BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3814—3817 (1973)

Photochemical Rearrangement of 2-Nitrophenyl Phenyl Sulfoxide to 2-Nitrosophenyl Phenyl Sulfone

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(Received May 14, 1973)

Irradiation of 2-nitrophenyl phenyl sulfoxide (I) gave 2-nitrosophenyl phenyl sulfone (II) as the sole product. The rearrangement was not affected by a quencher, but took a different course in the presence of a sensitizer or a halogen-containing solvent. When I with an electron-donating substituent at a 4′-position or electron-withdrawing one at a 4-position was irradiated, the corresponding II was obtained in a lower yield. 2-Nitrophenyl phenyl sulfide was photochemically stable. From the results, it is proposed that in the excited singlet state of I the oxyanion of a nitro group attacks the positive sulfur atom, and oxygen transfer takes place.

Organic nitrogen compounds, with an N→O bond such as $-N{=}\underset{|}{N}\rightarrow O$, $-CH{=}\underset{|}{N}\rightarrow O$ or $O{=}\underset{|}{N}\rightarrow O$, are known to undergo photochemical oxygen transfer reactions. Both rearrangements of azoxybenzene to 2-hydroxyazobenzene and of *N*,α-diphenylnitrone to 2,3-diphenylaziridine are postulated to proceed *via* the excited singlet state.[1,2]

In an aromatic nitro compound, a number of photochemical oxygen transfer reactions are also reported, but the reaction mechanism is not always straightforward.[3] In the rearrangements of 2-nitrobenzaldehyde to 2-nitrosobenzoic acid and of 2-nitrostilbene to 2-phenylisatogen, it is presumed that the reaction starts from an n→π* excitation and the oxygen atom of the nitro group in the (n,π*) triplet state abstracts a hydrogen atom or adds to an unsaturated system like the oxygen of a carbonyl group.

On the other hand, both azoxybenzene and nitrobenzene are known to be stronger bases in the excited

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[1] R. Tanikaga, This Bulletin, **41**, 2151 (1968).

[2] K. Shinzawa and I. Tanaka, *J. Phys. Chem.*, **68**, 1205 (1964); **69**, 2545 (1965).

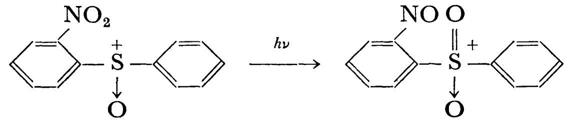
[3] H. A. Morrison, "The Chemistry of the Nitro and Nitroso Groups," Part 1, ed. by H. Feuer, Interscience Publishers, New York, N. Y. (1969), p. 165.

singlet state than in their ground state.[4,5] Thus a nitro compound might undergo an oxygen transfer reaction from the excited singlet state like an azoxy compound. 2-Nitrophenyl phenyl sulfoxide was found to rearrange to 2-nitrosophenyl phenyl sulfone possibly from the excited singlet state.[6]

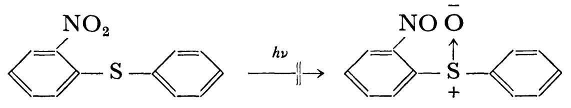
The principal objective of this work is to discuss the effect of a sensitizer, a quencher, a solvent, or a substituent on this new type of reaction, and to propose the mechanism.

Results and Discussion

A solution of 2-nitrophenyl phenyl sulfoxide (I) in benzene was irradiated with a high-pressure mercury lamp. Thin-layer chromatography analysis on silica gel revealed that 2-nitrosophenyl phenyl sulfone (II) was formed as the sole product, but not 2-nitrophenyl phenyl sulfide (III) or 2-nitrophenyl phenyl sulfone. This shows that an intramolecular oxygen transfer reaction took place. Neither thermal nor reverse photochemical rearrangement occurred. III was photochemically stable and gave no 2-nitrosophenyl phenyl sulfoxide. This suggests that the oxygen atom can attack only the positive sulfur atom.



(I) (II)



(III)

Effect of Sensitizer and Quencher. The results of the irradiation of I in benzene using a Pyrex filter are given in Table 1.

Table 1. Irradiation of I (10^{-2} M) for 3 hr

Sensitizer (M)	Quencher (M)	Yield (%) I	II	III
None	Degassed	84	12	0
None	O_2	84	12	0
None	1,3-Pentadiene (10^{-2})	85	11	0
$(C_6H_5)_3N$ (10^{-1})	Degassed	88	3	4
$(C_6H_5)_3N$ (10^{-1})	O_2	92	3	1

The rearrangement of I to II was not affected by oxygen or 1,3-pentadiene. Thus the oxygen transfer may occur directly from the excited singlet state.

