

p-Nitrobenzenesulfenate Esters as Precursors for Laser Flash Photolysis Studies of Alkyl Radicals

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Abstract: A series of *p*-nitrobenzenesulfenate esters was used in laser flash photolysis (LFP) studies to generate alkoxyl radicals that fragmented to give the (2,2-diphenylcyclopropyl)methyl radical. Rate constants for the β -scission reactions increased as a function of the carbonyl compound produced in the fragmentation reaction in the order CH₂O < MeCHO < Me₂CO < PhCHO < Ph₂CO and increased with increasing solvent polarity. For alkoxyl radicals that fragment to produce benzaldehyde and benzophenone, the β -scission reactions are faster than 1,5-hydrogen atom abstractions when the incipient carbon radical is as stable as a secondary alkyl radical, and this entry to carbon radicals can be used in LFP kinetic studies.

Laser flash photolysis (LFP) kinetic studies of radicals are conveniently conducted when one can generate the desired radical in high yield from a laser photolysis reaction, but many photochemical bond-cleavage reactions are not useful for LFP. Small quantum yields and/ or rapid electron-transfer processes following the bond homolysis reaction result in low yields of transients. When high-energy light is required for radical production, experimental difficulties are encountered if additives or the radical transients absorb laser light. We report here an evaluation of *p*-nitrobenzenesulfenate (PNBS) esters as precursors of carbon-centered radicals in LFP studies.

Benzenesulfenates react with stannyl radicals in radical chain reactions to give alkoxyl radicals,¹ and PNBS esters have been used as alkoxyl radical precursors in steady-state photolysis reactions^{2,3} and in LFP studies.⁴ The PNBS esters are yellow-colored compounds that have a long wavelength absorbance centered at ca. 350 nm. The photochemical homolysis reaction gives an alkoxyl radical and the *p*-nitrobenzenethiyl radical, and previous LFP studies demonstrated that the cleavage reactions of PNBS esters occur with high efficiency using 355-nm laser light (third harmonic of a Nd:YAG laser).⁴ Our interest in exploring PNBS esters as sources of alkyl radicals for kinetic studies was based on the facility of alkoxyl radical β -scission reactions, which have been extensively studied for the *tert*-butoxyl radical⁵⁻⁸ and the cumyloxyl radical,^{9,10} and the observation that PNBS

SCHEME 1



esters are relatively stable and can be purified by silica gel chromatography with little decomposition.^{2,4}



The series of PNBS esters 1 was prepared from reactions of the corresponding alcohols with 4-nitrobenzenesulfenyl chloride in the presence of Et₃N. Upon photolysis with 355-nm light, precursors 1 react as shown in Scheme 1. The initial photolysis gives alkoxyl radicals **2**. β -Scission of radicals **2** produces a carbonyl compound and the (2,2-diphenylcyclopropyl)methyl radical (3). Radical **3** is an ultrafast "reporter" radical¹¹ that ring opens with a rate constant of $5\times 10^{11}\,s^{-1}$ at ambient temperature¹² to give the 1,1-diphenyl-3-butenyl radical (4) that is readily detected in the UV due to its strong long wavelength absorbance with λ_{max} at ca. 335 nm.¹³ The rates of signal growth for radical 4 give the rates of the β -scission reactions of the alkoxyl radicals. Because radical **3** was produced in all reactions, the kinetic effects of the substituents on the β -scission reaction can be evaluated

Reactions with PNBS esters **1** were conducted in (trifluoromethyl)benzene (trifluorotoluene, TFT), acetonitrile, and acetic acid. Figure 1 shows the time-resolved growth spectrum following photolysis of precursor **1b** where the formation of the diphenylalkyl radical **4** is apparent from its characteristic spectrum with λ_{max} at

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FIGURE 1. Time-resolved spectrum from the reaction of radical **2b** in acetonitrile. The time slices are at 70, 100, 200, and 350 ns with the spectrum at 50 ns subtracted to give a baseline. Symbols on the 350-ns trace show the wavelengths that were monitored. The inset shows the kinetic trace at 334 nm.

