DMAZ+Hg(^3P_1)\rightarrow CO+DMA+Hg(^1S_0)$, DMA is formed with a large excess of energy and may isomerize and/or decompose. From Reactions (3) and (8)—(10), the following equation is derived:

$$\frac{\text{Yield of DMA}}{\text{Yield of CO}} = \frac{k_{10}[\text{DMAZ}]}{k_9 + k_{10}[\text{DMAZ}]}.$$

This equation shows that the relative yield of DMA increases with an increase in the DMAZ pressure; this explains the pressure dependence of the DMA yield given in Fig. 4.

As mentioned previously, the influence of products on the productions of carbon monoxide and isobutene can not be neglected. The following reaction scheme can possibly explain the influence of the products:

$$Hg^* + DMAZ \rightarrow Hg + DMAZ^*, \qquad (11)$$

$$Hg^* + X_i \rightarrow Hg + X_i^*, \qquad (12)$$

$$DMAZ^* \rightarrow \text{CO, isobutene, DMA}, \qquad (13)$$

and

$$X_i^* \rightarrow \text{Minor products observed and others.} \qquad (14)$$

As products $X_i$ build up in the system, the contribution of Reaction (12) becomes larger, and the yields of carbon monoxide and isobutene decrease; those of the minor products increase. These tendencies are emphasized at lower pressures. Although $X_i$ could not be identified, the above-mentioned reactions qualitatively account for the results regarding the dependences of the pressure, time, and light intensity on the product yields shown in Figs. 1—5. The production of minor products is certainly not simple, and further speculation concerning mechanism is not justified.

The mechanism for the formation of ammonia is not clear. Judging from the fact that ammonia was not detected in the mercury-photosensitized decomposition of DMAZ, ammonia is probably produced after hydrogen transfer in the biradical, B-1. Brinton[22] studied the photolysis of acetaldehyde azine and observed ammonia as a product. He pointed out that ethanimine, which is formed during the primary process, must play an important role in the production of ammonia: that is, ammonia is released during some rearrangement or polymerization reactions of ethanimine. This idea is in agreement with the abovementioned suggestion that hydrogen transfer occurs in the case of AZ, but not for DMAZ.

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