

Photolysis of 1,2-Naphthoquinone in Oxygen-Doped Argon Matrix at Low Temperature

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Photolysis of 1,2-naphthoquinone (**1**) in argon matrix either with or without oxygen at 10 K was investigated by IR spectroscopy in combination with DFT calculations. The results indicate that **1** gave bis(ketene) **2** as a main product along with a small amount of inden-1-one (**4**), most probably as a result of Type I cleavage, followed by electron reorganization and decarbonylation in the resulting diacyl radical, respectively. Bis(ketene) **2** was shown to transform to isomeric ketene **3** upon continued irradiation under these conditions. When the irradiation was carried out in argon matrix doped with 20% oxygen, **1** decomposed much more efficiently than that in argon matrix and six- and eight-membered cyclic peroxides presumably formed by trapping of initial diradical originating from α -cleavage by molecular oxygen were detected at complete expense of **3** and **4**. The formation of **2** even in the presence of oxygen suggested that **2** may partly be formed by a concerted pathway in the singlet excited state. The present observation reveals that photolysis of α -diketones in oxygen-doped matrix at low temperature provides useful information concerning the reaction pathway of the diketone upon photoexcitation.

Photolysis of α -diketones in the presence of oxygen in solution attracts considerable attention.^{1–5} Under these conditions, diketones are converted apparently to intermediate peroxy radicals, and observed final products are carboxylic anhydrides or the corresponding acids. When alkenes are present, the intermediate peroxy radicals react with the double bond to give the corresponding epoxides, thus providing a mild procedure for epoxidation of alkenes.

It has been proposed that the most plausible peroxy radicals are ketone–oxygen adduct diradical (I) formed as a result of attack of triplet oxygen on the carbonyl carbon in the excited triplet state of the diketones. Since the β -scission of an alkoxy radical is a facile process, the diradical I then decays to radical pair II. Formation of anhydride is explained in terms of attack of acyl radical on the carbonyl oxygen of acyl peroxide in II leading to III. Since acyl radical in II is known to efficiently react with oxygen,⁶ acyl radical in II is trapped by a second oxygen thus generating an acyl peroxy radical (IV), which eventually produces acids (Scheme 1).

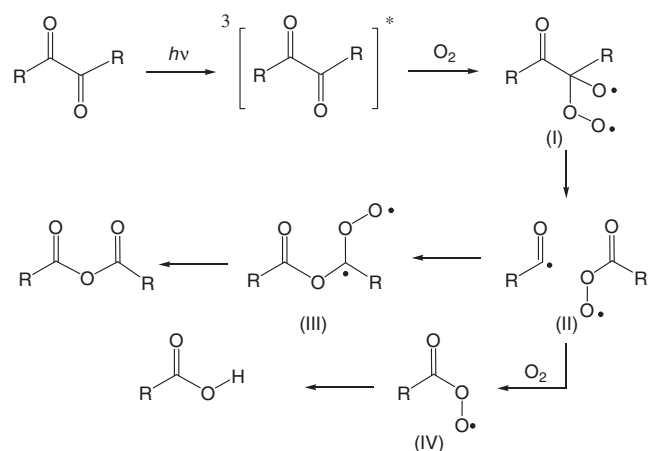
These intermediates have been proposed mostly based on product analysis studies and it is only recently that the initial ketone–oxygen adduct (I) has been detected by using time-resolved UV spectroscopy.⁷ We have shown⁸ that IR studies of photolysis of ketones in argon matrix in the presence of oxygen at low temperature provide useful information on reaction pathway of ketone upon photoexcitation. As an extension of such studies, we carried out similar spectroscopic studies in the photolysis of 1,2-naphthoquinone.

Results

1,2-Naphthoquinone (**1**) was deposited in an Ar matrix at 20 K and irradiated ($\lambda > 390$ nm) at 10 K (Figure 1). IR moni-

toring of the irradiation of **1** indicated that the peaks due to **1** decreased in intensity as new absorption bands showing peaks in the region of 1700 to 2400 cm^{-1} appeared. The absorption bands due to products after 24 h irradiation are shown in Figure 1b. A careful analysis of those product bands by plotting their intensities as a function of irradiation time (Figure 2, dotted lines) revealed that there were at least three products designated as A, B, and C. The band due to A (at 2100 cm^{-1}) arose rapidly at the initial stage of the irradiation and started to decrease as the irradiation was continued, while the band due to B (2144 cm^{-1}) formed rather slowly at initial stage but increased as the bands due to A decreased. The bands due to C (1741 cm^{-1}) appeared to form and increase independently.

