

Formation of Sulfur-Centered Cation Radicals by Photofragmentation

Richard S. Glass* and Jeffrey L. Broeker

Department of Chemistry, The University of Arizona, Tucson, AZ 85721, U.S.A.

Elke Anklam and Klaus-Dieter Asmus

Hahn-Meitner Institut Berlin, Bereich S, Abteilung Strahlenchemie,
Postfach 39 01 28, 1000 Berlin 39, GERMANY

Key Words: Sulfur-centered cation radical formation; laser flash photolysis;
perester fragmentation

Abstract: The selected dialkyl dithioethers 1,5-dithiocane, 1,4-dithiepane, 1,4-dithiane, and 2,6-dithiaheptane are readily monoalkylated in nitromethane by tert-butyl 0-trifluoromethanesulfonyl-3-hydroxyperoxypropanoate, **6**, to give the corresponding sulfonium salt peresters **2a-c**, and **3** in good yield. Laser flash photolysis of these compounds affords the known two-sulfur, three-electron stabilized cation radicals **2a**, **b**, and **5** which were characterized by optical absorption spectroscopy.

The structures and reactions of dialkylsulfide cation radicals have been the subject of considerable current experimental and theoretical interest.¹ Despite the numerous reports²⁻¹⁴ of their formation as observed species or presumed intermediates the study of these generally reactive species is associated with certain limitations. Thus a method for chemo- and regioselective production of these species is lacking. In addition, generation of these species by pulse radiolysis, which is one of the most general and useful methods is usually limited to water as solvent. Consequently, these studies necessarily involve $(R_2S \cdot OH_2)^+$, an adduct of the molecular $R_2S^{+\cdot}$ cation radical to a single water molecule.^{15,16} Formation of "free" sulfur-centered cation radicals or species with bonds, between sulfur and some electron-rich center, which are weaker than the bond in $(R_2S \cdot OH_2)^+$ are not observed. Because of the restriction to studies in water there is a paucity of information on solvent effects on the structures and reactions of these moieties.

Our recent¹⁷ studies on the photodecomposition of sulfonium salt peresters **1a** led to the speculation that the sulfur-centered cation radicals $R_2S^{+\cdot}$ are produced as shown in eq 1. Since

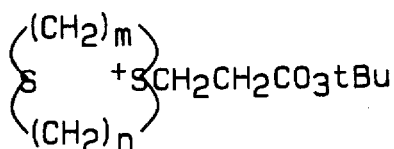


1a, R = R' = Me
b, R' = H

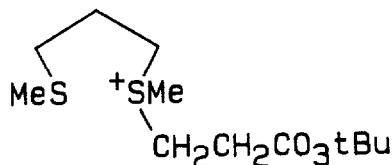
such photolysis would provide a potentially useful method for generating sulfur-centered cation radicals which would complement the previously reported methods this reaction was studied in more

detail. In this paper formation of sulfur-centered cation radicals by photodecomposition of sulfonium salt peresters **1b**, *t*-butyl 3-(*S,S*-dialkyl) sulfonioperoxypropanoates, is proven and, thereby, a potentially general procedure for selective generation of sulfur-centered cation radicals is at hand.

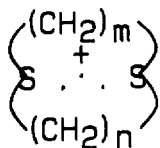
To prove that sulfur-centered cation radicals are formed on photolysis of sulfonium salt peresters **1b**, compounds **2a-c**, and **3** were studied, because the stabilized cation radicals expected to be produced on photolysis, i.e. **4a-c** and **5**, respectively have been reported previously^{3,9,18-20} and characterized spectroscopically.



