Electron Transfer and Singlet Oxygen Mechanisms in the Photooxygenation of Dibutyl Sulfide and Thioanisole in MeCN Sensitized by *N*-Methylquinolinium Tetrafluoborate and 9,10-Dicyanoanthracene. The Probable Involvement of a Thiadioxirane Intermediate in Electron Transfer Photooxygenations

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Abstract: Photooxygenations of PhSMe and Bu_2S sensitized by *N*-methylquinolinium (NMQ^+) and 9,10-dicyano-anthracene (DCA) in O_2-saturated MeCN have been investigated by laser and steady-state photolysis. Laser photolysis experiments showed that excited NMQ^+ promotes the efficient formation of sulfide radical cations with both substrates either in the presence or in absence of a cosensitizer (toluene). In contrast, excited DCA promotes the formation of radical ions with PhSMe, but not with Bu_2S. To observe radical ions with the latter substrate, the presence of a cosensitizer (biphenyl) was necessary. With Bu_2S, only the dimeric form of the radical cation, $(Bu_2S)_2^{+\bullet}$, was observed, while the absorptions of both $PhSMe^{+\bullet}$ and $(PhSMe)_2^{+\bullet}$ were present in the PhSMe time-resolved spectra. The decay of the radical cations followed second-order kinetics, which in the presence of O_2, was attributed to the reaction of the radical cation (presumably in the monomeric form) with $O_2^{-\bullet}$ generated in the reaction between $NMQ^\bullet$ or $DCA^{-\bullet}$ and O_2. The fluorescence quenching of both NMQ^+ and DCA was also investigated, and it was found that the fluorescence of the two sensitizers is efficiently quenched by both sulfides (rates controlled by diffusion) as well by O_2 ($k_q = 5.9 \times 10^9$ M^{-1} s^{-1} with NMQ^+ and 6.8×10^9 M^{-1} s^{-1} with DCA). It was also found that quenching of $^1NMQ^*$ by O_2 led to the production of $^1O_2$ in significant yield ($\phi_\Delta = 0.86$ in O_2-saturated solutions) as already observed for $^1DCA^*$. The steady-state photolysis experiments showed that the NMQ^+- and DCA-sensitized photooxygenation of PhSMe afford exclusively the corresponding sulfoxide. A different situation holds for Bu_2S: with NMQ^+, the formation of Bu_2SO was accompanied by that of small amounts of Bu_2S_2; with DCA, the formation of Bu_2SO_2 was also observed. It was conclusively shown that with both sensitizers, the photooxygenations of PhSMe occur by an electron transfer (ET) mechanism, as no sulfoxidation was observed in the presence of benzoquinone (BQ), which is a trap for $O_2^{-\bullet}$, $NMQ^\bullet$, and $DCA^{-\bullet}$. BQ also suppressed the NMQ^+-sensitized photooxygenation of Bu_2S, but not that sensitized by DCA, indicating that the former is an ET process, whereas the second proceeds via singlet oxygen. In agreement with the latter conclusion, it was also found that the relative rate of the DCA-induced photooxygenation of Bu_2S decreases by increasing the initial concentration of the substrate and is slowed by DABCO (an efficient singlet oxygen quencher). To shed light on the actual role of a persulfoxide intermediate also in ET photooxygenations, experiments in the presence of Ph_2SO (a trap for the persulfoxide) were carried out. Cooxidation of Ph_2SO to form Ph_2SO_2 was, however, observed only in the DCA-induced photooxygenation of Bu_2S, in line with the singlet oxygen mechanism suggested for this reaction. No detectable amounts of Ph_2SO_2 were formed in the ET photooxygenations of PhSMe with both DCA and NMQ^+ and of Bu_2S with NMQ^+. This finding, coupled with the observation that $^1O_2$ and ET photooxygenations lead to different product distributions, makes it unlikely that, as currently believed, the two processes involve the same intermediate, i.e., a nucleophilic persulfoxide. Furthermore, the cooxidation of Ph_2SO observed in the DCA-induced photooxygenation of Bu_2S was drastically reduced when the reaction was performed in the presence of 0.5 M biphenyl as a cosensitizer, that is, under conditions where an (indirect) ET mechanism should operate. This observation confirms that a persulfoxide is formed in singlet oxygen but not in ET photosulfoxidations. The latter conclusion was further supported by the observation that also the intermediate formed in the reaction of thianthrene radical cation with KO_2, a reaction which mimics step d (Scheme 2) in the ET mechanism of photooxygenation, is an electrophilic species, being able to oxidize Ph_2S but *not* Ph_2SO. It is thus proposed that the intermediate involved in ET sulfoxidations is a thiadioxirane, whose properties (it is an electrophilic species) seem more in line with the observed chemistry. Theoretical calculations concerning the reaction of a sulfide radical cation with $O_2^{-\bullet}$ provide a rationale for this proposal.