 TABLE 1. Rate Constants for Fragmentation of Alkoxyl Radicals 2^a

radical	byproduct	temp (°C)	k_{TFT} (s ⁻¹)	$k_{\rm ACN}$ (s ⁻¹)	$k_{ m AcOH}$ (s ⁻¹)
2a 2b 2c 2d 2e	CH ₂ O ^c MeCHO Me ₂ CO PhCHO Ph ₂ CO	22 22 22 -30 22 -40 22	$3.8 imes 10^5 \ 6.0 imes 10^6 \ 2.2 imes 10^{7 \ d}$	$\begin{array}{c} 7.5 \times 10^5 \\ 1.1 \times 10^7 \\ 5.7 \times 10^7 \\ 7.5 \times 10^7 \\ 5 \times 10^8 e \\ \geq 2 \times 10^8 \\ \geq 1.3 \times 10^9 e \end{array}$	${5.2\times10^6}_{>2\times10^8}$

^{*a*} Observed rate constants; typical errors are 3% of the stated value. ^{*b*} TFT = α, α, α -trifluorotoluene; ACN = acetonitrile; AcOH = acetic acid. ^{*c*} In aqueous acetonitrile solutions, radical **2a** fragmented at 22 °C with the following rate constants: *k* (ACN: water, v:v) = 9.0 × 10⁵ s⁻¹ (95:5), 1.5 × 10⁶ s⁻¹ (80:20), and 3.2 × 10⁶ s⁻¹ (50:50). ^{*d*} Reference 4. ^{*e*} Rate constants for **2d** and **2e** at 22 °C were estimated from the low-temperature kinetic values; see text.

ca. 335 nm.¹³ In principle, β -scission of radicals **1b** and **1c** might occur in part with elimination of methyl radicals, but that pathway was not important. For reactions of **1b** and **1c**, there was no obvious reduction in the yields of radical **4** relative to the byproduct *p*-nitrobenzenethiyl radical as determined from the ratio of the ultimate signal intensities at 335 nm (for radical **4**) and the instantaneous signal intensities at 490 nm (for the *p*-nitrobenzenethiyl radical).

The observed rate constants for β -scission of radicals **2** are given in Table 1. Phenyl-substituted radicals **2d** and **2e**, which fragment to give benzaldehyde and benzophenone, respectively, reacted faster than the instrument response at 22 °C. A rate constant for reaction of **2d** could be obtained at -30 °C in acetonitrile, and we estimated a rate constant of $k = 5 \times 10^8 \text{ s}^{-1}$ for reaction of **2d** at 22 °C from this kinetic value and a log *A* term of 12.4.¹⁴ Alkoxyl radical **2e** fragmented faster than the instrument limit even at -40 °C, and we estimated a lower limit for this fragmentation reaction of $k \ge 1.3 \times 10^9 \text{ s}^{-1}$ at 22 °C. A relatively large solvent polarity effect on the rate constants for β -scission of radicals **2a**, **2b**,

The change in the rate constants for β -scission for the series of radicals **2** is noteworthy. For radicals $2\mathbf{a} - \mathbf{c}$, the trend mirrors the activation energies for β -scission of the methyl radical from the series of radicals ethoxyl, isopropoxyl, and *tert*-butoxyl.⁸ A strong acceleration in the fragmentation rate results from replacement of a methyl group on the α -carbon with a phenyl group; e.g., radical 2d reacts about 50 times faster than radical 2b at 22 °C in acetonitrile. The direction, if not the magnitude, of this effect was expected because the rate constant for β -scission of a methyl radical from cumyloxyl in acetonitrile is 10 times larger than that for β -scisssion of a methyl radical from the tert-butoxyl radical in the same solvent.^{7,9,10} The second phenyl group at the $\alpha\text{-carbon}$ in radical **2e** resulted in further acceleration of the β -scission reaction to an unknown extent because the instrument limit was exceeded. Phenyl group migration in the 1,1-diphenylethoxyl radical to give the 1-phenyl-1-phenoxyethyl radical, a neophyl-like rearrangement reaction, is faster than β -scission of the methyl radical,¹⁶ but the rate constant for phenyl migration in acetonitrile at ambient temperature is only $(2-3) \times 10^6 \text{ s}^{-1, 17-19}$ about 3 orders of magnitude smaller than that for β -scission of radical 2e.

If PNBS esters are to be used as sources of carbon radicals, the β -scission reactions must be faster than intra- and intermolecular hydrogen atom transfer reactions. Unlike the β -scission reactions that have rate constants strongly dependent on the stability of the incipient radical, hydrogen atom abstractions are relatively insensitive to the stability of the radical product. For example, rate constants for 1,5-hydrogen atom transfer in radicals **5** and **6** at 20 °C in trifluorotoluene were 2.7 × 10⁷ and 1.2 × 10⁷ s⁻¹, respectively,⁴ even though the C–H bond energies should differ by 4 kcal/mol or more.



When alkoxyl radical **2c** was generated in THF at 20 °C, the signal intensity from product radical **4** was reduced to 40% of that observed when **2c** was produced in the nonreactive solvent trifluorotoluene. This indicates that 60% of the radical reacted with THF. The observed rate constant in THF at 20 °C, which is the sum of all first-order and pseudo-first-order rate constants for reactions of **2c**, was $k_{obs} = 7.7 \times 10^7 \text{ s}^{-1}$. Therefore, the

⁽¹⁴⁾ A log A value of 12.4 was determined for β -scission of radical **2c** in triflouormethylbenzene; see ref 4.

