The Photochemistry of Nitrosobenzene: Direct Observation of the Phenyl Radical–Nitric Oxide Triplet Radical Pair in Argon at 12 K

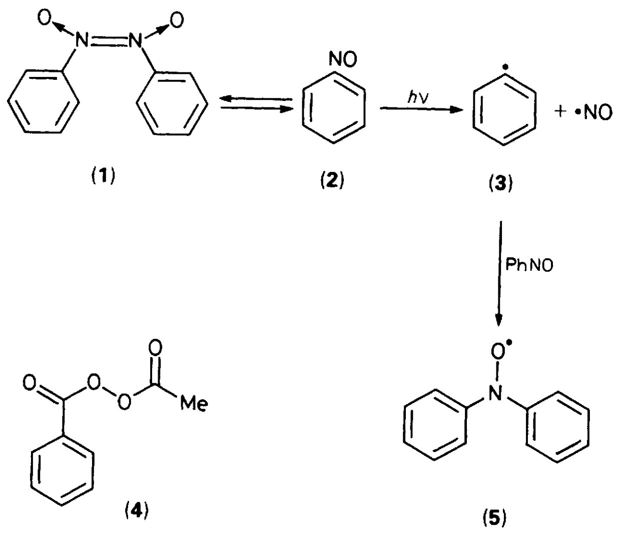
William G. Hatton, Nigel P. Hacker,* and Paul H. Kasai

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120 6099, U.S.A.

Photolysis of nitrosobenzene monomer in an argon matrix at 12 K efficiently yields the phenyl radical and nitric oxide as a triplet radical pair, which are characterized by IR, UV, and ESR spectroscopy; these species recombine upon warming to 25—40 K to regenerate nitrosobenzene.

C-Nitroso compounds can exist either as monomers or dimers in solution dependent on concentration and temperature.[1] Interconversion between dimer and monomer ceases at −60 °C and the photodissociation of the dimer to monomer has been reported.[2] Photolysis of nitrosobenzene solutions (monomer or dimer) at room temperature yields diphenylnitroxide.[3] Presumably, the nitrosobenzene dimer is photodissociated to the monomer which upon photolysis generates the phenyl radical and nitric oxide, and reaction of the phenyl radical with nitrosobenzene gives diphenylnitroxide (Scheme 1). However, trapping the phenyl radical, generated from nitrosobenzene photolysis, with solvent or other radical traps, has not been reported. Nitrosobenzene itself is frequently used for trapping radicals generated from aliphatic nitroso compounds.[4] We report here the photolysis of nitrosobenzene in argon at 12 K and direct observation of the phenyl radical and nitric oxide intermediates.

Nitrosobenzene, which exists as the yellow *cis*-dimer in the solid state at room temperature and starts to form the blue monomer at about 65 °C, was sublimed at room temperature and trapped in solid argon on a CsI window at 32 K.† The observation of a strong band at 1515 cm^{-1} (N=O stretch) and the absence of any bands stronger than 1% of the 1515 cm^{-1} band, expected for the dimer, in the regions 1000—1480, 1270—1260, and 855 cm^{-1}, indicate that the nitrosobenzene monomer was isolated in the argon matrix.[1,5] Irradiation (λ >300 nm) of the sample at 12 K led to disappearance of the IR bands of (**2**) and the appearance of a strong new band at 1871 cm^{-1}, due to nitric oxide.[6] In addition to the nitric oxide absorption, new bands at 3087vw, 3071m, 3060vw, 1442s, 1433s, 1062w, 1027m, 976w, 708s, 705vs, 656s, 605w, and 587vw cm^{-1}, due to the phenyl radical were recorded (Figure 1). Additional minor bands due to water in the 4000—3500 and 1600 cm^{-1} regions, and due to secondary photoproducts at 2343, 2270, 2224, and 2137 cm^{-1}, identified as CO_2,[7] N_2O,[8] C_3O_2,[9] and CO,[7] respectively, were also recorded. Warming the sample to 40 K followed by re-cooling to 12 K caused all the IR bands due to the phenyl radical and nitric oxide to disappear and the IR bands of nitrosobenzene to reappear.



Scheme 1. Products from photolysis of nitrosobenzene.

Most of the new IR bands recorded after photolysis of nitrosobenzene agree well with those previously reported for the phenyl radical by Pacansky, from photolysis of acetyl benzoyl peroxide (**4**) in argon at 10 K.[10] Unfortunately, photolysis of (**4**) also generates substantial amounts of CO_2, methyl benzoate, and methyl radical, in addition to the phenyl radical, and these by-products obscure much of the IR spectrum. However photolysis of nitrosobenzene ejects nitric oxide which has only one vibrational mode and does not obscure any of the IR region of interest. Hence the previously unreported bands at 3087, 3060, 1442, 976, 656, 605, and 587 cm^{-1} are readily observed from nitrosobenzene photolyses. The bands assigned to CO_2, N_2O, C_3O_2, and CO, do not disappear after annealing the matrix and are formed by secondary reactions of the phenyl radical and nitric oxide fragments. Prolonged photolysis of the sample causes a decrease in the phenyl radical peaks and an increase in the peaks in the 2400—2100 cm^{-1} region. Also, doping the argon matrices with 1% oxygen causes a relative decrease in the intensities of the peaks assigned to the phenyl radical and nitric oxide, and an increase in intensity of the CO_2 and CO peaks. Thus CO_2, C_3O_2, and CO are either products from oxidation of the excited state of nitrosobenzene or from oxidation of the phenyl radical. Peaks which could be assigned to C_3O_2 and CO were present in the IR spectra recorded from the photolysis of (**4**).[10] The observation of identical carbon oxides from two different precursors suggests that the phenyl radical is oxidized.‡