To characterize those products, DFT calculations were carried out at the B3LYP/6-31G(d) level of theory. Thus, the



Scheme 1.

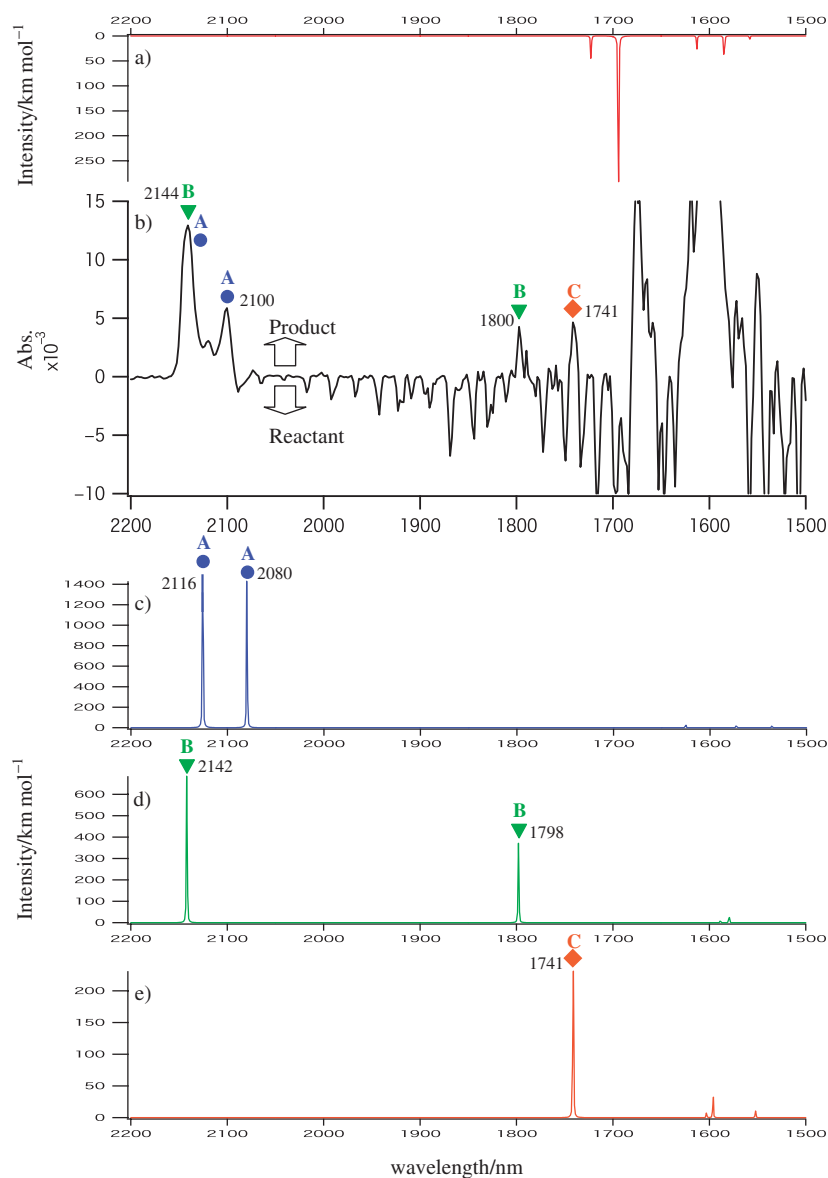


Figure 1. Photolysis of 1,2-naphthoquinone (**1**) in an Ar matrix at 10K. (a) Calculated [B3LYP/6-31G(d)] spectra of **1**. (b) IR spectrum of the photoproduct formed after 24 h of irradiation ($\lambda > 390$ nm) of **1**. (c, d, and e) Calculated [B3LYP/6-31G(d)] spectra of bis(ketene) **2** (c), keto-ketene **3** (d), and inden-1-one (**4**) (e), respectively.