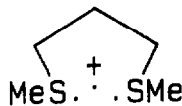
2a, $m=n=3$
b, $m=3, n=2$
c, $m=n=2$



3

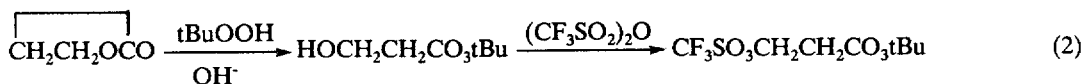


4a, $m=n=3$
b, $m=3, n=2$
c, $m=n=2$



5

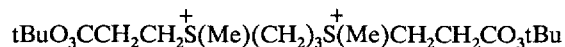
To develop a general method for synthesizing sulfonium salt peresters, alkylating agent **6** was prepared as shown in eq 2. Treatment of β -propio-lactone with *tert*-butylhydroperoxide in base



6

affords *tert*-butyl 3-hydroxypropanoate which was converted to the unstable trifluoromethanesulfonate **6**. In analogy with the work of Vedejs and coworkers,^{21,22} **6** was expected to alkylate dialkyl sulfides, readily. Indeed reaction of **6** with 1,5-dithiocane, 1,4-dithiepane, and 1,4-dithiane proceeded smoothly in nitromethane at room temperature to produce sulfonium salt peresters **2a-c** in 70, 94, and 78% yield, respectively, after recrystallization. Alkylation of 2,6-dithiaheptane with **6** gave sulfonium salt perester **3** but ¹H NMR spectroscopic analysis revealed that a mixture of **3** and

the dialkylated product **7** was also formed. The yield of **6** was approximately 80% and that of **7** ca. 20%. This product could not be purified by recrystallization but the mixture was studied.



7

Sulfonium salt perester **2a** absorbs with a maximum of 230 nm in the UV. Irradiation of this salt in acetonitrile with light from a high pressure mercury vapor lamp through a Vycor filter resulted in the formation of ethene in 84% yield as analyzed by GC. In addition, ethane, propene, methane, and isobutene were formed in 1, 3, 10, and 30% yields, respectively. Methane and ethane are the expected products from the decomposition of the tert-butoxy radical.²³ Isobutene suggests the formation of acid and subsequent acid-catalyzed decomposition of the tert-butyl ester.²⁴ After irradiation, however, the solution showed no measurable absorption at 412 nm which is the reported²⁵ absorption maximum for **4a** in acetonitrile. A solution of **4a** in acetonitrile prepared following the procedure of Musker and coworkers^{19,20} showed absorption maxima at 412²⁵ and at 235 nm as well.²⁶ Consequently, cation radical **4a**, if formed may photolyze (either directly or via the corresponding dication). Indeed irradiation of a solution of **4a** in acetonitrile resulted in its decomposition.^{24,27}

To avoid the photolysis of the presumed primary product **4a**, laser flash photolysis of **2a** was studied. The hope was that with flash irradiation over a very short time period sulfonium salt perester **2a** would photolyze but the light would be off before **4a** forms so that the latter would survive the irradiation. Flash photolysis of sulfonium salt perester **2a** in acetonitrile with an approximately 20 ns pulse of 248 nm light from a KrF excimer laser resulted in a solution absorbing with λ_{max} at 405 nm in reasonable agreement with that reported for **4a** in acetonitrile (412 nm)^{19,20,25} and in water (400 nm).¹⁸ The absorbing species decomposed with a half-life of approximately 8 μ s. Similar flash photolysis of **2b** resulted in a species with an absorption maximum of 460 nm (**4b** is reported¹⁸ to show a λ_{max} at 460 nm in water) and a half-life of approximately 5 μ s. Flash photolysis of **2c** gave a solution with too weak an absorption maximum to be accurately measured. However, flash photolysis of **3** provided a transient with an absorption maximum of 440 nm (**5** is reported¹⁸ to exhibit an absorption maximum of 440 nm in water) and a half-life of 12 μ s.

These preliminary results provide strong evidence for the formation of sulfur-centered cation radicals on photolysis of sulfonium salt peresters **1b** as shown in eq 1. Note that the lifetimes for the species produced in this way is shorter than those reported previously from the pulse radiolysis and chemical oxidation studies in aqueous solution. The reason for this is not known at present but could be due to reaction of the sulfur-centered cation radical with the other radical species produced in this photolysis.

Acknowledgment: RSG and JLB gratefully acknowledge support of this work by the U.S. Public Health Service, National Institutes of Health, Grant No. HL 15104. Part of this work was conducted with the help of Dr. S. Steenken at the Max Planck Institut für Strahlenchemie (Mülheim), which E.A. thanks for its gracious hospitality.

