Self-Induced, Photochemical, Singlet-Oxygen Oxidation of 4-Nitrobenzenesulfenates to 4-Nitrobenzenesulfinates

Daniel J. Pasto,* Francois Cottard, and Sandra Horgan

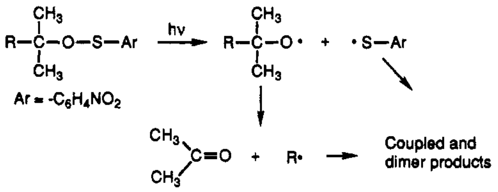
Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received March 25, 1993

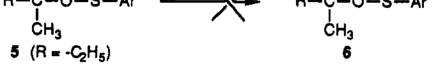
It has been previously reported that the photo-induced homolytic dissociation of homoallyl and alkyl 4-nitrobenzenesulfenates, followed by β-scission of the alkoxy radicals to allyl and alkyl radicals, leads to the formation of sulfides. In the presence of dioxygen the alkyl sulfenates undergo oxidation to the corresponding alkyl sulfinates. The results of theoretical studies suggest that the absorption of the photon results in the excitation of an electron from the π-type sulfur nonbonded-pair MO (the HOMO) to a π* MO of the aromatic ring (the LUMO). Quenching studies indicate that a triplet excited state is ultimately formed which then reacts with triplet dioxygen to form singlet dioxygen, which can be trapped with 1,3-cyclohexadiene, which then reacts with ground-state sulfenate.

Recent studies in the author's laboratories have focused on gaining an understanding of the factors controlling the regioselectivity of H-atom transfer to, and coupling of, substituted allyl radicals,[1] and in the ring-closure of the diradical intermediates formed in the [2 + 2] cycloaddition[2] and cyclodimerization reactions[3] of substituted allenes. Alternative methods were sought for the generation of substituted allyl radicals in which more specific information could be gained from the data. Dialkyl and diacyl peroxides (ROOR') have been extensively used for the generation of C-centered radicals (by β-scission of the initially formed O-centered radicals); however, there appeared to be no reasonable methods available for the synthesis of the required peroxide derivatives. The use of azo compounds similarly did not appear to be attractive. Alkyl hypochlorites have also been employed for the generation of alkoxy radicals;[4] however again, the methods used to prepare the alkyl hypochlorites proved to be incompatible with the presence of a C=C in the alkyl group. It was thus decided to investigate the photo-induced decomposition of alkyl arenesulfenates as a potential source of organic free radicals; the bond dissociation energy of the O–S bond being lower than that of the O–O bond, and the energy level of the nonbonded pair of electrons on the sulfur atom being higher in energy and thus requiring less energy (longer wavelength light) for electronic excitation. The results of our initial studies on the photo-induced homolytic decomposition of *tert*-homoallyl and alkyl 4-nitrobenzenesulfenates indicated that homolytic scission of the O–S bond occurred efficiently, which was followed by β-scission, producing allyl and alkyl radicals which then underwent coupling with the 4-nitrobenzenethiyl radical to form sulfides in up to 70% yields.[5] These results suggested that this procedure would provide a new and efficient approach for the generation of alkoxy and alkyl radicals.

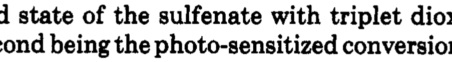
During more recent investigations on the photo-induced decomposition of variously substituted alkyl 4-nitrobenzenesulfenates it was noticed that small quantities of 4-nitrobenzenesulfinates were formed when the reaction solutions were not freeze-degassed. When chloroform



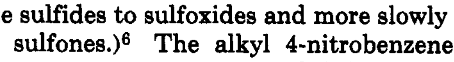
solutions of the alkyl 4-nitrobenzenesulfenates were irradiated under an oxygen atmosphere, using a Rayonet apparatus at 350 nm, isolated yields of up to 50–65% of the corresponding sulfinates were obtained. The yields of the "normal" radical products were greatly reduced. Primary and secondary alkyl 4-nitrobenzenesulfenates undergo oxidation to the sulfinates (the later to a mixture of diastereomers) [eq 1 and 2]; however, tertiary alkyl 4-nitrobenzenesulfenates do not undergo such oxidation [eq 3].



