Photolysis of 1,2,4,5-Benzenetetracarboxylic Dianhydride in a Low-Temperature Argon Matrix. Direct Observation of Reactive Intermediates Stepwise Produced

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(Received March 2, 1995)

Irradiation of 1,2,4,5-benzenetetracarboxylic dianhydride produced stepwise a cyclopropenone and benzyne intermediates with the release of CO_2 and CO in a low-temperature argon matrix. In the final stage the further extrusion of CO_2 and CO gave 1,3,5-hexatriyne which was a potential product in the ring-opening reaction of benzdiyne.

Arynes are interesting intermediates in their structures and reactivities. Benzyne, the most fundamental species of them, has been observed directly by IR and UV-Vis spectroscopies employing a matrix isolation technique.[1] On the other hand, benzdiynes having two triple bonds in an aromatic ring have been discussed only theoretically.[2,3] Although some reports have predicted that the photolysis or thermolysis of benzene-tetracarboxylic dianhydrides could produce benzdiynes,[3,4] there has been yet no experimental evidence for it. We wish to report the photolysis of 1,2,4,5-benzenetetracarboxylic dianhydride (**1**, pyromellitic dianhydride) in a low-temperature argon matrix.

The photolysis was followed for the matrix isolated sample prepared on a CsI plate at 17 K by means of IR spectroscopy. Irradiation of **1** with a high pressure mercury lamp (>290 nm) afforded a new carbonyl species (1794 cm^{-1}) together with extrusion of CO_2 (2343 cm^{-1}) and CO (2142 cm^{-1}) from **1**. Continued irradiation of the 1794-cm^{-1} species with a low pressure mercury lamp caused the disappearance of the 1794-cm^{-1} band with further increasing the absorption of CO_2 and CO. These results suggest that the 1794-cm^{-1} species still had the carbonyl sites which were able to decompose to CO_2 and CO. Together with the disappearance of the 1794-cm^{-1} species, other new bands appeared at 2250, 2246, and 2234 cm^{-1} assigned to ketene, and gave a new intermediate **A** (3335, 3317, and 623 cm^{-1}) not assigned at the present stage.

In order to study on the reaction mechanism in detail, the narrow-band irradiation was carried out with an XeCl excimer laser at 308 nm. The irradiation of **1** gave a carbonyl species (1859, 1843, and 1801 cm^{-1}) which was a precursor of the 1794-cm^{-1} species with increasing the absorption of CO_2, and then, the 1859-cm^{-1} species decreased with the increase of CO and the 1794-cm^{-1} species (Figure 1). Subsequent irradiation finally gave the same IR spectrum as given upon the irradiation of **1** with the high pressure mercury lamp (>290 nm). Consequently, it was confirmed that the photolysis of **1** produced the 1794-cm^{-1} species through the 1859-cm^{-1} intermediate in the initial stage.

On the basis of above-mentioned IR spectra and the following trapping analysis, the photolytic process which is dependent on irradiation wavelength would be shown in Scheme 1. In the

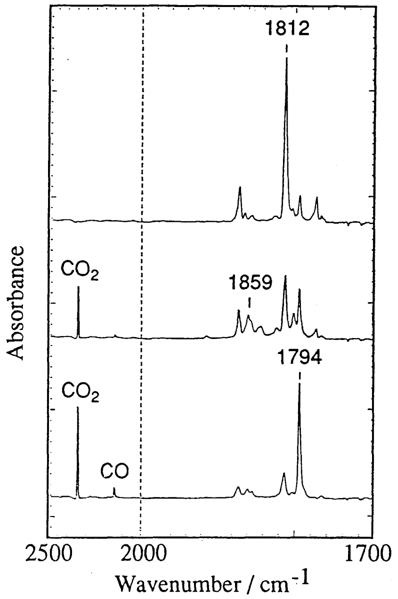
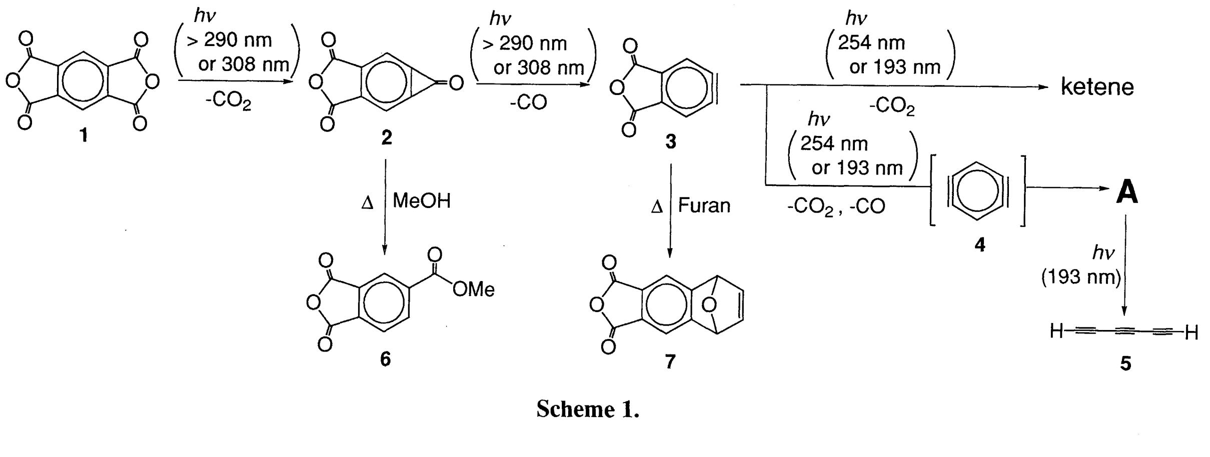