Introduction

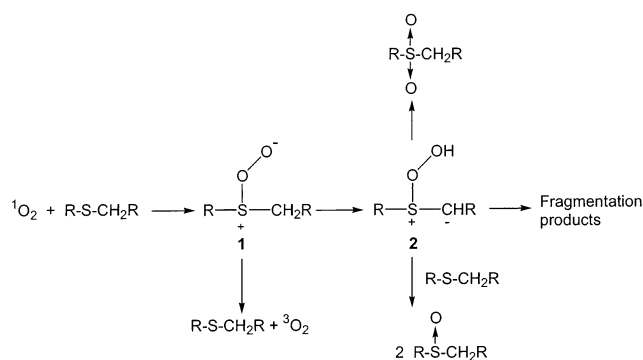Photooxygenation of sulfides is a topic attracting continuous interest both from the practical and the mechanistic point of view.[1−8] Presently, two main photooxidation mechanisms are clearly recognized: (a) photooxidation promoted by singlet
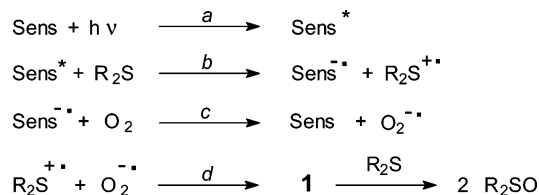
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Scheme 1

Scheme 2

oxygen [O_2 ($^1\Delta_g$), henceforth indicated as $^1O_2$] and (b) photo-oxidation with triplet oxygen [O_2 ($^3\Sigma_g^-$), henceforth referred to simply as O_2] via electron transfer (ET) sensitization.

It is generally thought that, in aprotic solvents, the two mechanisms should involve the same key intermediate, the per-sulfoxide **1**, albeit of course formed by different routes. In $^1O_2$ photooxygenations,[9-12] **1** is directly formed by reaction of $^1O_2$ with the sulfide and, as shown in Scheme 1, it can then collapse to the starting sulfide and O_2 or be converted to a second reaction intermediate, probably a *S*-hydroperoxysulfonium ylide (**2**). The main pathway of the latter species is the reaction with another sulfide molecule to produce the sulfoxide, but also rearrangement to sulfone and formation of fragmentation products are possible. ET photosulfoxidations have been studied in much less detail than $^1O_2$ photosulfoxidations. Nevertheless, the mechanism reported in Scheme 2 is generally accepted.[13] The excited sensitizer (step *a*) reacts with the sulfide in an electron-transfer process (step *b*) to form a sulfide radical cation and the reduced form of the sensitizer. The latter can then react with O_2 to regenerate the sensitizer and to produce $O_2^{-\bullet}$ (step *c*), which by reaction with the sulfide radical cation (step *d*) forms the persulfoxide **1**. However, while the role of **1** in singlet oxygen sulfoxidations has received strong support, both theo-

retically and experimentally, no evidence in this respect is available concerning ET photooxygenations of sulfides. Nor has it ever been tested if the same product pattern is found in $^1O_2$ and ET photooxygenations, which is required if **1** is an intermediate in both reactions.

Moreover, the possibility that ET sensitizers can also induce singlet oxygen photooxygenation of sulfides leading to a competition between the two mechanisms, as observed with alkenes, has never been investigated in detail.[14-17]

With the aim of shedding light on some of these aspects, the photooxygenation of dibutyl sulfide (Bu$_2$S) and thioanisole (PhSMe) sensitized by *N*-methylquinolinium tetrafluoborate (NMQ$^+$) and 9,10-dicyanoanthracene (DCA) in MeCN has been investigated by laser and steady-state photolysis. NMQ$^+$ appears to be particularly well suited to promote ET processes since ^{1}NMQ^{+*} reacts with the substrate to produce a neutral radical/radical cation pair whose separation is facilitated by the lack of any electrostatic barrier.[18] The reduction potential of ^{1}NMQ^{+*} is very high (2.7 V vs SCE),[19] much higher than the oxidation potentials of Bu$_2$S (1.5 V vs SCE)[20] or PhSMe (1.4 V vs SCE),[21] and moreover, its reduced form (NMQ$^\bullet$) is able to convert O_2 into $O_2^{-\bullet}$. However, no information is available concerning the capacity of ^{1}NMQ* to induce the formation of $^1O_2$.

^{1}DCA* is also an efficient ET sensitizer with a reduction potential (1.90-2.00 V)[22] sufficient to oxidize both sulfides; however, it has been clearly demonstrated that ^{1}DCA* can also be efficiently trapped by O_2 to give $^1O_2$, mainly through reactions 1 and 2, and so it can promote $^1O_2$-induced photo-oxygenations as well.[14-17]

$$^1DCA* + {}^3O_2 \rightarrow {}^3DCA* + {}^1O_2 \qquad (1)$$

$$^3DCA* + {}^3O_2 \rightarrow DCA + {}^1O_2 \qquad (2)$$
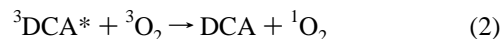
This mechanistic dichotomy has been clearly demonstrated by Foote and his associates for the DCA-promoted photoxy-genations of alkenes.[14-17] However, the studies that have so far dealt with the photooxygenation of alkyl and aryl sulfides sensitized by DCA have concluded that an ET mechanism (Scheme 2) is operating.[13,23]

