PHOTOREDUCTION OF 2-NITROSO-1-NAPHTHOL

K. PAK and A. C. TESTA

Department of Chemistry, St. John's University, Jamaica, NY 11439 (U.S.A.)

(Received January 27, 1981; in revised form March 17, 1981)

Summary

The photoreduction of 2-nitroso-1-naphthol in isopropyl alcohol proceeds through an upper triplet excited state, presumed to be the T_2 state, and can be reversed by the addition of oxygen. Hydrogen abstraction, which is the primary process, leads to only one photoproduct, namely 2-hydroxylamine-1-naphthol. Quantum yields for the disappearance of 2-nitroso-1-naphthol in air-saturated and degassed solutions were determined to be 0.034 ± 0.002 and 0.045 ± 0.002 respectively. The azoxy compound formed from the dark coupling reaction between the hydroxylamine and nitroso compound was isolated in large-scale photolysis, and its photochemistry in vacuum-degassed solutions is shown to involve a reversible photocyclization step.

1. Introduction

In a previous study in this laboratory we demonstrated that the photolysis of nitrosobenzene at 313 nm in isopropyl alcohol leads to only one photoproduct, phenylhydroxylamine, and that this process can be reversed in the presence of oxygen [1]. We suggested that an upper triplet was involved since irradiation into the S_1 state (730 nm) did not result in photochemistry, while 313 nm excitation led to hydrogen abstraction. The overall cyclic process is shown in Fig. 1. A dark reaction, which can be minimized in dilute solutions, occurs between phenylhydroxylamine and nitrosobenzene, leading to the formation of azoxybenzene. The azoxybenzene was isolated in large-scale photolysis together with 2-hydroxyazobenzene, which results from the photochemistry of azoxybenzene [2].

Aromatic nitroso compounds possess two low-lying $^1n,\pi^*$ transitions which are separated by about $18\,000$ cm^{-1} [3]. The $n_N \rightarrow \pi^*$ transition is lowest in energy and appears at about 720 nm while the $n_0 \rightarrow \pi^*$ transition appears at about 310 nm. Figure 2 is an energy level diagram showing these states and the large separation between the T_1 and T_2 states.

As an extension of our interest in the excited state behavior of aromatic nitroso compounds and also to provide further evidence for the involvement
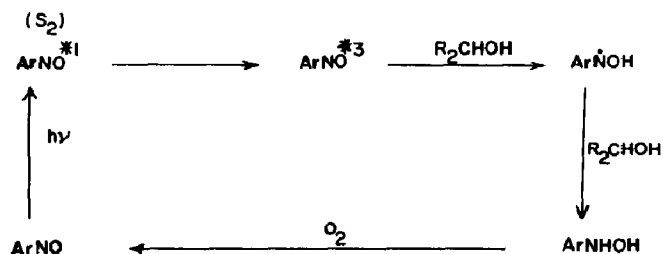
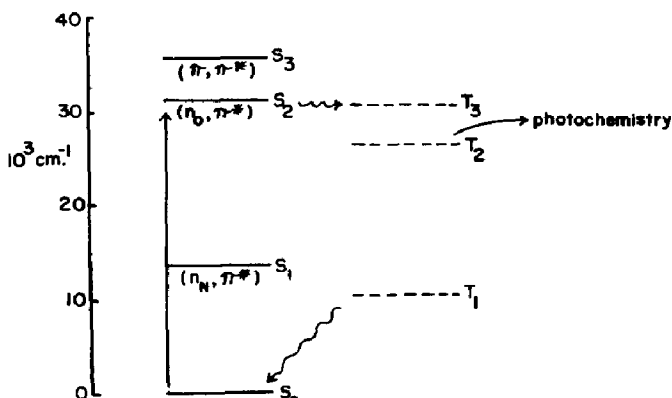Fig. 1. The photolysis of nitrosobenzene at 313 nm in isopropyl alcohol.

Fig. 2. Reversible photoreduction of aromatic nitroso compounds from high-lying excited states: an energy level diagram illustrating two ^{1}n,π^* states and photochemistry arising from the T_2 state.

of an upper triplet state in the photoreduction of aromatic nitroso compounds, we have undertaken an investigation of the photochemistry of 2-nitroso-1-naphthol with the aim of elucidating the primary photochemical event and the potential reversibility of the photochemistry that such a molecule may exhibit. In view of the hydrogen abstraction reaction, the formation of the hydroxylamine derivative as the only photoproduct and the involvement of an upper excited state in the observed photoreduction of nitrosobenzene, photolysis experiments were initiated for 2-nitroso-1-naphthol in isopropyl alcohol.

