The Intermediates in the Low-Temperature Photolysis of Bis(diazo)cyclohexatetraone in an Argon Matrix

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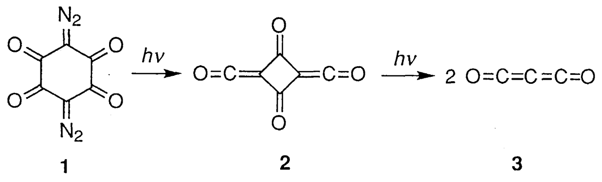
The photolysis of bis(diazo)cyclohexanetetraone (**1**) was investigated in an argon matrix at 17 K. Two intermediates were formed by a consecutive decomposition of two diazo groups of **1**, which were identified by UV-vis and IR spectroscopies.

Photolysis of diazo ketones has been widely investigated in carbene chemistry. In particular, ketocarbenes are interesting in their high reactivity to follow Wolff rearrangement.[1-3] Recently Maier and his co-workers reported preliminary results of the photolysis of bis(diazo)cyclohexanetetraone (**1**) in an argon matrix at low temperature from the viewpoint of preparation of new carbon oxides.[4,5] Although they found that the photolyzed **1** gave a carbon suboxide (C_3O_2) (**3**) as a final photoproduct *via* cyclic bisketene (**2**) as an intermediate (Scheme 1), they did not describe the reaction mechanism including the formation of **2**. In this paper we report the identification of transient intermediates in the photolysis of **1** in a low-temperature argon matrix on the basis of UV-vis and IR spectroscopies.



Scheme 1.

A matrix-isolated sample of **1** with argon was prepared by deposition of **1** on a CsI substrate for IR spectroscopic study or a sapphire plate for UV-vis spectroscopic study at 17 K. The sample was photolyzed with a monochromatic light (310 nm) of a high pressure mercury lamp (500 W) through a monochromator (JASCO CT-10). The photolysis of **1** was followed by UV-vis and FT-IR spectroscopies.

UV-vis spectral change is shown in Figure 1. With the increase of irradiation time, a new peak at 245 nm appeared with the decrease of the maxima at 274 and 318 nm. Upon further irradiation another new maximum appeared at 234 nm, while no absorption peaks appeared in the longer wavelength region. These results suggest that the photolysis of **1** proceeded *at least* in two steps.

On the other hand, FT-IR spectroscopic analysis indicated that **1** was photolyzed in three steps as shown in Figure 2. Upon the irradiation for 10 min, many peaks appeared with the decrease of the peaks at 1681 and 2150 cm^{-1} which were ascribed to carbonyl and diazo groups, respectively. However, the peaks at 1697, 2165, and 2131 cm^{-1}, which were three of the many peaks, decreased upon further irradiation. These three peaks belong to a sole intermediate (A), because the decreasing rates of those were similar.[6]

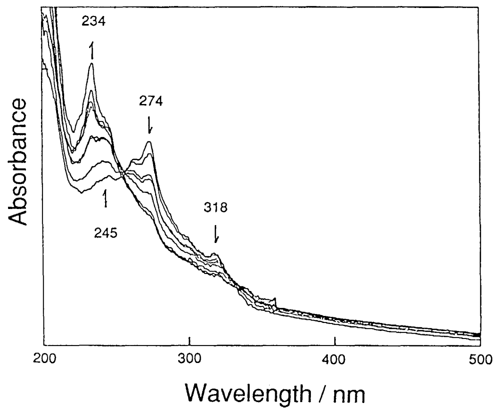


Figure 1. UV-vis spectra obtained by irradiation (310 nm light) of bis(diazo)cyclohexatetraone (**1**) in an argon matrix at 17 K.