The results reported herewith have allowed us to establish with certainty the ET character of the photooxygenations sensitized by NMQ$^+$ of both Bu$_2$S and PhSMe, even though it has been discovered that irradiation of this sensitizer in the presence of oxygen produces large amounts of singlet oxygen. With DCA, however, the ET mechanism is operating only for PhSMe, whereas for Bu$_2$S, clear evidence has been found that the photooxygenation mainly involves singlet oxygen. These results have also demonstrated that ET and $^1O_2$ photooxygen-

(1) Tung, C.-H.; Guan, J.-Q. *J. Am. Chem. Soc.* **1998**, *120*, 11874−11879.
(2) Bonesi, S. M.; Nella, M.; d'Alessandro, N.; Aloisi, G. G.; Vanossi, M.; Albini, A. *J. Org. Chem.* **1998**, *63*, 9946−9955.
(3) Toutchkine, A.; Clennan, E. L. *J. Org. Chem.* **1999**, *64*, 5620−5625.
(4) Bonesi, S. M.; Albini, A. *J. Org. Chem.* **2000**, *65*, 4532−4536.
(5) Toutchkine, A.; Aebisher, D.; Clennan, E. L. *J. Am. Chem. Soc.* **2001**, *123*, 4966−4973.
(6) Clennan, E. L.; Zhou, W.; Chan, J. *J. Org. Chem.* **2002**, *67*, 9368−9378.
(7) Lacombe, S.; Cardy, H.; Simon, M.; Khoukh, A.; Soumillion, J. Ph.; Ayadim, M. *Photochem. Photobiol. Sci.* **2002**, *1*, 347−354.
(8) Zen, J. M.; Liou, S. L.; Kumar, A. S.; Hsia, M. S. *Angew. Chem., Int. Ed.* **2003**, *42*, 577−579.
(9) Liang, J. J.; Gu, C. L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717−4721.
(10) Ishiguro, K.; Hayashi, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7265−7271.
(11) Jensen, F.; Greer, A.; Clennan, E. L. *J. Am. Chem. Soc.* **1998**, *120*, 4439−4449 and references therein.
(12) Clennan, E. L. *Acc. Chem. Res.* **2001**, *34*, 875−884.
(13) Soggiu, N.; Cardy, H.; Habib Jiwan, J. L.; Leray, I.; Soumillion, J. Ph.; Lacombe, S. *J. Photochem. Photobiol. A: Chem.* **1999**, *124*, 1−8 and references therein.

(14) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083−6088.
(15) Steichen, D. S.; Foote, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 1855−1857.
(16) Silverman, S. K.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 7672−7675.
(17) Araki, Y.; Dobrowolski, D. C.; Goyne, T. E.; Hanson, D. C.; Jiang, Z. Q.; Lee, K. J.; Foote, C. S *J. Am. Chem. Soc.* **1984**, *106*, 4570−4575.
(18) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876−1883.
(19) Yoon, U. C.; Quillen, S. L.; Mariano, P. S.; Swanson, R.; Stavinoha, J. L.; Bay, E. *J. Am. Chem. Soc.* **1983**, *105*, 1204−1218.
(20) Gassman, P. G.; Mullins, M. J. *Tetrahedron Lett.* **1980**, *21*, 2219−2222.
(21) Goto, Y.; Matsui, T.; Ozaki, S.; Watanabe, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **1999**, *121*, 9497−9502.
(22) Chanon, M.; Eberson, L. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part A, p 470.
(23) Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455−6456.

ations lead to different products distributions. The latter observation coupled with results of trapping experiments, has cast serious doubts on the current belief that persulfoxide **1** is a key reaction intermediate in ET photosulfoxidations. A thiadioxirane structure seems more likely, a conclusion that also appears to be justified by theoretical calculations.

Experimental Section

Materials. Dibutyl sulfide (Aldrich) was used as received. Thioanisole (Aldrich) was purified by distillation. Diphenyl sulfoxide was prepared by perchloric acid-catalyzed reaction of diphenyl sulfide (Aldrich) with hydrogen peroxide,[24] purified by chromatography (diethyl ether/petroleum ether 1:1 on silica gel), followed by three recrystallizations from dichloromethane/hexane to obtain a >99.97% purity (gas chromatograph). Benzoquinone (Aldrich) was purified by recrystallization from dichloromethane/hexane. Reaction products dibutyl sulfoxide, dibutyl sulfone, dibutyl disulfide, methyl phenyl sulfoxide, and phenyl sulfone were purchased from Aldrich and used as received. *N*-Methylquinolinium tetrafluoborate was prepared by a literature procedure.[25] 9,10-Dicyanoanthracene (Kodak), acetonitrile (Carlo Erba, HPLC plus grade), biphenyl (Aldrich), and toluene (Aldrich, RPE) were used as received.