2. Experimental procedure

2.1. Materials
2-Nitroso-1-naphthol was vacuum sublimed prior to use. Spectrograde isopropyl alcohol was used as received.

2.2. Equipment
Solutions to be photolyzed were typically 10^{-3} - 10^{-5} M in concentration and were vacuum degassed (1 cm cells with graded seals) at 10^{-4} Torr

prior to flame sealing. The 313 nm excitation line was isolated from a high pressure mercury lamp with a 10 nm bandwidth interference filter, and light intensities were typically 2.0×10^{15} quanta s^{-1}, as determined with a potassium ferrioxalate actinometer. Quantum yields were measured for solutions in which less than 15% of the molecules were converted and polarographic analysis in acetic acid—sodium acetate buffers was employed to determine the concentration changes resulting from photolysis.

Large-scale photolyses were performed with a 450 W Hanovia mercury lamp and typically an 800 ml solution of 10^{-1} M 2-nitroso-1-naphthol in isopropyl alcohol, constantly purged with nitrogen, was used. Solvent evaporation followed by thin layer chromatography using acetone as the eluent resulted in the separation and identification of two yellow photoproducts (the azoxy and cyclized dihydrocompound). A Cary 14 spectrophotometer was used to follow the disappearance of nitroso compound and a Beckman IR-8 spectrophotometer was employed to identify the azoxy compound formed from the known coupling reaction between the hydroxylamine and the nitroso compound.

3. Results

The photolysis of 4.05×10^{-5} M 2-nitroso-1-naphthol at 313 nm in isopropyl alcohol can be readily followed by UV absorption, as is shown in Fig. 3. It is seen that the peaks at 265 and 290 nm disappear and are replaced by a new band at 235 nm, which is from the hydroxylamine derivative. The system exhibits an isosbestic point at 245 nm, which suggests a simple two-component system. After irradiation a dark reaction arises due to the presence of oxygen and reconverts the hydroxylamine derivative to the starting nitroso compound. Spectrum (4) in Fig. 3 is constructed from the difference between the absorption spectra after photolysis for 1592 min and after dark reaction for 6480 min. It is evident that the return of the nitroso compound occurs in the dark. The overall process, which involves hydrogen abstraction as the primary photochemical event, is represented as follows:
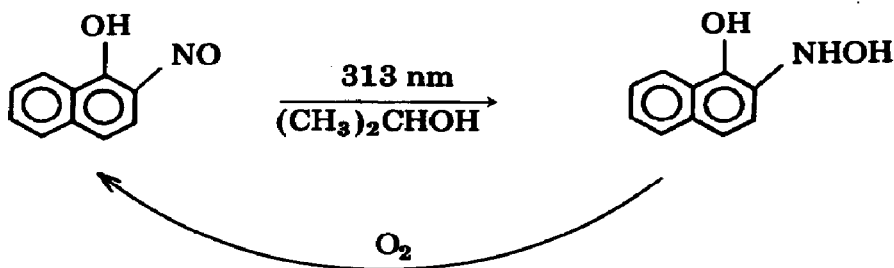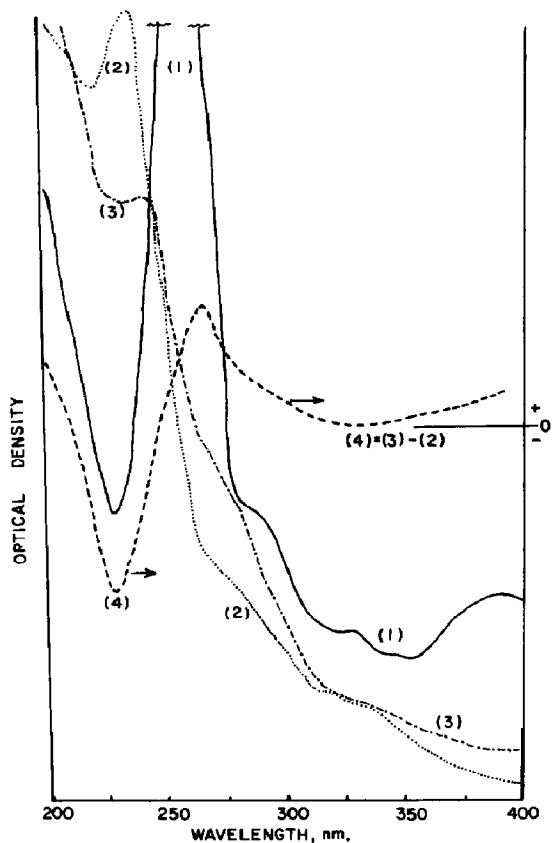
Fig. 3. The variation in the UV absorption spectrum during the photolysis of (air-saturated) 4.05×10^{-5} M 2-nitroso-1-naphthol at 313 nm in isopropyl alcohol: curve (1) (———), before photolysis; curve (2) (· · ·), after photolysis for 1592 min; curve (3) (— · —), after dark reaction for 6480 min; curve (4) (— — —), constructed from curve (3) minus curve (2), indicating that the peak for 2-nitroso-1-naphthol returns during the dark reaction.