The peaks at 2101 and 1747 cm^{-1}, which were also appeared at the initial stage of the photolysis, seemed to be constant during the further irradiation. However, additional irradiation led to a final photoproduct (**C**), having the peaks at 3073, 2272, and 541 cm^{-1}, with a slight decrease of the peaks at 2101 and 1747 cm^{-1}. It means that the intermediate (**B**) having the peaks at 2101 and 1747 cm^{-1} was converted to photoproduct **C**.[7]

In the case of UV-vis spectra the photolysis proceeded in two steps, whereas a three step process was indicated in the IR spectra, as mentioned above. This result can be explained by the overlapping of the absorptions of the intermediates **A** and **B**.

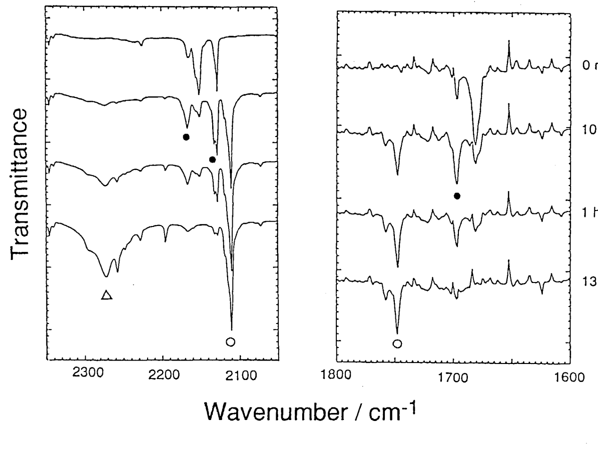
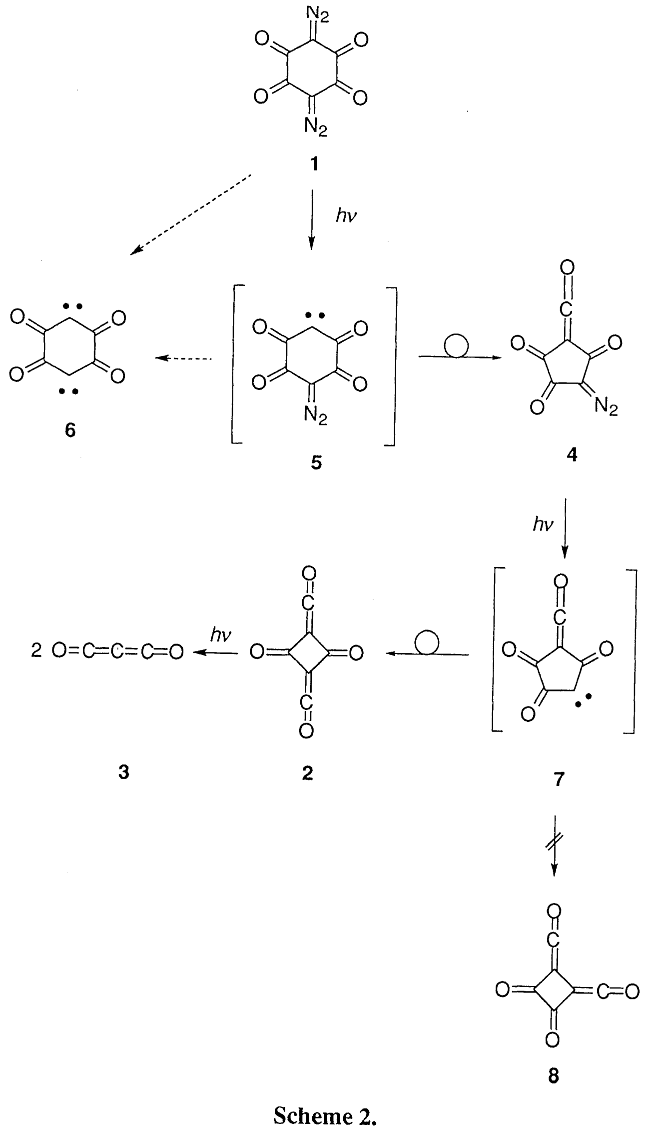


Figure 2. FT-IR spectra obtained by irradiation (310 nm light) of bis(diazo)cyclohexateraone (**1**) in an argon matrix at 17 K. The peaks marked with ●, ○, and △ are assigned to the bands due to **4**, **2**, and **3**, respectively.