Photooxidation General Procedure. Photooxidation reactions were carried out in a Rayonet reactor equipped with 16 lamps (3500 Å; 24 W each). A solution (4 mL) containing the sulfide (0.01 or 0.1 M) and the sensitizer (2 or 20×10^{-4} M) in oxygen-saturated acetonitrile was irradiated in a rubber cap-sealed tube for 10 min under magnetic stirring. An internal standard (4-methylbenzophenone) was added, and the mixture was analyzed by GC and GC-MS. A cosensitizer (1 M toluene for NMQ$^+$ and 0.5 M biphenyl for DCA) was added in some experiments. Photooxidations were also carried out in the presence of benzoquinone (BQ, 5×10^{-4} or 2.5×10^{-3} M) or of variable concentrations of Ph$_2$SO (0.02–0.1 M). Experiments in the presence of DABCO ($3-6 \times 10^{-4}$ M) were also carried out. Products analysis (comparison with authentic specimens) was carried out on a Varian CP-3800 gas chromatograph and on a HP 5890 gas chromatograph equipped with a 5972 mass selective detector.

Fluorescence Quenching. Measurements were carried out at 25 °C on a Shimadzu RF5001PC spectrofluorophotometer. For quenching of ^{1}NMQ^{+*} ([NMQ$^+$] = 5×10^{-5} M) by sulfides (0 to 5×10^{-4} M) in argon-saturated acetonitrile, the relative emission intensities at 390 nm (NMQ$^+$ emission maximum) were measured by irradiating at 315 nm (NMQ$^+$ absorption maximum). For quenching of ^{1}DCA* by sulfides, the relative emission intensities at 440 nm (DCA emission maximum) were measured by irradiating (at 350 nm) argon-saturated MeCN solutions containing DCA (5×10^{-5} M) and the sulfide (from 0 to 5×10^{-3} M). In the case of quenching of ^{1}NMQ^{+*} and ^{1}DCA* by O$_2$, argon-saturated, air-equilibrated (O$_2$, 1.7×10^{-3} M), and O$_2$-saturated (O$_2$, 8.0×10^{-3} M) MeCN solutions of the sensitizer (5×10^{-5} M) were irradiated.

Laser Flash Photolysis. An excitation wavelength of 355 nm from a Nd:YAG laser (Continuum, third harmonic) was used in nanosecond flash photolysis experiments (pulse width ca. 7 ns and energy <3 mJ per pulse).[26,27] The transient spectra were obtained by a point-to-point technique, monitoring the change of absorbance (ΔA) after the laser flash at intervals of 5–10 nm over the spectral range 300–900 nm, averaging at least 10 decays at each wavelength. The $t_{1/2}$ values (the time at which the initial signal is halved, experimental error of $\pm 10\%$) are reported for transients showing second-order kinetics. All solutions

were flowed through a quartz photolysis cell while nitrogen or oxygen was bubbled through them. All measurements were carried out at 22 ± 2 °C.

Singlet Oxygen. The phosphorescence emission of ^{1}O$_2$ was detected by a germanium diode detector in O$_2$-saturated solutions.[28] At least 200 transients were averaged for each measurement. Stern–Volmer linear plots built with the ^{1}O$_2$ lifetimes recorded at different concentrations of Bu$_2$S and PhSMe gave the corresponding ^{1}O$_2$ quenching rate constants.

Quantum Yields. For NMQ$^+$, a 3 mL O$_2$-saturated solution of the sensitizer (3.9×10^{-4} M) and PhSMe ($1.0-4.7 \times 10^{-2}$ M) or Bu$_2$S ($4.7-9.4 \times 10^{-2}$ M) in MeCN was placed in a quartz cell and irradiated with a high-pressure Hg lamp at 313 nm as selected with a Balzer interference filter. For DCA, a 2.5 mL O$_2$-saturated MeCN solution of the sensitizer (7.2×10^{-4} M) and PhSMe ($1.05-6.8 \times 10^{-2}$ M) or Bu$_2$S ($0.97-4.7 \times 10^{-2}$ M) was placed in a quartz cell and irradiated at 366 nm. In both cases, the photoproducts were quantified by GC analysis; 4-methylbenzophenone was used as an internal standard, and the substrate conversion was held below 10%. The light intensity (ca. 3.4×10^{14} photons/s) was measured by potassium ferric oxalate actinometry.

Reaction of Thianthrene Radical Cation. Thianthrene radical cation tetrafluoroborate[29] (0.05 mmol) and 1 mmol of Ph$_2$SO were added to a suspension of KO$_2$ (0.1 mmol in 5 mL of dry MeCN). The color of the thianthrene radical cation tetrafluoroborate immediately disappeared. After GC and GC-MS analysis, the only reaction products detected were thianthrene and thianthrene 5-oxide (yield 49%); no appreciable formation of Ph$_2$SO$_2$ was observed.