geometries of plausible products expected to be formed in the photolysis of **1** were optimized and the vibrational frequencies were calculated. Since both A and B have intense and sharp bands at around 2000–2200 cm⁻¹, they are most likely ketenes. Thus, ketenes **2**, expected to be formed by cleavage of CO–CO bonds, and **3**, presumably produced by cyclization of **2** were optimized. Two isomers of **2** (**2A** and **2B**) (Chart 1) are close in energy (0.85 kcal mol⁻¹) and are shown to have almost indistinguishable frequencies but with slight difference in the intensities. Those bands match relatively well with that due to product A, assuming that the band at 2116 cm⁻¹ calculated for **2** is included in the hem of a rather broad band with maximum at 2144 cm⁻¹. On the other hand, the bands calculated for **3** match well with that due to product B. The band at 1741 cm⁻¹ due to C is obviously due to ketone carbonyl group. Among several possible products including keto-carbenes to be formed as a result of ring-contraction (see Supporting Information), the

vibrational frequencies calculated for inden-1-one (**4**) match best with that due to C (Scheme 2).

In order to know a rough ratio of those three products, calibrations were made by dividing experimentally observed absorbance of each peak with that calculated (1426 km mol⁻¹ at 2116 cm⁻¹ for **2**, 685 km mol⁻¹ at 2142 cm⁻¹ for **3**, and 231 km mol⁻¹ at 1741 cm⁻¹ for **4**, respectively).⁹ The results displayed in Figure 2 (solid lines) indicate that the main initial pathway is the formation of ketene **2**, which is converted to **3** upon photoexcitation and that the formation of **4** is a minor process.

When the irradiation was carried out in the presence of oxygen, appreciably different spectral changes were obtained. Thus, when **1** matrix-isolated in argon doped with 20% oxygen was irradiated ($\lambda > 390$ nm) at 10 K, the bands due to **1** appeared to diminish much more efficiently than that in an undoped matrix. The absorption bands due to products after

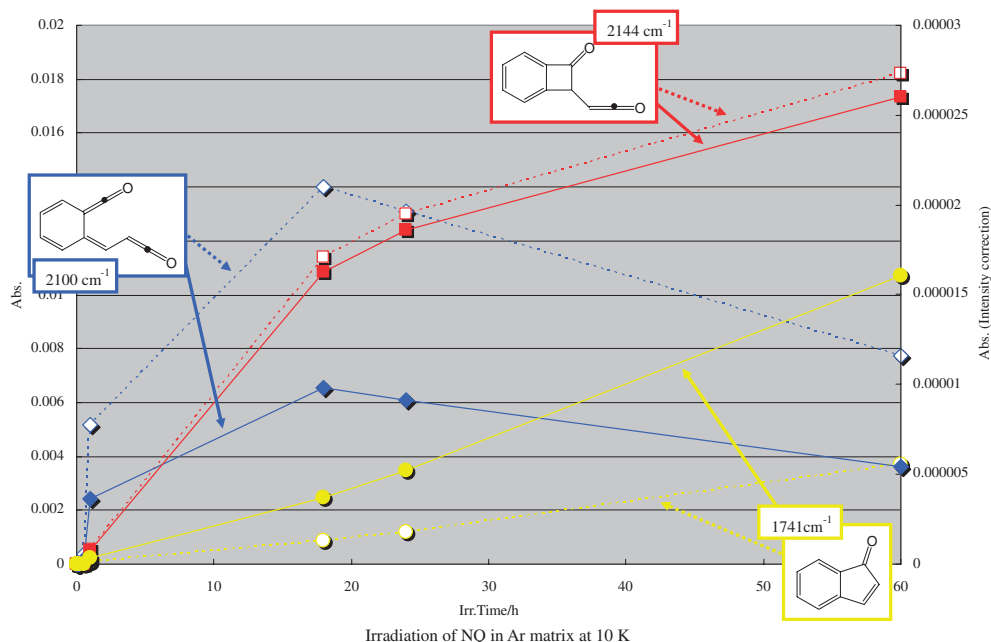
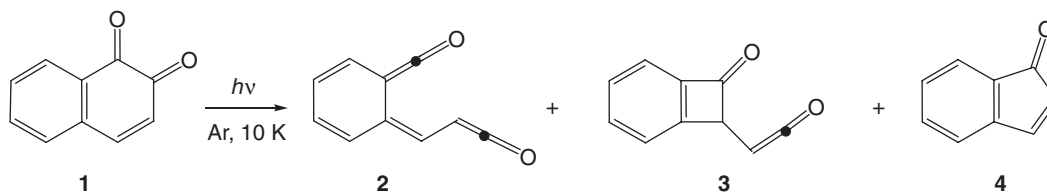


Figure 2. Plot of peaks due to **2**, **3**, and **4** as a function of irradiation time. Dotted and solid lines are for the observed absorbance and for the corrected absorbance obtained by dividing with the calculated intensities, respectively.