Benzophenone, frequently used as a sensitizer, has one weak absorption band ($\lambda_{max}=343$ nm, $\varepsilon_{max}=130$) in benzene due to an n→π* transition in the wavelengths above 310 nm, whereas I has much stronger absorption in the same region (for example, $\varepsilon_{343nm}=925$). Therefore, a large excess of benzophenone should be used for photochemical sensitization, but such a reaction condition does not seem suitable because of the possibility of a chemical sensitization.

On the other hand, triphenylamine has a strong absorption band ($\lambda_{max}=302$ nm, $\varepsilon_{max}=2290$) in benzene, and its intersystem crossing efficiency is known to be high. When triphenylamine was used as a sensitizer, two different reactions appear to have occurred at the same time; a direct photorearrangement of I in its excited singlet state to II, and a photosensitized reaction of I to III, that is, the reduction of the S→O bond of I presumably in its excited triplet state. One plausible explanation for the low yield of III is to assume that I in the excited triplet state can not easily be reduced to III.

Effect of Solvent. The results of the photolysis of I in various solvents using a Pyrex filter are given in Table 2. Irradiation was stopped at an early stage of the reaction to prevent the product from absorbing light.

It was not possible to determine what excitation occurred, since no electronic spectrum of I has yet been assigned. Nitrobenzene in heptane has a long-wavelength absorption maximum at 330 nm ($\varepsilon=165$) which has been assigned as an n→π* band.[7] An ethanol solution of I shows only one absorption band at 235 nm ($\varepsilon=11000$) presumably arising from a π→π* transition, and other absorptions are completely submerged under this high intensity band. It appears attractive to assume that the reaction of I starts from its π→π* transition, since the yield of II was higher in quartz tube in spite of a weak radiation of the lamp used at 254 nm. Although there remain some possibilities that the reaction starts from another type of excitation, the possibility of an n→π* excitation may be excluded, since the absorption of I around 330 nm

Table 2. Irradiation of I (10^{-2} M) for 3 hr

Solvent	Yield (%) I	II	III
n-Hexane	81	14	0
n-Hexane[a]	76	17	0
Benzene	84	12	0
Ethanol	79	10	0
Acetonitrile	85	6	0
1-Chloropropane	86	3	0
1-Bromopropane	88	1	1
1,3-Dibromopropane	87	1	3

a) Quartz was used.

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[4] H. H. Jaffé, D. L. Beveridge, and H. L. Jones, *J. Amer. Chem. Soc.*, **86**, 2932 (1964); H. H. Jaffé and H. L. Jones, *J. Org Chem.*, **30**, 964 (1965).

[5] a) H. E. Zimmerman, "Advances in Photochemistry," Vol. 1, ed. by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Interscience Publishers, New York, N. Y. (1963), p. 200. b) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **89**, 6917 (1967). c) J. A. Barltrop and N. J. Bunce, *J. Chem. Soc., C*, **1968**, 1467. d) B. Tiniand and C. Décoret, *Tetrahedron Lett.*, **1971**, 2467.

[6] R. Tanikaga, Y. Higashio, and A. Kaji, *ibid.*, **1970**, 3273.

[7] S. Nagakura, M. Kojima, and Y. Maruyama, *J. Mol. Spectrosc.*, **13**, 174 (1964).

is rather strong ($\varepsilon > 1000$).

The spectra of I in various solvents are very similar. II was obtained in a higher yield in a non-polar solvent.

The irradiation of I in a halogen-containing solvent tended to afford III in place of II. In that solvent I in the excited singlet state is expected to undergo an intersystem crossing as a result of a heavy-atom effect. Thus it seems reasonable that the yield of II *via* the excited singlet state decreased, and that of III *via* the excited triplet state increased. The possibility of excitation of the solvent must be excluded, since the absorption intensity of the solvent is much lower in the wavelengths above 310 nm than that of I in 10^{-2} M concentration. Pyridine *N*-oxide is reported to be reduced to pyridine through the excited triplet state by the photolysis in a halogen-containing solvent.[8]

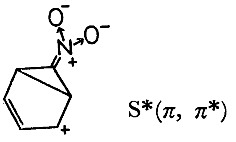
Effect of Substituent. The results of the photolyses of 2-nitrophenyl phenyl sulfoxide with a substituent in benzene using a Pyrex filter are given in Table 3. Irradiation was stopped at an early stage of the reaction to prevent the product from absorbing light.

