

Reaction of (4-Nitrophenyl)nitrene with Molecular Oxygen in Low-temperature Matrices: First IR Detection and Photochemistry of Aryl Nitroso Oxide

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(Received December 22, 2004; CL-041585)

The thermal reaction of (4-nitrophenyl)nitrene with oxygen in low-temperature matrices produced a new molecular species, which was identified as 4-nitrophenylnitroso oxide on the basis of its IR spectrum in combination with isotopic labeling with $^{18}\text{O}_2$ and vibration analyses by the DFT method. This is the first report for the infrared detection of an aryl nitroso oxide. We could monitor also the wavelength-dependent N–O and O–O bond cleavage of the nitroso oxide.

It has been assumed that the photooxidation of aryl azide in solution afforded aryl nitroso oxide as an intermediate, which was thought to convert to the corresponding nitro compound either by unimolecular rearrangement via the dioxaziridine or by intermolecular *O*-transfer.¹ While a little attempt to observe the intermediates involved was made by means of the laser flash photolysis and the matrix isolation technique, these studies were limited to the detection of UV–vis² and ESR^{2b–d} spectra. We have monitored the photo-oxidation process by means of FT-IR with using cryosystems to obtain more clear information. We describe here definitive evidences for aryl nitroso oxide and its photochemistry.

We used 4-nitrophenyl azide (**1**) instead of simple phenyl azide as a precursor of aryl nitrene, because the latter azide yielded not phenylnitrene but the dihydroazepine having the seven membered ring, under our experimental conditions. In the case of **1**,³ only triplet (4-nitrophenyl)nitrene (**2**; 1557, 1497, 1338, 1321, 845, 833, and 743 cm^{-1}) could be accumulated in 5% O_2 -doped Xe matrices at 10 K under irradiation with light of 365 nm from a 250-W deep-UV lamp with using a band-pass filter. Although the photoisomerization of **2** into 5-nitro-1,2-dihydroazepine (**7**; 1887, 1568, 1511, 1331, and 970 cm^{-1}) was induced by the irradiation at 313 or >400 nm, **2** could be easily regenerated with light of 365 nm.

Upon warming a Xe matrix containing **2** to 50 K in the absence of oxygen, small IR peaks remained, which suggested the sole generation of dimerized product, namely, 4,4'-dinitroazobenzene (871, 863 cm^{-1}). In a 5% O_2 -doped Xe matrix, however, at heating to 50 K, the bands due to **2** almost disappeared and the bands from new molecular species⁴ (designated as **X**) appeared, together with weak intensity peaks of the azobenzene. When the same reaction was carried out with $^{18}\text{O}_2$ (99% doubly labeled) instead of $^{16}\text{O}_2$, most of the IR bands of **X** shifted.⁴ In particular, the medium intensity bands at 1131 and 1017 cm^{-1} , which appeared in the O–O stretching region of the peroxide, showed the large isotopic shifts of –62 and –49 cm^{-1} , respectively. In conjunction with this, the photoreaction of **X** was also examined. When the matrix containing **X** was irradiated with light of >590 nm at 10 K, the precursor nitrene was regenerated slowly and no other reaction could be observed. On the other hand, as shown in Figure 1, irradiation of **X** with >415 nm