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calculated pseudo-first-order rate constant for reaction with THF is 4.6 × 10⁷ s⁻¹, and that for β -scission is k =3.1 × 10⁷ s⁻¹. There is good agreement in the value for the β -scission reaction in THF with that in TFT as expected given that the polarities of THF and TFT are similar.^{20,21} Using a molarity for THF of 12.3 M, the second-order rate constant for reaction of **2c** with THF is 3.7 × 10⁶ M⁻¹ s⁻¹, which is in good agreement with the reported second-order rate constant of 4.6 × 10⁶ M⁻¹ s⁻¹ for reaction of the *tert*-butoxyl radical with THF at 25 °C.²²

The β -scission reactions of radicals **2d** and **2e**, which eliminate benzaldehyde and benzophenone, respectively, are more than 1 order of magnitude faster than typical 1,5-hydrogen atom abstractions and reaction with neat THF. Therefore, PNBS esters that give such alkoxyl radicals should be useful as carbon-radical precursors when the incipient carbon radical is as stable as a secondary alkyl radical. It is possible that this entry to carbon radicals will not be useful for primary alkyl radicals, however, due to the strong dependence of the β -scission reaction on the stability of the product radical.

Experimental Section

General Method for the Preparation of Alkyl 4-Nitrobenzenesulfenates. To a stirred solution of the appropriate alcohol (1 equiv) and distilled triethylamine (1.5 equiv) in anhydrous CH_2Cl_2 at 0 °C was added dropwise a solution of 4-nitrobenzenesulfenyl chloride (1.2 equiv) in CH_2Cl_2 . After 10 min, the solution was warmed to room temperature and stirred for an additional 15 min. After addition of water to the reaction mixture, the organic layer was washed with 10% aqueous NH_4 -Cl solution and saturated NaCl solution, dried over MgSO₄, and concentrated in vacuo. Column chromatography on silica gel (hexanes/EtOAc) yielded the desired 4-nitrobenzenesulfenate ester as a reddish oil or solid in high yield.

2-(2,2-Diphenylcyclopropyl)ethyl 4-Nitrobenzenesulfenate (1a). The general procedure was used with 300 mg (1.3 mmol) of 2-(2,2-diphenylcyclopropyl)ethanol to yield **1a** as a red oil (370 mg, 75% yield). ¹H NMR: δ 1.20 (t, J = 7.0 Hz, 1H), 1.29 (d, J = 7.2 Hz, 2H), 1.81 (m, 2H), 3.94 (t, J = 6.4 Hz, 2H), 7.10–7.32 (m, 12H), 8.12 (d, J = 9.1 Hz). ¹³C NMR: δ 20.1 (CH₂), 22.3 (CH), 31.7 (CH₂), 35.2 (C), 79.0 (CH₂), 119.8 (CH), 127.7 (CH), 128.3 (CH), 130.4 (CH), 141.0 (C), 145.1 (C), 146.6 (C), 151.5 (C).

2-(2,2-Diphenylcyclopropyl)-1-methylethyl 4-Nitrobenzenesulfenate (1b). The general procedure was used with 300 mg (1.2 mmol) of 1-(2,2-diphenylcyclopropyl)-2-propanol to yield **1b** a red oil (375 mg, 78% yield). A mixture of diastereoisomers was obtained, whose NMR peaks were mostly overlapping. ¹H NMR of the mixture: δ 0.98 and 1.17 (m, 1H), 1.29–1.38 (m, 5 H), 1.75 and 1.99 (m, 2H), 3.85 (m, 1H), 7.13–7.31 (m, 12H), 8.04 and 8.11 (d, J = 9.1 Hz and J = 9.0 Hz, 2H). ¹³C NMR of the mixture: δ 20.4 (CH₃), 20.5 and 21.1 (CH₂), 22.3 and 22.4 (CH), 34.7 and 35.2 (C), 38.0 and 38.1 (CH₂), 85.0 and 85.5 (C), 120.0 and 120.1 (CH), 124.0 (CH), 125.88 and 125.9 (CH), 126.5 and 126.6 (CH), 127.4 (CH), 127.8 (CH), 128.3 (CH), 128.4 (CH), 130.3 and 130.5 (CH), 141.0 and 141.1 (C), 144.98 and 145.04 (C), 146.7 (C), 152.3 and 152.4 (C).