TABLE 3. IRRADIATION OF I (10^{-2} M) WITH SUBSTITUENT FOR 3 hr

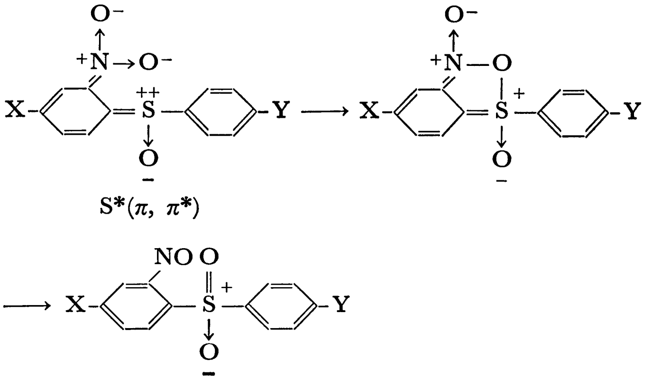
Substituent	Yield (%)	
	I	II
4′-CH_3O	88	8
4′-CH_3	91	6
4′-Cl	85	12
H	84	12
3′-Cl	82	16
4′-CH_3CO	83	14
4′-NO_2	86	11
4-NO_2	100	0

The electronic spectra of these compounds have only one strong absorption band in the wavelengths around 250 nm, and show similar intensities in wavelengths longer than 290 nm (Table 5). Although there will be problems in the discussion of the substituent effect, it is interesting to note that 2-nitrophenyl phenyl sulfoxide with an electron-donating group at a 4′-position tends to give the corresponding sulfone in a lower yield, and I with nitro group at a 4-position does not give any sulfone. These substituent effects are in contrast to those in the case of the oxygen transfer reaction of 2-nitrostilbene,[9] in which an electron-donating group at a 4′-position and an electron-withdrawing group at a 4-position promote the rearrangement.

Reaction Mechanism. In the excited (presumably (π,π^*)) singlet state, an aromatic nitro compound is known to have a higher electron density at the oxygen atom of the nitro group and a lower one at the meta-position of the phenyl ring.[5] This phenomenon can be illustrated by means of the following valence bond picture.[5a)]



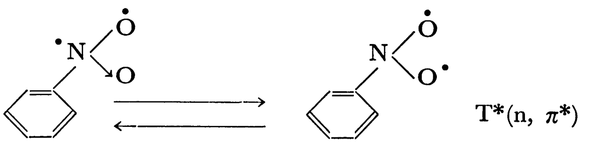
Thus, the most reasonable mechanism of the photochemical oxygen transfer reaction of I is as follows. In the excited (π,π^*) singlet state the oxyanion of a nitro group attacks the positive sulfur atom, and the oxygen transfer takes place without a spin inversion. This mechanism of the reaction of I is similar to that of azoxybenzene[1] and of *N*,α-diphenylnitrone.[2]



X: electron-donating group
Y: electron-withdrawing group

The above mechanism, in which the rearrangement occurs directly from the excited singlet state, can be explained by the effects of a sensitizer, a quencher and a halogen-containing solvent. The mechanism, in which an intramolecular nucleophilic attack occurs on the sulfur atom, can also be explained by the effect of a substituent on the rearrangement of I and the photochemical stability of III. The interesting intermolecular nucleophilic substitution on a sulfur atom was reported in the photochemistry of 2,4-dinitrobenzenesulfenyl derivatives.[10] The oxygen-bridged transition state may be supported by the effect of a solvent polarity.

On the other hand, in the excited (presumably (n,π^*)) triplet state a nitro compound is believed to have the following biradical structure.[3]



Thus, the oxygen atom of the nitro group in the excited state can have two opposite behaviors, a nucleophilic property in the excited (π,π^*) singlet state and an electrophilic one in the excited (n,π^*) triplet state. The former case was observed in the photochemical rearrangement of I to II, and the latter one is reported by de Mayo[11] in the photochemical electrophilic addition of an aromatic nitro compound

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8) N. Hata, Preprints for the 20th Annual Meeting of the Chemical Society of Japan (1967), Vol. 1, p. 483.

9) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955).

10) D. H. R. Barton, T. Nakano, and P. G. Sammes, *J. Chem. Soc., C*, **1968**, 322.

11) J. L. Charlton, C. C. Liao, and P. de Mayo, *J. Amer. Chem. Soc.*, **93**, 2463 (1971).

to an alkene. A similar biradical property of the nitro group in the excited (n,π^*) triplet state also appears to be observed in the intramolecular electrophilic attack of the nitro group to the double bond in the photochemical reaction of 2-nitrostilbene to 2-phenylisatogen.[9]

In conclusion, the property of an aromatic nitro compound in the excited (π,π^*) singlet state differs a great deal from that in the excited (n,π^*) triplet state.