Scheme 2.

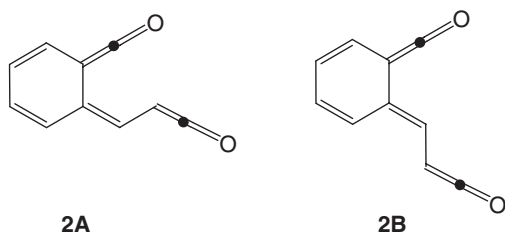


Chart 1.

13 h irradiation are shown in Figure 3b. New bands formed after photoirradiation were significantly different from that observed in the irradiation of **1** in undoped matrix. The bands at 2100 and 2142 cm^{-1} are very similar to those observed for **A** (**2**) in the irradiation of **1** in undoped matrix. The other bands were not observed in the undoped run and hence they are most probably ascribable to oxidation products. Again analysis was made on those product bands by plotting their intensities as a function of irradiation time (Figure 4, dotted lines), which revealed that there were at least three products designated as D to F, all of which increased monotonously with the irradiation time in this case. DFT calculations were carried out on plausible oxidation products expected to be formed during the photooxidation of **1**. The bands due to D with a strong peak at 2143 cm^{-1} match well with that calculated for **5**, while a band

at 1763 cm^{-1} is in agreement with that calculated for **6** (Figure 3 and Scheme 3). Again calibrations were made to estimate a rough ratio of the products by using calculated intensities (560 km mol^{-1} at 2145 cm^{-1} for **5** and 461 km mol^{-1} at 1768 cm^{-1} for **6**, respectively) (Figure 4, solid lines), which indicate that **5** was formed as major product while **6** was produced in only approximately 20% of **5** and that unoxidized product **2** was formed as a minor product.

Discussion

Cyclic diketones are known to undergo Type I cleavage upon photoexcitation to generate two acyl radicals that can lead to decarbonylation. In a conjugated diketone, bis(ketene) formation is also possible.¹⁰ Irradiation of *o*-benzoquinone in matrix at low temperature was monitored by IR spectroscopy, which indicated the formation of bis(ketene) as a main product along with the formation of cyclopentadienone.¹¹ Although the mechanism of the reaction has not been proposed, the initial cleavage of the C–C bond between the two carbonyl groups leading to diacyl radical, followed by either electronic reorganization forming bis(ketene) or decarbonylation forming cyclopentadienone is presumed to be the most likely pathway. The formation of **2** and **4** in the photolysis of **1** in argon matrix can be easily understood as the reaction of a benzo analogue of *o*-quinone. On the other hand, ketene **3** is likely to be formed from **2** upon photoexcitation, although **3** can also be produced