(1)



(2)



(3)

There are two reasonable mechanisms for this oxidation reaction, one being the direct reaction of the electronically-excited state of the sulfenate with triplet dioxygen and the second being the photo-sensitized conversion of triplet dioxygen to singlet dioxygen which then reacts with the ground-state sulfenate. (Singlet oxygen is well known to oxidize sulfides to sulfoxides and more slowly sulfoxides on to sulfones.)[6] The alkyl 4-nitrobenzenesulfenates possess a λ_{max} at ~337 nm. *Ab initio* calculations on structure 7 at the 3-21G level with partial geometry

---

[1] Pasto, D. J.; L'Hermine, G. *J. Org. Chem.* **1990,** *55,* 685–694. Pasto, D. J.; Cottard, F. *Tetrahedron* **1992**, submitted.

[2] Pasto, D. J.; Kong, W. *J. Phys. Org. Chem.* **1992,** *5,* 160–170.

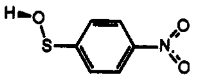
[3] Pasto, D. J.; Yang, S.-H. *J. Org. Chem.* **1986,** *51,* 3611–3619.

[4] Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963,** *85,* 1593–1597.

[5] Pasto, D. J.; L'Hermine, G. *J. Org. Chem.* **1990,** *55,* 5815–5816.

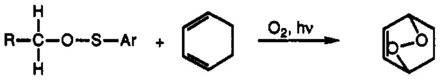
[6] Schenck, G. O.; Krauch, C. H. *Angew. Chem.* **1962,** *74,* 510. Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983,** *105,* 4717–4721.

0022-3263/93/1958-4110$04.00/0 © 1993 American Chemical Society



7

optimization,[7] indicate that the photo-excitation probably involves the excitation of an electron from the π-type nonbonded pair MO on the sulfur atom (the HOMO) to the π^* MO of the aromatic ring (the LUMO).[8] When the oxidation reaction is carried out in the presence of an excess (2.5 equiv) of 1,3-cyclohexadiene, the oxidation of the sulfenate is quenched and the endoperoxide of the diene is formed.[9] When the 1,3-cyclohexadiene had completely reacted, the normal oxidation of the sulfenate resumed.



These results suggest that singlet oxygen is involved in the oxidation of the sulfenates to the sulfinates. When the oxidation reaction is carried out in the presence of *trans*-piperylene, the oxidation of the sulfenates and the "normal" radical reactions are quenched, and the piperylene slowly disappears. After the complete disappearance of the piperylene, the oxidation and "normal" radical reactions resume. These results suggest that it is the triplet excited state of the 4-nitrobenzenesulfenates which is sensitizing the conversion of triplet oxygen to singlet oxygen which then reacts with ground-state sulfenate.[10]

Further studies are being carried out on this oxidation process, including the stereochemical features of the oxidation process.

Experimental Section

General. All ^1H NMR (300 mHz) and ^{13}C NMR (75 mHz) spectra were recorded on a General Electric GN 300 instrument connected to a General Electric 1280 data station. Deuteriochloroform (99.98% $CDCl_3$) was used as solvent and the chemical shifts were assigned relative to tetramethylsilane. The mass spectral analyses were carried out on a Finningan-Mat 8340 mass spectrometer equipped with a Varian 3400 gas chromatograph. TLC analyses were carried out using commercially available 0.2-mm thick silica gel F_{254} on aluminum. Column chromatography was performed using 230–400 mesh silica gel.