The quantum yields measured for air-saturated and degassed solutions are 0.034 ± 0.002 and 0.045 ± 0.002 respectively and there is no significant concentration effect on the quantum yield as seen in the data given in Table 1.

TABLE 1

Quantum yields for the disappearance of 2-nitroso-1-naphthol in isopropyl alcohol

Concentration (M × 10³)	ϕ_{air}	$\phi_{degassed}$
1.25	0.031	0.041
6.24	0.034	0.045
12.5	0.035	0.048

The contribution of a dark reaction involving coupling of the 2-hydroxylamine-1-naphthol with 2-nitroso-1-naphthol was minimized in the quantum yield determinations by using dilute solutions, *i.e.* 10^{-3} M. From the data in Table 1 it is evident that dimers do not appear to play a significant role in this system. Further, the nitroso compound did not phosphoresce when irradiated at 77 K in ether–isopentane–ethanol (volume ratio, 5:5:2).

Large-scale photolyses were performed with the aim of identifying the photoproducts and in these experiments the azoxy compound generated by the following dark reaction was isolated and identified by IR spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.
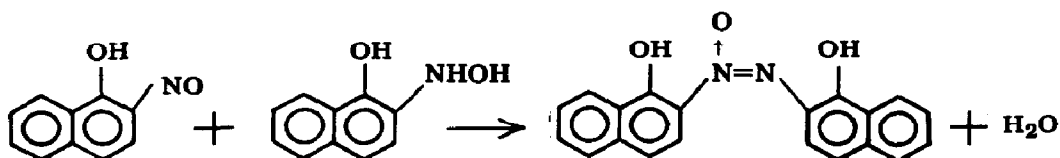
Separation of the photolysis products after solvent evaporation using thin layer chromatography (elution with acetone) yielded two yellow compounds I and II. The IR spectrum of I exhibited azoxy bands at 6.4 and 7.9 μm as well as additional bands at 2.9, 6.2, 7.35, 10.2, 12.0, 12.9 and 13.8 μm. The UV spectrum of this compound in isopropyl alcohol exhibited peaks at 217, 265 (most intense), 292 and 330 nm. Further evidence for the identification of this compound as the azoxy derivative was the presence of two different hydroxyl protons in the NMR spectrum, which disappeared on addition of deuterated water. Compound II, also yellow, was identified as the dihydro-cyclized compound since its IR spectrum was found to be identical with that of the azoxy compound