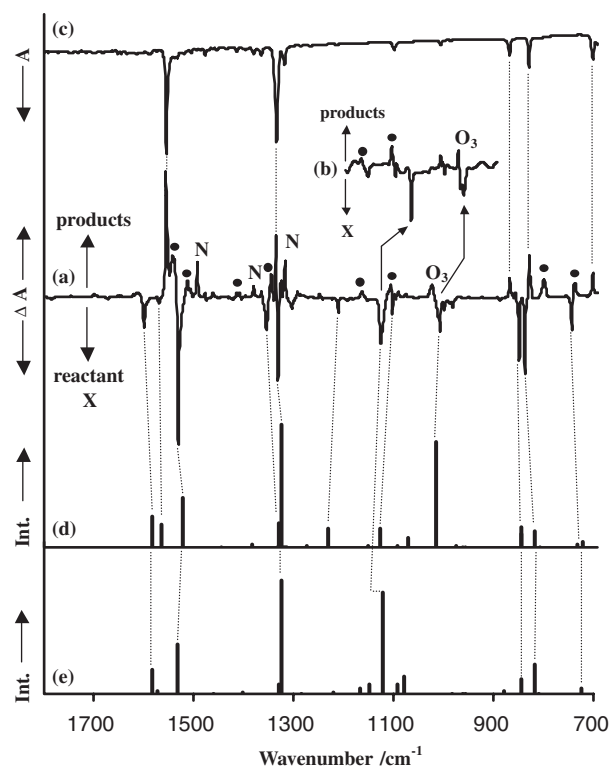


Figure 1. Difference IR spectra recorded after irradiation of **X** (down bands) matrix-isolated in Xe doped with $^{16}\text{O}_2$ (a) and $^{18}\text{O}_2$ (b) at 10 K with light of >415 nm. In product bands, bands labeled solid circles, N, and O_3 assigned **5**, **2**, and ozone, respectively. (b) shows $^{18}\text{O}_2$ -isotopic effects for the bands of **X** in the region 900–1200 cm^{-1} . (c) IR spectrum of **4** matrix-isolated in O_2 -doped Xe at 10 K. (d) and (e) UB3LYP/6-31+G* calculated IR spectra for *cis*- and *trans*-**3**, respectively (scaled by 0.9614).⁶

caused the rapid disappearance of **X** and afforded 1,4-dinitrobenzene (**4**; 1558, 1339, 875, 836, and 709 cm^{-1}) along with 4-nitro-nitrosobenzene (**5**; 1545, 1518, 1414 1349, 1167, 1111, 806, and 745 cm^{-1}) and ozone ($^{16}\text{O}_3$; 1029, $^{18}\text{O}_3$; 977 cm^{-1}). IR peaks of these product species could be readily assigned by comparison with the IR spectra of authentic samples isolated in O_2 -doped Xe matrices at 10 K.⁵ From these experimental results, we thought that the new species **X** might be the nitroso oxide.

In order to confirm this idea, the theoretical analyses for the nitroso oxide were carried out using the DFT calculations at the unrestricted B3LYP/6-31+G* level of theory. Geometry optimization of the nitroso oxide revealed that two conformers *cis*- and *trans*-**3** existed as true energy minimum structures in their singlet states and that *cis*-form is slightly more stable than *trans*-form by 2.5 kJ mol^{-1} . On the basis of the spin and charge densities calculated for **3**, both isomers are thought to have

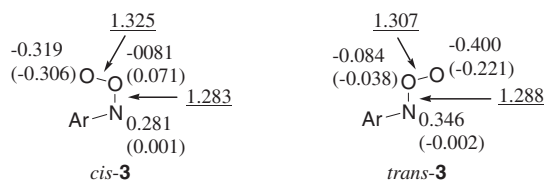
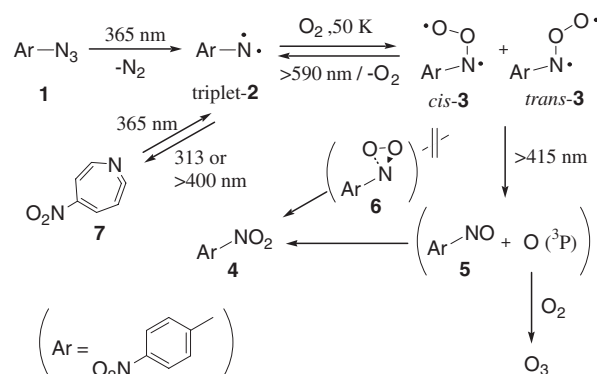


Figure 2. Spin densities, NPA atomic charges (in parentheses), and bond lengths (underlines, Å) of **3** calculated at the UB3LYP/6-31+G* level of theory. (Ar = 4-nitrophenyl).