Experimental

Starting Materials. The sulfides were prepared by the reaction of sodium thiophenolates and aryl halides. The sulfoxides were prepared by controlled oxidation of the corresponding sulfides with hydrogen peroxide. They were purified by column chromatography and recrystallization until their thin-layer chromatography showed only one spot, and were identified by elemental analysis, and NMR and IR spectra. (Tables 4 and 5)

TABLE 4. 2-NITROPHENYL PHENYL SULFIDES

Substituent	Mp (°C)
H	72.5
4'-CH_3O	97.5
4'-CH_3	83.0
4'-Cl	93.0
3'-Cl	107.5
4'-CH_3CO	156.5
4'-NO_2	162.0
4-NO_2	121.0

TABLE 5. 2-NITROPHENYL PHENYL SULFOXIDES

Substituent	Mp (°C)	$\varepsilon_{313\text{nm}}^{\text{benzene}}$
H	93.5	2250
4'-CH_3O	109.0	2830
4'-CH_3	139.5	2450
4'-Cl	117.5	2610
3'-Cl	115.5	2470
4'-CH_3CO	134.0	2640
4'-NO_2	153.5	5480
4-NO_2	114.0	4320

Photolysis of 2-Nitrophenyl Phenyl Sulfoxides to 2-Nitrosophenyl Phenyl Sulfones. A solution of 2 g of 2-nitrophenyl phenyl sulfoxide (I) in 500 ml of benzene was internally irradiated for 3 hr with a 300 W high-pressure mercury lamp using a Pyrex filter. Removal of the solvent gave a dark oil which was chromatographed on preparative thin-layer plates (Merck silica gel G). Development with chloroform three times gave two separated bands, the second band arising from I. The material from the first band was recovered by extraction with chloroform. Slow recrystallization from chloroform and *n*-hexane gave 400 mg of pale crystals Z; mp 145 °C; UV (benzene) $\lambda_{\max}$ 783 nm (nitroso); IR (KBr) 1320, 1150 cm^{-1} (sulfone).

Found: C, 58.58; H, 3.66; N, 5.59; S, 12.85%. Calcd for $C_{12}H_9NO_3S$: C, 58.29; H, 3.67; N, 5.66; S, 12.97%.

Compound Z was positive to the Liebermann test, and yielded 2-nitrophenyl phenyl sulfone by oxidation with hydrogen peroxide. Consequently, Z was assigned to 2-nitrosophenyl phenyl sulfone (II).

Other 2-nitrosophenyl phenyl sulfone derivatives were isolated and identified as described above. (Table 6)

TABLE 6. 2-NITROSOPHENYL PHENYL SULFONES

Substituent	Mp (°C)	$\nu_{\max}^{\text{KBr}}$ (cm^{-1})
H	145	1320, 1150
4'-CH_3O	152	1320, 1150
4'-CH_3	200	1300, 1150
4'-Cl	169	1330, 1160
3'-Cl	195	1330, 1165
4'-CH_3CO	154	1320, 1150
4'-NO_2	161	1300, 1160

Photolysis of I in the Presence of Sensitizer or Quencher. A Pyrex tube (inner diameter, 0.9 mm) containing a degassed or oxygen-saturated solution (2 ml) of I (10^{-2} M), with or without 1,3-pentadiene (10^{-2} M) or triphenylamine (10^{-1} M), was kept standing in a "merry-go-round" apparatus. The solution was irradiated for 3 hr with a 100 W high-pressure mercury lamp fitted with a water-cooled immersion well, and thermostated at 25 °C. Five ml of chloroform was added after irradiation and 0.5 ml of the resulting solution was developed on the thin-layer plate (silica gel G), and each component was extracted with chloroform. The yield was determined from the intensity of the absorption of the extract in an electronic spectrum, whose extinction coefficient had previously been determined with an authentic sample.

Reproducibility of the data obtained by this method was satisfactory. The results are given in Table 1.

Photolysis of I in Various Solvents. A solution (2 ml) of I (10^{-2} M) in each solvent was irradiated in a Pyrex or quartz tube for 3 hr. The yield of each product was determined as described above. The results are shown in Table 2.

Photolysis of 2-Nitrophenyl Phenyl Sulfoxide with Substituent. A solution (2 ml) of 2-nitrophenyl phenyl sulfoxide, with such substituents as shown in Table 3, in benzene, was irradiated in a Pyrex tube for 3 hr. The yield of each component was determined as described above. The results are shown in Table 3.