except for the presence of an additional band at 3.4 μm, which was attributed to the saturated C—H bond arising from the photocyclization process. The UV absorption of this compound exhibited peaks at 217 (most intense), 265, 295 and 309 nm. This behavior is similar to that observed for the cyclization of 2,2'-azoxy-naphthalene [4]. In order to test this hypothesis further the 1,1'-dihydroxy-2,2'-azoxynaphthalene separated from the large-scale photolysis was irradiated at 313 nm. Figure 4 shows the variation in optical density when a vacuum-degassed isopropyl alcohol solution of 1,1'-hydroxy-2,2'-azoxy-naphthalene was irradiated at 313 nm, and it can readily be seen that the photochemistry induced after 320 min is noticeably reversed in the dark. In fact this dark reverse reaction appears to be faster than that of the 2-hydroxylamine-1-naphthol conversion back to the nitroso compound. Two isosbestic points are evident at 250 and 295 nm, which indicates a simple photochemical system. The behavior is suggestive of the following cyclization.
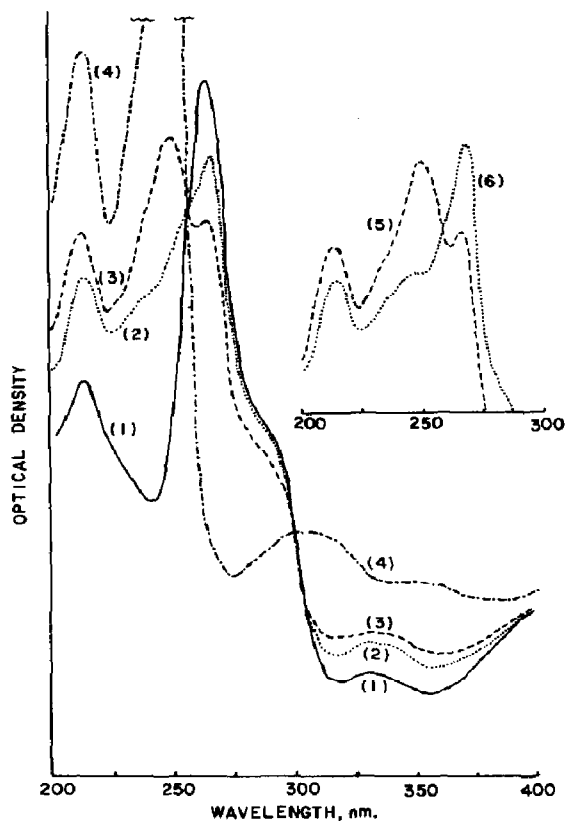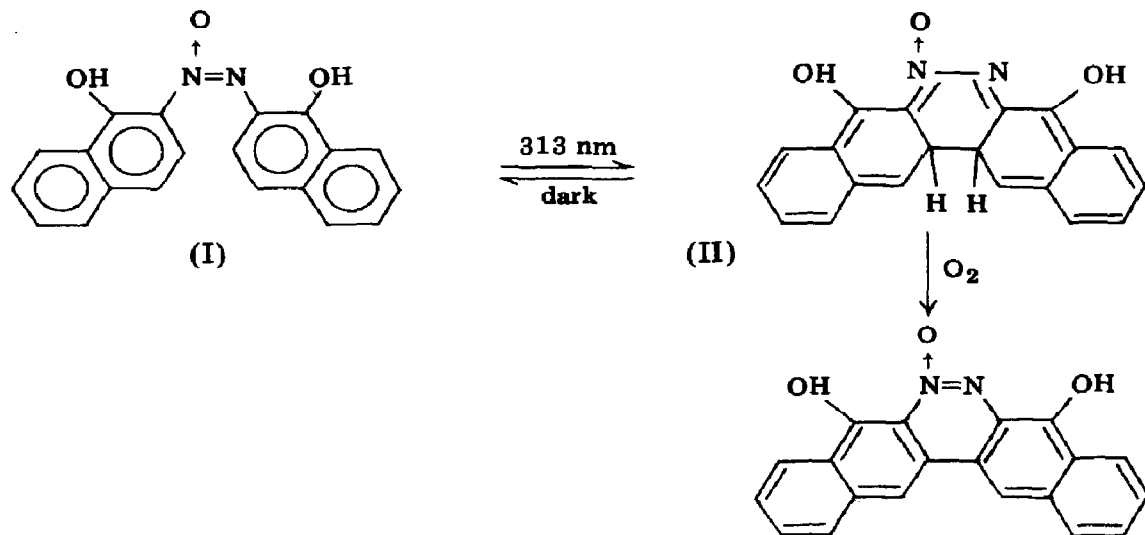
Fig. 4. The UV absorption changes induced by the photolysis of degassed 1,1'-hydroxy-2,2'-azoxynaphthalene at 313 nm: curve (1) (———), unphotolyzed; curve (2) (· ·), after photolysis for 50 min; curve (3) (———), after photolysis for 80 min; curve (4) (— · —), after photolysis for 320 min; curve (5) (inset, ———), after dark reaction for 20 h; curve (6) (inset, · · ·), after dark reaction for 44 h.

This scheme is similar to the photocyclization of *cis*-stilbene to dihydro-phenanthrene and phenanthrene [5]. The photocyclizations of related *cis* compounds have been studied extensively [6 - 9]. Fluorescence does arise after extended photolysis and it is inviting to suggest that this originates from the photocyclized aromatic compound, which arises after the dihydro compound reacts with oxygen.