General Procedure of the Synthesis of Alkyl 4-Nitrobenzenesulfenates. A 50-mL three-neck flask containing the alcohol (5 mmol), freshly distilled triethylamine (1.6 mL, 11.5 mmol), and 15 mL of anhydrous methylene chloride under an argon atmosphere was placed in dry-ice in a darkened hood. A solution of 4-nitrobenzenesulfenyl chloride (0.95 g, 5 mmol) in anhydrous methylene chloride (10 mL) was added with stirring. After the addition of the sulfenyl chloride the reaction mixture was stirred for 15 min and was then allowed to warm to room temperature for 30 min. The reaction mixture was washed with cold 3% hydrochloric acid (2 × 10 mL) and cold water (3 × 10 mL), and the extract was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure in an aluminum-wrapped flask giving the sulfenates in essentially quantitative yields (>90%). When sufficiently thermally and photochemically stable, the sulfenate was purified by rotating-disk, thin-layer chromatography using an eluent system composed of Skellysolve B and methylene chloride in a 3:1 ratio.

1-Butyl 4-nitrobenzenesulfenate (1, R = C_3H_7) was prepared from 1-butanol following the general procedure described above: dark red liquid; UV, λ_{max} 345 nm; ^1H NMR ($CDCl_3$) δ 0.95 (t, J = 7.36 Hz, 3H), 1.44 (m, 2H), 1.72 (m, 2H), 3.90 (t, J = 6.58 Hz, 2H), 7.25 (d, J = 9.00 Hz, 2H), 8.20 (d, J = 9.00 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 18.9, 32.3, 79.4, 119.8, 124.2, 145.0, 151.7; HR EIMS calcd for $C_{10}H_{13}NO_3S$ 227.0616, found 227.0614.

1-Pentyl 4-nitrobenzenesulfenate (1, R = C_4H_8) was prepared from 1-pentanol following the general procedure described above: dark red liquid: ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 6.87 Hz, 3H), 1.35 (m, 4H), 1.75 (m, 2H), 3.90 (t, J = 6.64, 2H), 7.25 (d, J = 8.95 Hz, 2H), 8.20 (d, J = 8.95 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 27.7, 30.0, 79.6, 119.9, 124.2, 145.0, 151.8; HR EIMS calcd for $C_{11}H_{15}NO_3S$ 241.0773, found 241.0765.

2-Hexyl 4-nitrobenzenesulfenates (3, R = C_4H_9) was prepared from 2-hexanol following the general procedure described above: dark red liquid; ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7.00 Hz, 3H), 1.33 (d, J = 6.21 Hz, 3H), 1.35 (m, 4H), 1.60 (m, 1H), 1.80 (m, 1H), 3.75 (m, 1H), 7.25 (d, J = 9.01, 2H), 8.20 (d, J = 9.01, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 20.1, 22.6, 27.4, 35.4, 85.4, 119.9, 124.0, 144.9, 152.6; HR EIMS calcd for $C_{12}H_{12}NO_3S$ 255.0929, found 255.0949.

2-Methyl-2-butyl 4-Nitrobenzenesulfenate (5). 5 was prepared from 2-methyl-2-butanol following the general procedure described above: dark red liquid; ^1H NMR ($CDCl_3$) δ 0.95 (t, J = 7.50 Hz, 3H), 1.28 (s, 6H), 1.70 (q, J = 7.5 Hz, 2H), 7.30 (d, J = 9.00 Hz, 2H), 8.15 (d, J = 9.00 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 8.6, 24.5, 35.5, 86.9, 119.9, 123.7, 144.5, 154.2; HR EIMS calcd for $C_{11}H_{15}NO_3S$ 241.0773, found 241.0793.

General Procedure for the Photooxidation of 4-Nitrobenzenesulfenates. A Rayonet Photochemical Chamber Reactor Model RPR-100 equipped with 350.0-nm lamps was used to irradiate the sample solutions. The reaction temperature was stabilized at ~35 °C by a cooling fan. A conical flask containing a 0.5 M solution of the sulfenate in $CDCl_3$ was irradiated under an oxygen atmosphere until complete disappearance of the sulfenate (as determined by periodic NMR analysis). A change in color was observed, the orange-red color of the starting sulfenate changing to the orange-yellow of the sulfinate. Purification by flash column chromatography (Skelly F/CH_2Cl_2) gave pure sulfinates.