References and Notes

1. "Sulfur-Centered Reactive Intermediates in Chemistry and Biology," Chatgililoglu, C.; Asmus, K.-D. Eds., Plenum: NY, 1990.
2. Rao, D.N.R.; Symons, M.C.R.; Wren, B.W. *J. Chem. Soc. Perkin Trans. 2* **1984**, 1681-1687 and references therein.
3. Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436-442.
4. Ando, W.; Takata, T. In "Singlet O₂," Vol. 3, Part 2, Frimer, A.A. Ed., CRC Press Inc.: Boca Raton, FL, 1985, chp 1.
5. Pienta, N.J. In "Photoinduced Electron Transfer," Part C, Fox, M.A.; Chanon, M., Eds., Elsevier: Amsterdam, 1988, pp 421-486.
6. Dektar, J.L.; Hacker, N.P. *J. Am. Chem. Soc.* **1990**, *112*, 6004-6015 and references therein.
7. Shine, H.J. In "The Chemistry of the Sulphonium Group," Stirling, C.J.M.; Patai, S., Eds., Wiley: NY, 1981, chp 14.
8. Joule, J.A. *Adv. Heterocycl. Chem.* **1990**, *48*, 301-393.
9. Musker, K. *Acc. Chem. Res.* **1980**, *13*, 200-206.
10. Dinnocenzo, J.P.; Banach, T.E. *J. Am. Chem. Soc.* **1986**, *108*, 6063-6065.
11. Miller, A.E.; Bischoff, J.J.; Bizub, C.; Luminoso, P.; Smiley, S. *J. Am. Chem. Soc.* **1986**, *108*, 7773-7778 and references therein.
12. Grimshaw, J. In "The Chemistry of the Sulphonium Group," Stirling, C.J.M.; Patai, S. Eds., Wiley: NY, 1981, chp 7.
13. Torii, S. "Electroorganic Synthesis," Kodansha: Tokyo, 1985, pp 210-217.
14. Iliés, A.J.; Livant, P.; McKee, M.L. *J. Am. Chem. Soc.* **1988**, *110*, 7980-7984.
15. Asmus, K.-D. in "Sulfur-Centered Reactive Intermediates in Chemistry and Biology," Chatgililoglu, C.; Asmus, K.-D., Eds. Plenum Press: NY, 1990 pp 155-172.
16. Clark, T. *ibid.* pp 13-18.
17. Broeker, J. Ph.D. Dissertation, University of Arizona 1988.
18. Asmus, K.-D.; Bahnmann, D.; Fischer, Ch.-H.; Veltwisch, D. *J. Am. Chem. Soc.* **1979**, *101*, 5322-5329.
19. Musker, W.K.; Wolford, T.L. *J. Am. Chem. Soc.* **1976**, *98*, 3055-3056.
20. Musker, W.K.; Wolford, T.L.; Roush, P.B. *J. Am. Chem. Soc.* **1978**, *100*, 6416-6421.
21. Vedejs, E.; Engler, D.A. *Tetrahedron Lett.* **1976**, 3487-3490.
22. Vedejs, E.; Engler, D.A.; Mullins, M.J. *J. Org. Chem.* **1977**, *42*, 3109-3113.
23. Pryor, W.A. "Free Radicals," McGraw-Hill: NY, 1966, pp 84-87, 165-167.
24. The propene may be generated by photolysis of cation radical **4a** because both propene and ethene are detected in the photodecomposition of **4a** (in 1 and 7% yield, respectively).
25. The λ_{\max} for **4a** in acetonitrile is reported as 412 nm in Ref. 19 but 420 nm in Ref. 20.
26. The absorption maximum at 235 nm may be due to the corresponding dithioether dication which is present in solutions of the cation radical: Ryan, M.D.; Swanson, D.D.; Glass, R.S.; Wilson, G.S. *J. Phys. Chem.* **1981**, *85*, 1069-1075; Brown, T.G.; Hirschon, A.S.; Musker, W.K. *J. Phys. Chem.* **1981**, *85*, 3767-3771. This dication is reported to exhibit a λ_{\max} of 233 nm in acetonitrile.²⁰
27. Except for propene and ethene²⁴ the products from this photodecomposition were not determined.