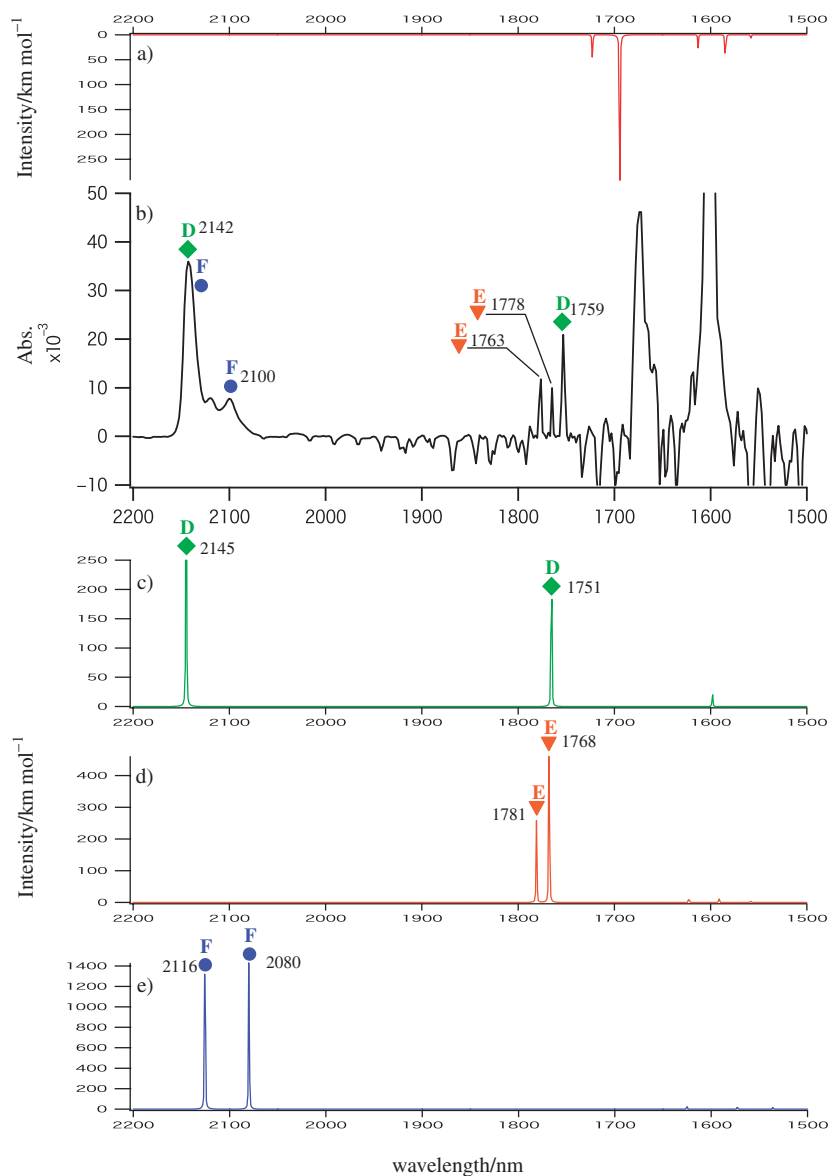
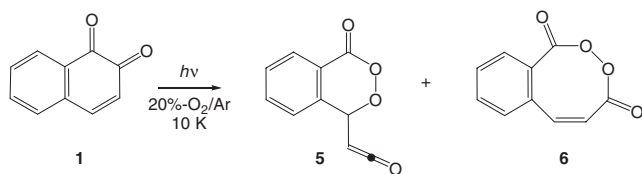


Figure 3. Photolysis of 1,2-naphthoquinone (**1**) in 20% O₂ doped Ar matrix at 10 K. (a) Calculated (B3LYP/6-31G(d)) spectra of **1**. (b) IR spectrum of the photoproduct formed after 13 h of irradiation ($\lambda > 390$ nm) of **1**. (c, d, and e) Calculated [B3LYP/6-31G(d)] spectra of six-membered cyclic peroxide **5** (c), eight-membered cyclic peroxide **6** (d), and keto-ketene **3** (e), respectively.



Scheme 3.

directly from the diacyl radical (DR) in its resonance form (DRb) (Scheme 4).

Irradiation of **1** in the presence of oxygen gave products as a result of trapping of intermediates involved in photochemical reaction of **1**. The formation of **6**, for instance, clearly supports the intervention of the another resonance form (DRa) in the photolysis of **1** leading to **2** and **4**. The formation of **5** can also be explained in terms of oxygen trapping of DR in its resonance form DRb.

It should be noted that **5** is formed predominantly over **6**. This is somewhat unexpected since ketene **2** presumably derived from resonance form DRa is formed as major product in an undoped matrix photolysis run. The profile of product-irradiation time plot in oxygen-doped matrix indicates that two oxidation products **5** and **6** are formed from the initial stage of the irradiation and do not isomerizes each other upon further irradiation and that ketene **2** is not likely to undergo photo-oxidation under these conditions.¹² The formation of oxidation products then may be interpreted as indicating a stepwise reaction between DR and triplet oxygen. Given the high reactivity of acyl radical toward oxygen,⁶ it is reasonable to assume that the benzoyl radical carbon of DR is trapped by oxygen to form peroxy-acyl diradical (DR-O₂). The oxygen radical center of the diradical either undergoes coupling at the acyl carbon in resonance form DRa forming **6** or at the benzyl