4. Discussion

It is evident from the results that the photochemistry of 2-nitroso-1-naphthol in isopropyl alcohol involves hydrogen abstraction by an upper triplet state reaction as the primary event, as was the case with nitroso-benzene. Further, the process is reversible in the presence of oxygen and the hydroxylamine derivative is the only photoproduct. The apparent small increase with concentration of the nitroso compound in the disappearance quantum yield (reflected in Table 1) is attributed to the increasing contribution of the dark coupling reaction between the hydroxylamine and nitroso compound, which forms the corresponding azoxy compound. The smaller disappearance yield for air-saturated solutions is due to triplet quenching by oxygen and reoxidation of the hydroxylamine back to the nitroso compound.

The presence of the azoxy compound appears in both nitrosobenzene and 2-nitroso-1-naphthol photochemistry; however, there is a difference between the photochemistry of azoxybenzene and 1,1'-dihydroxy-2,2'-azoxynaphthalene. For azoxybenzene, 2-hydroxyazobenzene appears as the photoproduct [2], while for 1,1'-dihydroxy-2,2'-azoxynaphthalene, as shown in this study, a reversible process involving photocyclization to the dihydro compound leads subsequently to the photocyclized aromatic derivative.

Bellaart [4] has shown that the photochemistry of azoxynaphthalene gives rise to an unidentified product that has the same UV and IR spectra as the starting material. On the basis of the present investigation it now appears that the photoproduct reported in the literature is the dihydro compound arising from cyclization.

In contrast with the photoreduction of aromatic ketones where n,π^* and π,π^* triplets are often difficult to distinguish, aromatic nitroso compounds provide an interesting case where two n,π^* transitions are separated by a large energy gap, thereby facilitating the assignment of an upper electronic state as the reactive state. Recently, Chernoff and Hochstrasser [10] reported that the lifetime of the S_2 state in nitrosobenzene is approximately 10^{-14} s, which supports the involvement of an upper triplet state rather than an upper singlet state in the observed hydrogen abstraction. On the basis of our photochemical studies with nitrosobenzene and 2-nitroso-1-naphthol, which involve excitation into an upper excited state, we conclude that aromatic nitroso compounds undergo photoreduction from the second triplet state and that the lowest triplet is efficiently coupled by a radiation-

less transition to the ground state. No photoreduction occurs for excitation into the S_1 state. We have not been able to observe phosphorescence at 77 K in either nitrosobenzene or 2-nitroso-1-naphthol. Taken together with the results of Lawrence *et al.* [11] on reactive upper singlet states of thioketones and the results of Liu and coworkers [12, 13] on the importance of upper triplet states in anthracenes it is reasonable to expect that the number of photochemical events involving upper electronically excited states will continue to increase.

References

1 K. Pak and A. C. Testa, *J. Phys. Chem.*, *76* (1972) 1087.
2 R. Tanikaga, K. Maruyama, R. Goto and A. Kaji, *Tetrahedron Lett.*, (1966) 5925.
3 K. Tabei and S. Nagakura, *Bull. Chem. Soc. Jpn.*, *38* (1965) 965.
4 A. C. Bellaart, *Tetrahedron*, *21* (1965) 3285.
5 F. B. Mallory, C. S. Wood and J. T. Gordon, *J. Am. Chem. Soc.*,*86* (1964) 3094.
6 K. A. Muszkat and A. Fischer, *J. Chem. Soc. B*, (1967) 662.
7 F. R. Stermitz, in O. L. Chapman (ed.), *Organic Photochemistry*, Vol. I, Dekker, New York, 1967, p. 247.
8 M. Scholz, F. Dietz and M. Mühlstadt, *Z. Chem.*, *7* (1967) 329.
9 A. V. Blackburn and C. J. Timmons, *Q. Rev. Chem. Soc.*, *23* (1969) 482.
10 D. A. Chernoff and R. M. Hochstrasser, *Chem. Phys. Lett.*, *70* (1980) 213.
11 A. H. Lawrence, C. C. Liao, P. deMayo and V. Ramamurthy, *J. Am. Chem. Soc.*, *98* (1976) 2219, 3572.
12 R. S. H. Liu and J. R. Edelman, *J. Am. Chem. Soc.*, *90* (1968) 213.
13 R. S. H. Liu and D. M. Gale, *J. Am. Chem. Soc.*, *90* (1968) 1897.