Computational Details. Theoretical calculations were carried out using the GAUSSIAN 98 system of programs[30] to determine the enthalpy for formation of dimethyl persulfoxide and dimethyl thiadioxirane from coupling of Me$_2$S$^{+\bullet}$ with O$_2^{-\bullet}$ along with the activation and reaction enthalpies for their dissociation to Me$_2$S + ^{1}O$_2$. The enthalpy of singlet oxygen was computed by adding the experimental singlet–triplet energy difference (22.5 kcal/mol)[31] to the computed enthalpy of triplet oxygen, as previously suggested by McKee,[32] since calculation of the δ state of ^{1}O$_2$ would require a complex wave function. Geometries were optimized by estimating electron correlation with the second-order Møller–Plesset perturbation theory (MP2) and with the quadratic configuration interaction, including single and double substitutions (QCISD). In all calculations, diffuse functions were added to the basis set on heavy atoms to properly describe superoxide, a negatively charged species, and the zwitterionic structure of dimethyl persulfoxide. A valence double-ζ basis set supplemented with two d-polarization functions on heavy atoms and a p-polarization function on hydrogen (6-31+G(2d,p)) was employed both in MP2 and QCISD calculations. Enthalpy corrections at 298.15 K were estimated at the MP2/6-31+G(d) level from frequency calculations using a scaling factor of 0.967 to account for anharmonicity.[33] The transition states for the dissociation of dimethyl persulfoxide and dimethyl thiadioxirane have only a single imaginary frequency. Inspection of the imaginary frequency indicates that the motion leads to dissociation.

(24) Cerniani, A.; Modena, G. *Gazz. Chim. Ital.* **1959**, *89*, 843–853.
(25) Donovan, P. F.; Conley, D. A. *J. Chem. Eng. Data* **1966**, *11*, 614.
(26) Romani, A.; Elisei, F.; Masetti, F.; Favaro, G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2147–2154.
(27) Görner, H.; Elisei, F.; Aloisi, G. G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 29–34.

(28) Elisei, F.; Aloisi, G. G.; Lattarini, C.; Latterini, L.; Dall'Acqua, F.; Guiotto, A. *Photochem. Photobiol.* **1996**, *64*, 67–74.
(29) Boduszek, B.; Shine, H. J. *J. Org. Chem.* **1988**, *53*, 5142–5143.
(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
(31) Krupenie, P. *J. Phys. Chem. Ref. Data* **1972**, *1*, 423–534.
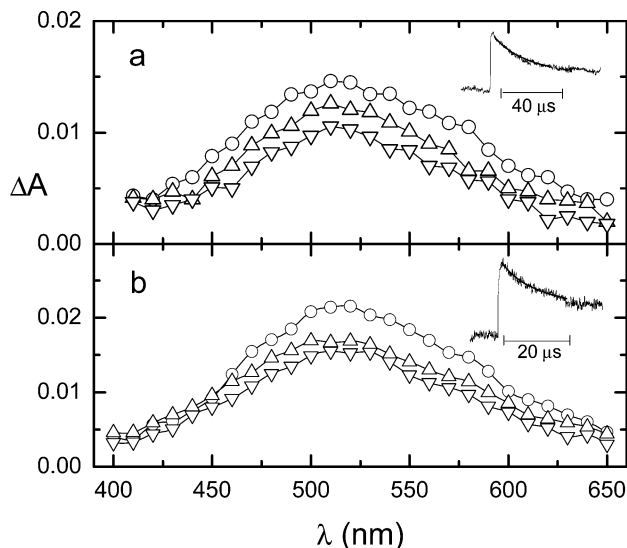(32) McKee, M. L. *J. Am. Chem. Soc.* **1998**, *120*, 3963–3969.
(33) Scott, P. A.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.