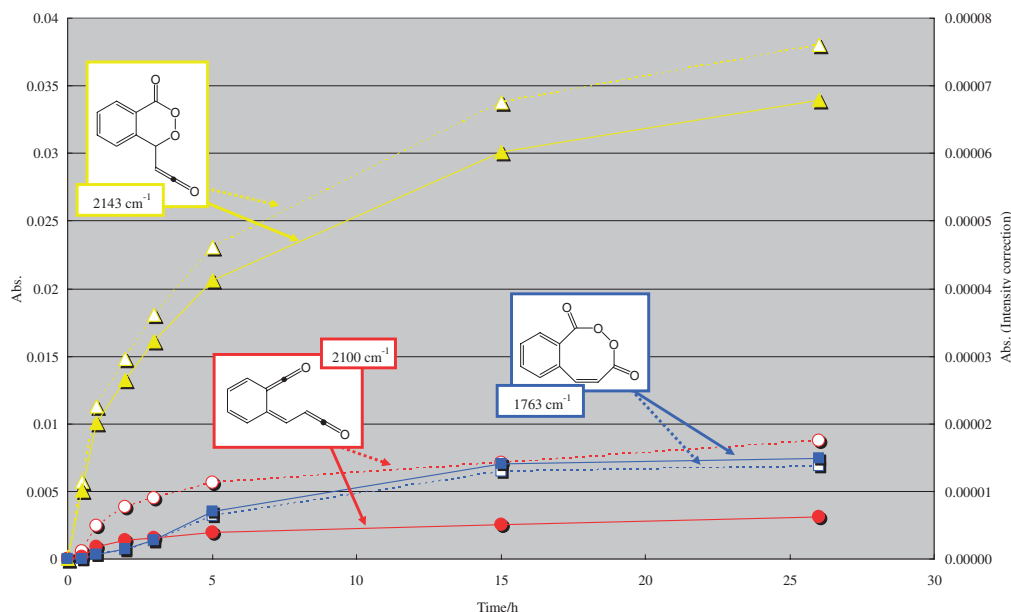
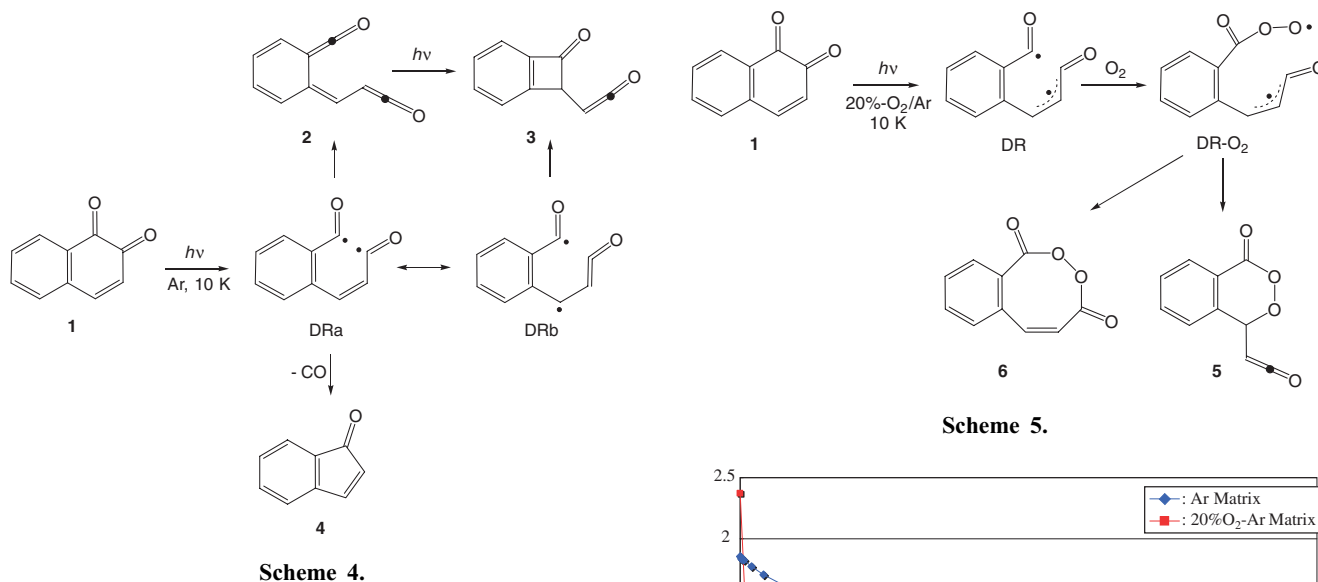


Figure 4. Plot of peaks due to **2**, **5**, and **6** as a function of irradiation time. Dotted and solid lines are for the observed absorbance and for the corrected absorbance obtained by dividing with the calculated intensities, respectively.



carbon in the resonance form DRb leading to **5**. The formation of **5** is favored partly because the contribution of DRb is more important than DRa due to benzyl stabilization and partly because the formation of six-membered ring **5** is favored over that of eight-membered ring **6** (Scheme 5).