diradical characters (Figure 2). Triplet-singlet energy differences for *cis*- and *trans*-**3** were calculated as 40.3 and 33.6 kJ mol⁻¹, respectively. These values indicate that the nitroso oxide populate in their singlet states at 50 K. The vibration frequencies calculated for *cis*- and *trans*-**3** were compared with experimental values after scaled by a factor of 0.9614 (Figure 1).⁶ IR spectrum observed for **X** seems to be similar to that calculated for more stable isomer *cis*-**3**. If the experimental spectrum consists of pure *cis*-**3**, band at 1131 cm⁻¹ must be assigned to the C–N–O symmetrical stretching mode of the theoretically calculated spectrum. The isotopic shift for the C–N–O stretching was calculated as –15 cm⁻¹, which is inconsistent with the large isotopic shift (–62 cm⁻¹) observed. While, considering that **X** is a *cis/trans* mixture of the nitroso oxide **3**, the calculated IR data fairly reproduce the observed data. Furthermore, theoretical isotopic shifts for O–O stretching modes of *cis*-**3** (–54 cm⁻¹) and *trans*-**3** (–62 cm⁻¹) are in fair agreement with experimental results described above. Thus it was concluded that the IR spectrum obtained by warming the matrix containing the nitrene **2** and oxygen molecules to 50 K corresponded to *cis*- and *trans*-4-nitronitrosobenzene *O*-oxide (**3**). We believe that this represents the first IR detection of aryl nitroso oxide, although Laursen et al. observed *trans*-HNOO formed in the reaction of NH and O₂ in a Xe matrix.⁷

Although the formation of singlet **3** from triplet **2** and O₂ is spin-allowed and calculated as exothermic of 22.0 kJ mol⁻¹, no **3** appeared in O₂-doped Ar or Xe matrices at 40 K where O₂ molecules could be rapidly diffuse.⁸ At 50 K, however, **2** reacted with O₂ to give the nitroso oxide **3** as shown above, indicating that this reaction needs some activation energy. Kinetic control may explain the presence of *trans*-**3** in spite of the energy difference (2.5 kJ mol⁻¹) between *trans*-**3** and more stable *cis*-**3**.

Next, the possible mechanism for the photochemical rearrangement of **3** into **4** is discussed. As mentioned in an introductory part, it was thought that the dioxaziridine may participate in this type of reaction. Assuming that the dioxaziridine **6** exists as an intermediate in this reaction process, the energy diagram calculated with the DFT method shows that the energy minimum structure of **6** (53.5 kJ mol⁻¹ above *cis*-**3**) lies in a deep potential well with activation barriers for the paths to *cis*-**3** (109.7 kJ mol⁻¹) and to **4** (96.9 kJ mol⁻¹). However, the theoretically calculated bands for **6**, which include the cyclic NO₂ deformation band at about 826 cm⁻¹ (¹⁸O-isotopic shift; –22 cm⁻¹), could not be detected in the photoreactions of **3**, regardless of the excitation at a variety of wavelengths ($\lambda > 590$, > 540 , > 460 , > 415 , or 365 nm). Therefore, we concluded that **6** is not an intermediate in the rearrangement of **3** into **4** in the matrix at 10 K. From the fact that **5** and ozone are observed in this photoreaction, it is predicted that **3** generates an oxygen atom photochemically. The formation of **4** could be achieved by the attack of



Scheme 1.

atomic oxygen on the nitroso moiety of **5** in matrix cage, though some of the atomic oxygen were captured by molecular oxygen to give ozone (Scheme 1). This mechanism could be also supported by the following experiment. A Xe matrix containing **5** and a large amount of ozone was irradiated (>520 nm) at 10 K, as the photolysis of ozone was known to give atomic oxygen (³P).⁹ It was observed that **5** was cleanly converted to **4** without any by-products.

Thus, it was found that the photoreaction of **3** with the long-wavelength light (>590 nm) caused the N–O bond cleavage to yield **2**, and that **4** was produced by the reaction of **5** with O(³P), which are derived from the photochemical O–O bond cleavage of **3** with light of >415 nm. At present, a systematic study for the photoreactions of aryl nitroso oxides using a variety of aryl azides is in progress.

This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology Japan (No. 15750040) and by the Sasakawa Scientific Research Grant from The Japan Science Society (No. 15-107).

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- IR bands of **1** (5% O₂-doped Xe, 10 K) 2133m, 2123s, 2102m, 2090m, 1608m, 1596m, 1593m, 1528s, 1492m, 1341m, 1304s, 1289s, 1176w, 1129w, 1105w, 860w, 847w, 748w cm⁻¹.
- IR bands of **X** (¹⁸O-isotopic shifts in cm⁻¹) 1602m (–1), 1571w (0) 1534s (–1), 1358m (–3), 1335s (–1), 1215w (–1), 1131m (–62), 1108w (–6), 1017m (–49), 856s (–1), 844s (–1), 751m (0) cm⁻¹.
- 5** was synthesized by the published method.¹⁰ Ozone was prepared with help of an ozonizer (Willbe ozonizer OZ-2, Ozone Shi-Nine inc.).
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