Figure 1. Time-resolved absorption spectra of the NMQ$^+$/Bu$_2$S system (3.5×10^{-3} and 1.0×10^{-2} M, respectively) in MeCN: (a) N$_2$-saturated, recorded 1.4 (○), 8.0 (△), and 16 μs (▽) after the laser pulse and (b) O$_2$-saturated, recorded 0.27 (○), 2.8 (△), and 6.4 μs (▽) after the laser pulse (λ_{exc} = 355 nm). Insets: decay kinetics recorded at 510 nm; the full lines represent the second-order best fittings of the experimental data.
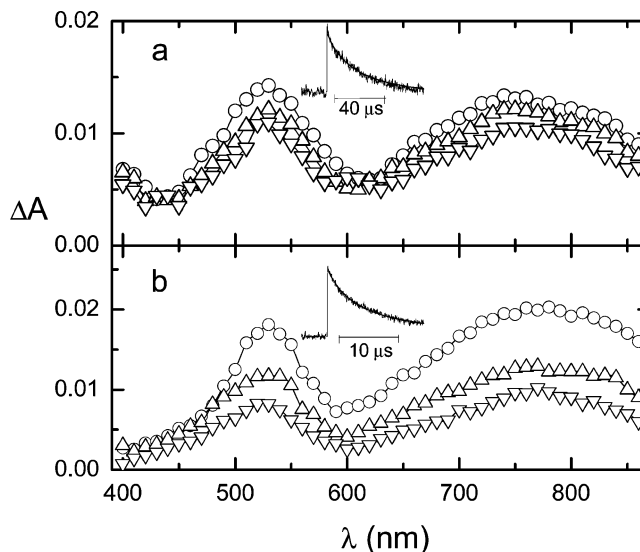
Calculations using high accuracy energy methods based on complete basis set models such as CBS-Q, CBS-QB3, and CBS-RAD failed since dimethyl persulfoxide **4** was computed to be unstable at the MP2/6-31G(d′), B3LYP/6-311G(2d,d,p) (i.e., two d-polarization functions on sulfur, a d-polarization function on first row atoms, and a p-polarization function on hydrogen), and QCISD/6-31G(d) levels, respectively. It should be noted that **4** (i) becomes unstable at the MP2 level changing the exponent of the polarization d-functions, (ii) remains unstable upon enlarging the basis set from 6-31G(d) to 6-311G(2d,d,p) using the DFT method with the B3LYP functional, (iii) and becomes unstable by improving the estimation of electron correlation passing from a perturbative (MP2) to a CI (QCISD) approach using the 6-31G(d) basis set. On the other hand, the high accuracy energy method G3 failed since the transition state for dissociation of dimethyl thiadioxirane **5** to dimethyl sulfide and singlet oxygen was not found at the HF/6-31G(d) level. However, this type of calculation provides only the enthalpy contribution to the total energy. This contribution was, then, estimated from frequency calculations at the MP2/6-31+G(d) level as in MP2 and QCISD calculations. Furthermore, geometries were optimized at the QCISD/6-31+G(2d,p) level instead of the MP2(full)/6-31G(d) level since preliminary calculations showed that addition of both diffuse functions and a second d-polarization function on heavy atoms affect significantly the equilibrium geometries.

The effect of solvent was taken into account both at the MP2 and QCISD levels by the polarizable continuum model (PCM)[34] employing the dielectric constant ϵ of acetonitrile (ϵ = 36.64).

Results

Laser Flash Photolysis Experiments with NMQ$^+$ and Singlet Oxygen Formation. Upon laser excitation (λ_{exc} = 355 nm) of MeCN solutions of NMQ$^+$//Bu$_2$S and NMQ$^+$//PhSMe, time-resolved absorption spectra and decay kinetics were recorded under N$_2$- and O$_2$-saturated conditions (Figures 1 and 2).

With Bu$_2$S, only one broad band centered at 525 nm is present in the case of N$_2$-saturated solution (Figure 1a), due to the overlap of the absorptions of NMQ$^\bullet$ (λ_{max} = 550 nm), and an

(34) Cossi, M.; Barone, V.; Cammi, R.; Tommasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327−335.

Figure 2. Time-resolved absorption spectra of the NMQ$^+$/PhSMe system (3.5×10^{-3} and 1.0×10^{-2} M, respectively) in MeCN: (a) N$_2$-saturated, recorded 0.94 (○), 3.8 (△), and 6.4 μs (▽) after the laser pulse and (b) O$_2$-saturated, recorded 0.13 (○), 1.9 (△), and 6.4 μs (▽) after the laser pulse (λ_{exc} = 355 nm). Insets: decay kinetics recorded at 520 nm; the full lines represent the second-order best fittings of the experimental data.

Table 1. Second-Order Decay Parameters of (Bu$_2$S)$_2$$^{\bullet+}$ and PhSMe$^{\bullet+}$ Sensitized by NMQ$^+$ and DCA in N$_2$- and O$_2$-Saturated MeCN

			k_2/ϵ (10^6 s^{-1} cm)	
compd	sensitizer	cosensitizer	N$_2$	O$_2$
Bu$_2$S	NMQ$^+$		2.9	4.7
	NMQ$^+$	toluene	2.3	4.9
PhSMe	NMQ$^+$		3.5	12
	NMQ$^+$	toluene	4.0	13
Bu$_2$S	DCA	biphenyl		7.2
PhSMe	DCA			16
	DCA	biphenyl		19

absorption at 510 nm, reasonably assigned to the (Bu$_2$S)$_2$$^{+\bullet}$ dimer,[35] formed just after the laser pulse. The decay kinetics recorded in the 400−700 nm range were well fitted by second-order laws (see Table 1 for the k_2/ϵ values recorded at 530 nm). In the presence of molecular oxygen, the absorption maximum was blue-shifted by 15 nm (λ_{max} = 510 nm) and the tail in the 400 nm region was less pronounced (Figure 1b); these changes are in agreement with an efficient quenching of NMQ$^\bullet$ (which no longer contributes to the absorption spectra) by molecular oxygen. Even under these experimental conditions, the decay kinetics were well fitted by a second-order law (see Figure 1b inset and Table 1 for the k_2/ϵ values recorded at 510 nm).