1-Butyl 4-Nitrobenzenesulfinate (2, R = C_3H_7) was obtained from in 65% yield following the general procedure described above as a pale yellow liquid: UV λ_{max} = 255 nm; ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.38 Hz, 3H), 1.35 (m, 2H), 1.60 (m, 2H), 3.66 (dt, J = 9.80, 6.50 Hz, 1H), 4.12 (dt, J = 9.80, 6.60 Hz, 1H), 7.90 (d, J = 8.85 Hz, 2H), 8.40 (d, J = 8.85 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5, 18.9, 31.6, 65.9, 124.2, 126.6, 150.0, 151.1; HR EIMS calcd for $C_{10}H_{13}NO_4S$, 243.0565, found 243.0568.

1-Pentyl 4-nitrobenzenesulfinate (2, R = C_4H_9) was obtained in 65% yield following the general procedure described above as a pale yellow liquid: ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.22 Hz, 3H), 1.3 (m, 4H), 1.65 (m, 2H), 3.65 (dt, J = 9.80, 6.60 Hz, 1H), 4.10 (dt, J = 9.80, 6.70 Hz, 1H), 7.90 (d, J = 8.90 Hz, 2H), 8.40 (d, J = 8.90, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.1, 27.8, 29.3, 66.2, 124.3, 126.6, 150.0, 151.1; HR CIMS (NH_3) calcd for $(M + NH_4)^+$ 275.1065, found 275.1079.

2-Hexyl 4-nitrobenzenesulfinate (4, R = C_4H_9) was obtained as a ~1:1 mixture of diastereomerers in 50% yield as a pale yellow liquid: ^1H NMR of one diastereomer ($CDCl_3$, characteristic distinguishing differences) δ 0.85 (t, J = 8.80 Hz, 3H), 1.30 (d, J = 6.25 Hz, 3H), 7.95 (d, J = 7.95 Hz, 2H), 8.40 (d, J = 7.95 Hz, 2H); ^1H NMR of second diastereomer δ 0.92 (t, J = 6.80 Hz, 3H), 1.45 (d, J = 6.20 Hz, 3H); ^{13}C NMR of the mixture of the two

---

(7) The bond lengths, bond angles, and dihedral angles in the NO_2 and H–O–S portions of 7 were optimized. The bond lengths of the C–C and C–H bonds of the aromatic ring were maintained at 1.396 and 1.078 Å, and the C–C–C and C–C–H bond angles were maintained at 120°. The optimized parameters for the C–N, N–O, S–C, O–S, and O–H bonds are 1.438, 1.245, 1.819, 1.725, and 0.971 Å, while the values for the C–N–O, C–S–O and S–O–H bond angles are 117.43, 98.92, and 109.74°, with the C–C–S–O and C–S–O–H dihedral angles being 12.65 and 97.66°.

(8) The energies (eV) and dominant contributions of the three highest occupied and three lowest unoccupied MO's of 7 are: −11.709 (NO_2 π, −10.369 (ring π), −9.539 (S_n) 3p, +0.952 (ring-NO_2, π^*), +2.976 (ring π^*), and +3.381 (O–S σ^*).

(9) The endoperoxide of 1,3-cyclohexadiene was identified by the comparison of the NMR spectrum of an authentic sample of the endoperoxide formed in the Rose Bengal-sensitized conversion of triplet oxygen to singlet oxygen in the presence of 1,3-cyclohexadiene (Foote, C. S.; Wexler, S.; Ando, W.; Higgins, R. *J. Am. Chem. Soc.* 1968, *90*, 975–981).

(10) The results of a theoretical study on the proposed intermediates formed in the singlet oxygen oxidation of sulfides has very recently appeared (Clennan, E. L.; Yang, K. *J. Org. Chem.* 1992, *57*, 4477–4487). See also the refs contained therein.

diastereoisomers ($CDCl_3$) δ 13.8–13.9, 21.7–21.9, 22.3–22.4, 27.2–27.3, 36.9–37.1, 78.4–78.7, 124–124.5, 126.3–126.4, 149.9–149.9, 152–152; HR-CIMS [isobutane, (EIMS produced no detectable parent ion)] highest *m/z* fragment ion calcd for $C_8H_8NO_4S$ 214.0174, found 214.0178.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds **1–5** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering formation.