The UV absorption spectrum of nitrosobenzene in argon at 12 K gave $\lambda_{max.}$ at 300 and 280 nm, slightly blue shifted from the room temperature absorption spectrum reported for the monomer.[2] Photolysis caused these UV absorbances to disappear. No new strong absorbances at λ >250 nm were observed, however a weak absorbance at λ 235 nm was detected. Annealing the matrix at 40 K caused the UV

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† The samples were irradiated with Oriel 500 W Hg or 1000 W Hg/Xe lamps equipped with a water filter with quartz windows to remove IR radiation and additional pyrex glass or 325 nm broad band filters. UV absorption spectra were measured with quartz windows and recorded on a Hewlett-Packard Model 8451A diode array UV spectrometer at 2 nm resolution. The IR and ESR matrix isolation equipment have previously been described.[13]

‡ In solution the phenyl radical normally reacts with oxygen without destruction of the aromatic nucleus and ultimately yields phenol. The destructive oxidation of the phenyl radical to CO_2 and CO is not necessarily from direct reaction with O_2, but possibly by other oxidative species, *e.g.*, ozone or nitrogen oxides.

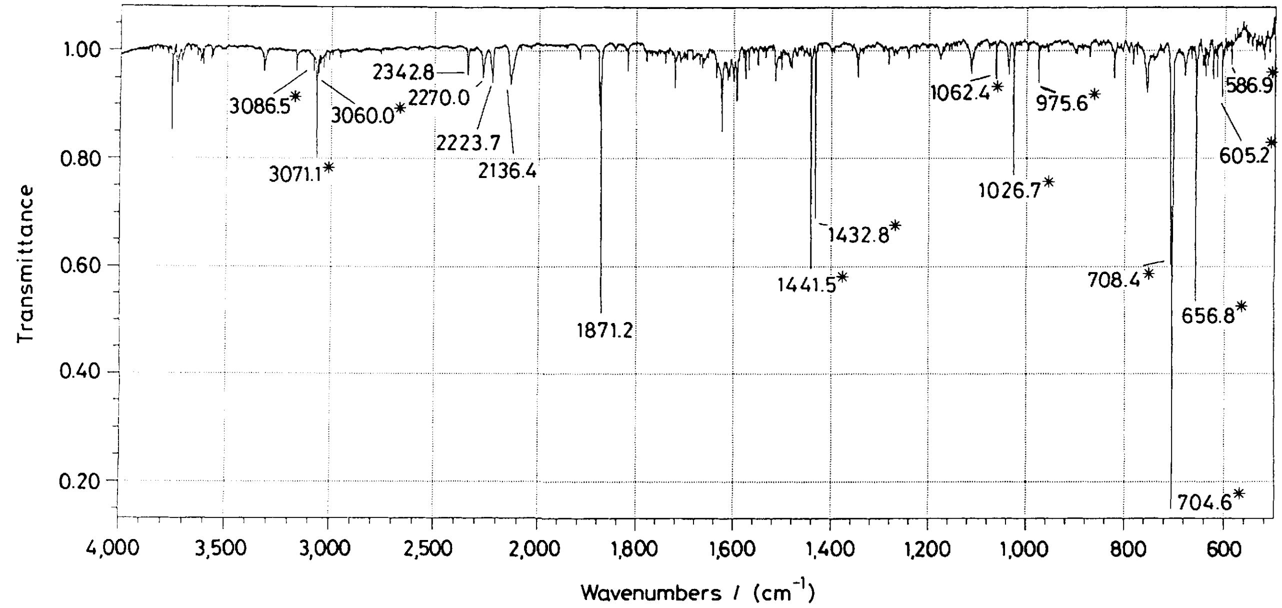

Figure 1. IR Spectrum at 12 K after 6 h photolysis of nitrosobenzene in argon (1 : 1000). The bands marked with an asterisk are assigned to the phenyl radical.