The observation that **2** is formed even in the presence of oxygen while **3** and **4** are almost completely quenched is also noteworthy. If all three products **2**, **3**, and **4** are formed from a common intermediate such as DR, they are expected to be quenched equally in the presence of oxygen. The formation of **2** even in the presence of oxygen means that some of **2** should be produced not by way of DR. A plausible pathway that is not quenched by oxygen is a concerted reaction in the singlet excited state of **1**.

Finally it is worth noting that the rate of photodecomposition of **1** was markedly increased in the O₂-doped matrix compared

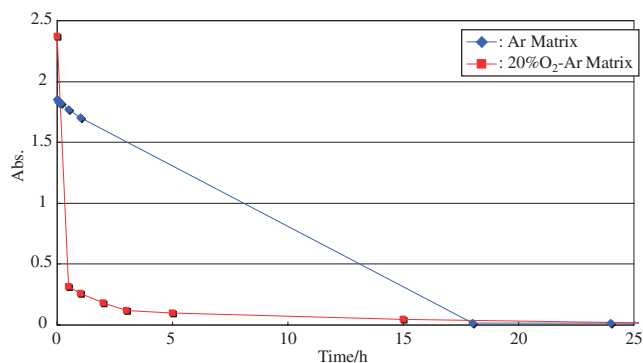


Figure 5. Plot of decay of the band due to **1** as a function of irradiation time in Ar (solid line) and in 20% O₂ doped Ar matrix (dotted line) at 10 K.

to that in the undoped matrix (Figure 5). This may be partly due to the intervention of the quenching pathway of the diradical by oxygen if one assumes that some of the initial diradicals undergo recombination to return to starting quinine **1**. On the other hand, oxygen is known to enhance the overall

$S_1 \rightarrow T_1$ process.¹³ Thus, in the presence of oxygen, the intersystem crossing efficiency of initially generated singlet state to the triplet is accelerated, which results in the increase in population of the triplet n, π^* state from which α -cleavage of the ketones takes place.

Conclusion

Present spectroscopic observations demonstrate that 1,2-naphthoquinone undergoes mainly α -cleavage to give diacyl diradical intermediate, which either leads to bis(ketene) or undergoes decarbonylation. Photooxidation of the quinone on the other hand, is completely different from that observed in solution phase but provides useful information concerning the reaction pathway of its reaction upon excitation.

Experimental

Materials. 1,2-Naphthoquinone was purchased from Tokyo Kasei Co., and used as provided.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by means of standard techniques^{14,15} using a closed-cycle helium cryostat. For IR experiments, a CsI window was attached to the copper holder at the bottom of the cold head. Two opposing ports of a vacuum shroud surrounding the cold head were fitted with KBr with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For UV experiments, a sapphire cold window and a quartz outer window were used. The temperature of the matrix was maintained by a controller (gold vs. chromel thermocouple).

All the samples used in this study were not easily vaporized and hence were directly deposited on the window from a glass tube equipped with a ceramic heater under a stream of argon. Therefore, the concentration of the sample on the window was different at each run.

Irradiations were carried out with a 500-W xenon high-pressure arc lamp. For broad-band irradiation, cutoff filters were used (50% transmittance at the specified wavelength). For monochromatic light irradiation, a monochromator was used. IR spectra were measured on a Shimadzu FTIR-4800S spectrometer, and UV–vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer.

Computational Procedures. DFT calculations were carried out using the Gaussian 94,¹⁶ programs. Optimized geometries were obtained at the B3LYP/6-31G(d)¹⁷ levels of theory. Vibrational frequencies obtained at the B3LYP level of theory were scaled by 0.961 and zero-point energies (ZPE) by 0.981.¹⁸ Transition states were located using Gaussain program (Rational Function Optimization-pseudo-Newton–Raphson method).¹⁹ The nature of each stationary point was confirmed with harmonic frequency calculations, i.e., minima have exactly one imaginary frequency related to the expected movement.

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Supporting Information

Cartesian coordinates of compounds 1–6 and Calculated [B3LYP/6-31G(d)] IR spectra of other products expected to be formed in the photolysis of 1. These materials are available free of charge on the Web at: <http://www.csj.jp/journals/bcsj/>.

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