The time-resolved absorption spectra recorded in the presence of PhSMe appear to be much more complex, due to the presence of three bands centered at 380, 530, and 780 nm (Figure 2a) in N$_2$-saturated solution. These spectra are due to the concomitant presence of NMQ$^\bullet$ (λ_{max} = 550 nm), PhSMe$^{+\bullet}$ monomer (λ_{max} = 520 nm),[36] and (PhSMe)$_2$$^{+\bullet}$ dimer (λ_{max} = 780 nm)[36] formed within the laser pulse. In O$_2$-saturated solution, where NMQ$^\bullet$ is efficiently quenched, the absorption spectra show λ_{max} at 520 and 780 nm (Figure 2b). Analogously to the case of Bu$_2$S, the

(35) In water, a λ_{max} value of 495 nm has been reported. Göbl, M.; Bonifacic, M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1984**, *106*, 5984−5988.
(36) Yokoi, H.; Hatta, A.; Ishiguro, K.; Sawaki Y. *J. Am. Chem. Soc.* **1998**, *120*, 12728−12733.

transients recorded under the different experimental conditions decay by second-order kinetics and the rate parameters are the same at 520 and 780 nm (Figure 2b inset and Table 1).
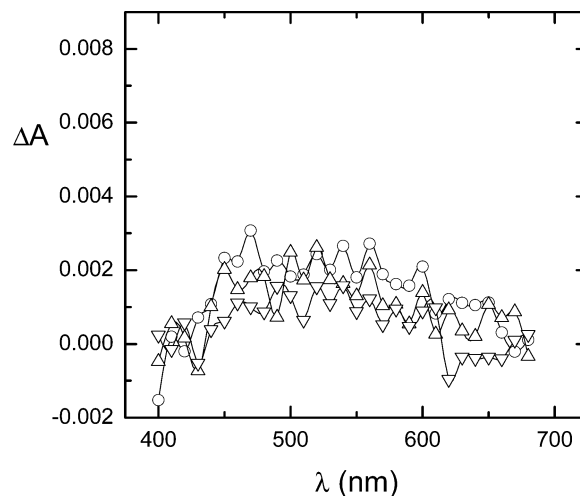
Flash photolysis experiments were also performed in the presence of toluene, which was used as a cosensitizer to reduce the efficiency of the back-electron-transfer process and, consequently, to increase the concentration of the transients formed within the laser pulse.[18] For both the sulfides, the time-resolved absorption spectra (Supporting Information: Figures S1 and S2), the decay order and rate constants were the same as in the absence of toluene (see Table 1 for the rate parameters). The only difference observed in the presence of toluene was the expected enhancements of the signals.

The observation that the fluorescence of NMQ$^+$ is quenched by O$_2$ with an efficiency that is only 3−5 times smaller than that with sulfides (vide infra) made it necessary to investigate if such a quenching was associated with the production of ^{1}O$_2$. Indeed, this was the case because, upon 355 nm irradiation, the luminescence emission of ^{1}O$_2$, sensitized by NMQ$^+$ in O$_2$-saturated MeCN, was observed and recorded at 1270 nm. The recorded signal was assigned to the emission of ^{1}O$_2$ because (a) it is formed within the time resolution of the experimental setup, (b) its decay follows first-order kinetic with a lifetime close to that already reported for ^{1}O$_2$ in MeCN (~50 μs),[37] (c) its intensity increases with the molecular oxygen concentration, and (d) it disappears in N$_2$-saturated solution and in the absence of NMQ$^+$. Thus, it appears that electronic excited states of NMQ$^+$ are able to induce the formation of ^{1}O$_2$ with high efficiency. A limiting value of 2.0 for the singlet oxygen yield (ϕ_Δ) was determined as reported in Supporting Information. This value suggests decay pathways 3 and 4 of the NMQ$^+$ excited states (similar to those reported for DCA excited states), which should occur with a very high efficiency (ca. 1).
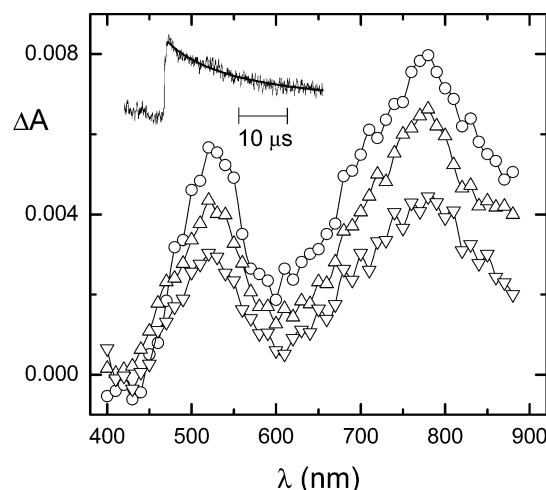
$$^1NMQ^{+}* + \, ^3O_2 \rightarrow \, ^3NMQ^{+}* + \, ^1O_2 \qquad (3)$$