The final photoproduct (**C**) was assigned to be carbon suboxide **3**, which Maier had reported,[4,5] by the comparison with the IR absorption spectrum given by Long and his co-workers.[8] This assignment was supported by the UV-Vis spectrum where the new peak appeared at 234 nm as a final photoproduct (Figure 1).[9]

The first-formed reactive intermediate **A** has two characteristic peaks at 2165 and 2131 cm^{-1}, as described above, which could be ascribed to ketene and diazo groups. As the results of the photodecomposition of one of the two diazo groups to follow Wolff rearrangement, the intermediate **A** was assigned to be the diazoketene **4**. This assignment is supported by semiempirical PM3 calculations. The IR absorption peaks of the diazo and ketene groups for **4** were calculated to be 2485 and 2349 cm^{-1}, respectively,10) and the spectral pattern well corresponded to that of the observed spectrum.



Scheme 2.

The second-formed intermediate **B** generated after further photolysis of another diazo group in **4** has two characteristic IR peaks which are ascribed to ketene and carbonyl groups. The intermediate **B** would be assigned tentatively to cyclic bisketene **2** or **8** as the results of the photodecomposition of diazo group and the Wolff rearrangement of reactive intermediate **7**. The structure of **B** was not **8** (C_{2v}) but **2** having a higher symmetrical structure (D_{2h}). It was confirmed by PM3 calculations, which showed a pattern of IR peaks similar to that of the observation. A selective formation of **2** from **7** would be explained thermodynamically because **2** was more stable than **8**. The heat of formation of **2** is 12.43 kcal/mol lower than **8**. Thus, the reaction mechanism for the formation of **2** from **4** is shown in Scheme 2.

An attempt was made to trap the carbenes **5** and **7** which were assumed in the mechanism. The photolysis of **1** in argon matrix was conducted in the presence of 2,3-dimethyl-2-butene. The matrix was annealed to room temperature; however, the carbene adducts were not observed by IR and mass analyses. In addition, ESR absorption peaks of carbenes were not detected in an argon matrix at 12 K and in 2-methyltetrahydrofuran at 4 K. Recently Tomioka and his co-workers have detected a diazo ketocarbene, which was stabilized with a phenylene group, in the photolysis of 1,3-bis(diazo)indan-2-one in cryogenic rigid matrices by IR and ESR spectroscopies.[3] On the contrary, ketocarbenes **5** and **7** should be highly reactive; therefore, rapid rearrangement must have taken place even at cryogenic temperature so that the clear evidence for the existence of the carbenes was not obtained.

Although biscarbene **6** was not detected in the experiments, the participation of **6** in the photolysis can not be excluded. Therefore, we conclude that the photolysis of **1** proceeded as shown in Scheme 2. It is expected that **6** can be formed by multi-photon processes. Thus, further investigation on high-intensity laser photolysis is in progress.

Reference and Notes

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6 The peaks ascribed to the intermediate **A** were observed before irradiation with 310 nm light. It would be explained by the fact that a small amount of **1** was decomposed during deposition of **1** (the deposition temperature; 80 °C).
7 The intermediate **B** was decomposed effectively to the photoproduct **C** upon the irradiation with a low-pressure mercury lamp, while the quantum yield of conversion of **B** was quite low with 310 nm light.
8 D. A. Long, F. S. Murfin, and R. L. Willams, *Proc. Roy. Soc.*, **A223**, 251 (1954).
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10 The *ab initio* caluclation of **4** was also perfomed at the HF/6-31G* level: 2543 cm^{-1} ($\nu_{C=N=N}$) and 2419 cm^{-1} ($\nu_{C=C=O}$).