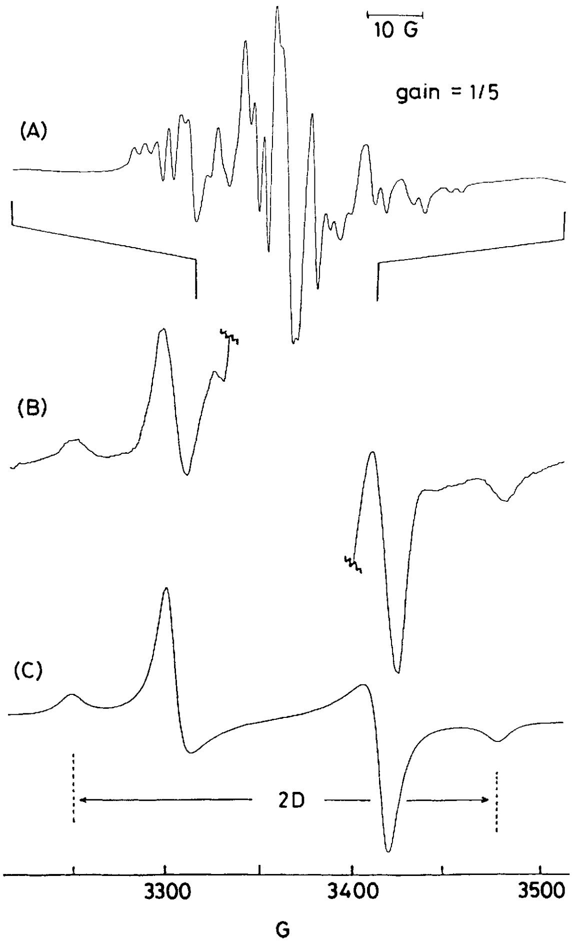

Figure 2. (A), (B) ESR spectra recorded after 20 min photolysis of nitrosobenzene in argon; (C) simulated ESR spectrum.

absorbances at 280 and 300 nm to reappear (usually >70% yield), but the fate of the λ 235 nm absorbance could not be determined due to the large increase in background absorption after annealing. The UV absorption studies confirm that photolysis of nitrosobenzene at 12 K gives an intermediate which regenerates nitrosobenzene after warming the matrix. The weak absorbance at λ 235 nm, and the absence of any absorbances at longer wavelengths, also supports the assignment of the phenyl radical. A weak transient absorption at 245 nm has been reported for vibrationally relaxed phenyl radical from gas phase nanosecond laser flash photolysis studies on chlorobenzene at room temperature.[11]

In order to further characterize the radicals formed from photolysis of nitrosobenzene, an argon matrix containing nitrosobenzene was prepared in a matrix-isolation ESR spectrometer system, and its ESR spectrum was examined. Prior to irradiation, the matrix showed no ESR signal. After photolysis for 20 min the matrix gave strong ESR signals which were recognized as a superposition of three sets of powder patterns. The most intense pattern was due to isolated phenyl radicals; the pattern was identical with that obtained earlier from photolysis of iodobenzene.[12] The second and third patterns were recognized as those of triplet-state species and, in light of the results obtained from the IR and UV studies, were assigned to radical pairs Ph$^{\bullet}\cdots$NO$^{\bullet}$ of different separations. The observed spectra of the phenyl radical region and the region showing the features associated with the Ph$^{\bullet}\cdots$NO$^{\bullet}$ pair of larger separation (hence smaller fine structure splitting) are shown in Figures 2(A) and 2(B). Figure 2(C) is a simulated powder pattern of a triplet-state species based on the spin Hamiltonian 1 and the splitting factor D of 115 G [equation (1)]. The pattern due to the second Ph$^{\bullet}\cdots$NO$^{\bullet}$ pair was similar to that of the first pair [Figure 2(B)] except for its much larger splitting factor of 350 G.

For the triplet-state of the radical pair the splitting factor D is dependent on the average separation, R, between the two unpaired electrons as in equation (2). Equation (2) and the observed D values of 115 and 350 G then yield 6.2 and 4.3 Å as the average separation of the unpaired electrons in these radical pairs. It is not apparent why the Ph$^{\bullet}\cdot\cdot$NO$^{\bullet}$ pairs in argon matrices should hold these particular separations. Intriguingly, though, they are close to the nearest and the second nearest neighbour separations of the argon lattice (3.8 and 5.3 Å).

$$H_{\text{spin}} = \beta SgH + D[S_z^2 - S(S + 1)/3] \qquad (1)$$

$$D = 3g^2\beta^2/(2R^3) \qquad (2)$$

The apparent signal strength of the phenyl radical was ~5 times stronger than that of the radical pair with D of 115 G, and the latter was, in turn, ~5 times stronger than the signal due to the pair with D of 350 G. The relative ratios of the concentrations of the three species (estimated from the strengths and overall spreads of the patterns) are 0.1 : 0.3 : 0.6 for the phenyl radical, the radical-pair of 6.2 Å separation, and the radical-pair of 4.3 Å separation, respectively. The matrix ESR study thus revealed that only 10% of photochemically cleaved nitrosobenzene yields isolated phenyl radicals, while 90% of the products remain as radical-pairs in the triplet state, in such proximity that recombination on warming, albeit spin-forbidden, occurs with extreme facility. Further studies on the photochemistry of other nitrosoarenes are in progress.

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