2-(2,2-Diphenylcyclopropyl)-1,1-dimethylethyl 4-Nitrobenzenesulfenate (1c). The general procedure was used with 500 mg (1.88 mmol) of 1-(2,2-diphenylcyclopropyl)-2-methyl-2-propanol to yield **1c** as a red oil (535 mg, 68% yield). ¹H NMR: δ 0.80 (dd, J = 14.4, 10.4 Hz, 1H), 1.30 (s, 3H), 1.33 (m, 1H), 1.36 (s, 3H), 1.70 (m, 1H), 2.08 (dd, J = 4.3, 3.1 Hz, 1H), 7.09–7.30 (m, 12H), 8.09 (d, J = 9.1 Hz, 2H). ¹³C NMR: δ 21.7 (CH₂), 22.0 (CH), 25.3 (CH₃), 25.7 (CH₃), 33.6 (C), 42.3 (CH₂), 87.2 (C), 120.1 (CH), 120.2 (CH), 123.8 (CH), 123.9 (CH), 125.8 (CH), 126.4 (CH), 127.6 (CH), 128.2 (CH), 130.3 (CH), 141.2 (C), 144.8 (C), 146.8 (C), 153.9 (C).

2-(2,2-Diphenylcyclopropyl)-1-phenylethyl 4-Nitrobenzenesulfenate (1d). The general procedure was used with 300 mg (9.5 mmol) of 2-(2,2-diphenylcyclopropyl)-1-phenylethanol to yield **1d** as an orange solid (312 mg, 70% yield). Mp: 40 °C dec. The product was a mixture of diastereoisomers that was not further purified. ¹H NMR of the mixture: δ 1.19, 1.33, 1.47, 1.67, 1.89 and 2.20 (m, 5H), 4.57 and 4.65 (t, J = 7.1 and 6.5 Hz, 1H) 7.07–7.39 (m, 15H), 7.97 and 8.09 (d, J = 8.9 Hz and J = 8.9 Hz, 2H). ¹³C NMR of the mixture: δ 20.0 and 21.1 (CH₂), 22.1 and 22.9 (CH), 35.1 and 35.6 (C), 38.4 and 39.2 (CH₂), 90.1 and 90.8 (CH), 120.1 (CH), 120.2 (CH), 120.3 (CH), 124.1 and 124.2 (CH), 126.0 (CH), 126.7 (CH), 127.4 (CH), 128.0 (CH), 128.4 (CH), 128.6 (CH), 130.2 (CH), 130.6 (CH), 140.1 and 140.4 (C), 140.8 and 141.1 (C), 145.0 and 145.1 (C), 146.5 and 146.6 (C), 151.5 and 151.6 (C).

2-(2,2-Diphenylcyclopropyl)-1,1-diphenylethyl 4-Nitrobenzenesulfenate (1e). The general procedure was used with 750 mg (1.9 mmol) of 2-(2,2-diphenylcyclopropyl)-1,1-diphenylethanol to give **1e** as an orange solid (783 mg, 75% yield). Mp: 55 °C dec. ¹H NMR: δ 0.77 (m, 1H), 0.91 (m, 1H), 1.43–1.60 (m, 2H), 2.93 (d, J = 11.9 Hz, 1H), 6.91 (d, J = 6.6 Hz, 2H), 7.06–7.30 (m, 20H), 7.91 (d, J = 9.0 Hz, 2H). ¹³C NMR: δ 21.3 (CH2), 21.9 (CH), 34.1 (C), 39.3 (CH2), 91.9 (C), 121.6 (CH), 121.7 (CH), 123.3 (CH), 123.4 (CH), 125.8 (CH), 126.4 (CH), 127.7 (CH), 127.9 (CH), 128.2 (CH), 130.2 (CH), 141.3 (CH), 142.0 (CH), 142.5 (CH), 144.9 (CH), 146.7 (CH), 151.5 (C).

Laser flash photolysis studies were performed with Applied Photophysics LK50 and LK60 kinetic spectrometers by conventional methods. In brief, solutions of precursors in the appropriate solvent were prepared such that the absorbance at 355 nm was ca. 0.5. The solutions were allowed to flow through a 1 cm \times 1 cm quartz cell and were irradiated with 355-nm light (Nd:YAG, third harmonic) in 5- or 7-ns pulses of 50–90 mJ. Data were collected at individual wavelengths via oscilloscopes with temporal resolution up to 125 ps. The measured photomultiplier response was 2 \times 10⁸ s⁻¹, which represents the kinetic limit of the instruments.

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Supporting Information Available: Experimental details for preparation of the alcohols used in the preparation of PNBS esters 1 and ¹H and ¹³C NMR spectra of the alcohols and PNBS esters 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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