Figure 1. IR spectra of **1** (top), after irradiation of 500 pulses (center) and after irradiation of 6000 pulses (bottom) with XeCl excimer laser in an argon matrix at 17 K.



Scheme 1.

first, the release of CO_2 from **1** gives a cyclopropenone intermediate **2** having the carbonyl absorption at 1859 cm^{-1} , and, in the second, the release of CO from **2** gives a benzyne intermediate **3** having the carbonyl absorption at 1794 cm^{-1}. The band of **2** at 1859 cm^{-1} is in good agreement with that due to cyclopropenone structure.[5] The formation of **2** and **3** was confirmed by trapping in an argon-methanol (ca. 100:2.5) and argon-furan (ca. 100:2.3) matrices, respectively. The trapped products were examined by GC-MS, which revealed the formation of ester **6** (M^+=206) and **3**-furan adduct **7** (M^+=214).

The conversion of **1** to **3** through **2** was also followed by UV-Vis spectroscopy using the same matrix as the IR spectra were measured. Irradiation of **1** with the laser at 308 nm resulted in the disappearance of **1** with concomitant appearance of new maxima at 287 and 296 nm due to **2** (Figure 2). Continued irradiation of **2** caused the disappearance of the maxima due to **2** and then, gave the intermediate **3**, which has no absorption maxima in near 300 nm although the small maxima due to **1** and **2** still remained.

Moreover a high energy photolysis with an ArF excimer laser at 193 nm was investigated in order to discuss on the final stage of the reaction. The photolysis of **1** proceeded along two different paths. One was the formation of the ketene which was same as given upon the irradiation with the low pressure mercury lamp. The other was the formation of 1,3,5-hexatriyne (**5**, 3324 and 627 cm^{-1}, assigned in the literature[6]) through the intermediate **A**. Although the formation of **5** from **1** by flash vacuum pyrolysis has been reported without detailed mechanism by McNaughton et. al,[7] we revealed the formation of **5** through the stepwise decarboxylation and decarbonylation from **1**. This finding suggests that 1,4-benzdiyne (**4**) may participate in the reaction from **1** to **5**, because it has been indicated from the MO calculation that **5** is assumed as the product in the ring-opening reaction of **4**.[2] In the present work, however, we could not obtain a direct evidence of **4** by IR and UV-Vis spectroscopies. If **4** is stable in the low-temperature matrices, a Raman spectroscopy technique would be needed to observe the matrix isolated **4** because the IR intensities of **4** are mostly low from the theoretical predictions.[3]

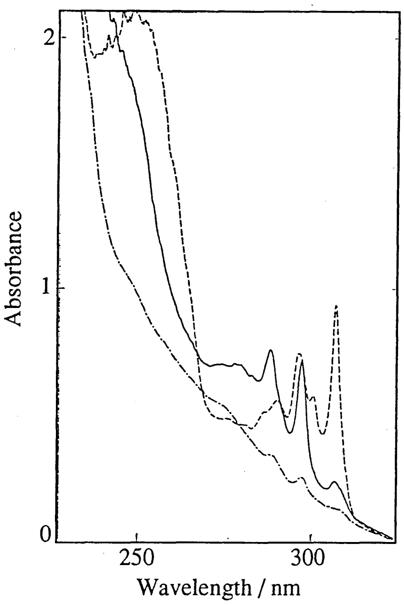


Figure 2. UV-Vis spectra of the cyclopropenone intermediate **2** (solid line) and the benzyne intermediate **3** (dotted line) formed on irradiation of **1** (dashed line) (500 and 6000 pulses, respectively, with XeCl excimer laser) in an argon matrix at 17 K.

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