$$^3NMQ^{+}* + \, ^3O_2 \rightarrow NMQ^{+} + \, ^1O_2 \qquad (4)$$

The high efficiency of path 3 is in line with an energy gap between ^{1}NMQ$^+$* and ^{3}NMQ$^+$* (ca. 21 kcal/mol),[38] which practically corresponds to the ^{1}O$_2$ energy (23 kcal/mol) if one takes into account the experimental errors. Furthermore, the results are also in agreement with a negligible S$_1$ → T$_1$ intersystem crossing for ^{1}NMQ$^+$* in the absence of additives, as also shown by the fluorescence quantum yield of 0.85 reported for air-equilibrated MeCN solution of NMQ$^+$, where about 16% of singlet NMQ$^+$* is quenched by molecular oxygen (Table S1). The ^{1}O$_2$ lifetime was reduced by both Bu$_2$S and PhSMe with rate constants, measured by Stern−Volmer plots, of 2.9 × 10^7 and 8.2 × 10^6 M^{-1} s^{-1}, respectively. It should also be noted that in the presence of 1 M toluene (cosensitizer), the ^{1}O$_2$ luminescence disappeared completely even in O$_2$-saturated solutions, due to the highly efficient quenching of singlet NMQ$^+$* by the cosensitizer.

Laser Flash Photolysis Experiments with DCA. For the DCA/Bu$_2$S and DCA/PhSMe systems, time-resolved absorption

Figure 3. Time-resolved absorption spectra of the DCA/Bu$_2$S system (1.0 × 10^{-4} and 2.1 × 10^{-2} M, respectively) in O$_2$-saturated MeCN recorded 1.3 (○), 7.2 (△), and 16 μs (▽) after the laser pulse (λ_{exc} = 355 nm).

Figure 4. Time-resolved absorption spectra of the DCA/PhSMe system (1.0 × 10^{-4} and 2.4 × 10^{-2} M, respectively) in O$_2$-saturated MeCN recorded 0.56 (○), 5.5 (△), and 16 μs (▽) after the laser pulse (λ_{exc} = 355 nm). Inset: decay kinetics recorded at 520 nm.

spectra and decay kinetics were obtained in O$_2$-saturated MeCN solutions. No evidence for the formation of radical cations was obtained with Bu$_2$S, as no significant signal at 510 nm for (Bu$_2$S)$_2$$^{+•}$ is observed in the spectrum (Figure 3). In contrast the time-resolved spectrum for PhSMe (Figure 4) was similar to that found with NMQ$^+$, showing the presence of PhSMe$^{+•}$ (λ_{max} = 520 nm) and (PhSMe)$_2$$^{+•}$ (λ_{max} = 780 nm). The decay of the band at 520 nm followed second-order kinetics (see inset) with a k_2/ϵ value quite close to that obtained with NMQ$^+$ (Table 1), which supports the hypothesis that the decay is presumably due to the reaction of the monomer radical cation (the most reactive species) with O$_2$$^{-•}$.

Further experiments were also carried out in the presence of biphenyl (BP) as a cosensitizer to reduce the efficiency of the back-electron-transfer process and, consequently, to increase the concentration of the transients formed within the laser pulse.[39] Under these conditions, formation of the radical cations was observed also with Bu$_2$S (Figure 4S, Supporting Information).

(37) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663−1021.
(38) Probably, the actual value of the singlet−triplet energy gap for NMQ$^+$* is slightly higher than that (20.6 kcal/mol) reported in the literature. Abraham, W.; Glänzel, A.; Stösser, R.; Grummt, U. W.; Köppel, H. *J. Photochem. Photobiol.* **1990**, *51*, 359−370.

(39) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663−664.

Table 2. Photooxygenation of Bu_2S and PhSMe Sensitized by NMQ^+ in O_2-Saturated MeCN[a]

			products after 10 min of irradiation (μmol)[b]	
entry	substrate (M)	additive (M)	sulfoxide	disulfide
1	PhSMe (0.01)		8.8	c
2	PhSMe (0.01)[d]		38	c
3	PhSMe (0.01)	BQ (2.5×10^{-3})	c	c
4	Bu_2S (0.01)		4.0	0.18
5	Bu_2S (0.1)		8.0	0.28
6	Bu_2S (0.01)[e]	Toluene (1)	2.1	0.06
7	Bu_2S (0.01)[f]	BQ (2.5×10^{-3})	c,g	c

[a] Volume: 4 mL. In all cases, the sensitizer concentration was 0.2 mM. [b] Determined by GC analysis. [c] Not detected ($<5 \times 10^{-3}$ μmol). [d] Irradiation time: 60 min. [e] Irradiation time: 90 s. [f] $[NMQ^+] = 2 \times 10^{-3}$ M, irradiation time 2 min. [g] Traces of butyl sulfoxide, probably due to some photosulfoxidation sensitized by BQ, were observed.

Table 3. Photooxygenation of Bu_2S and PhSMe Sensitized by DCA in O_2-Saturated MeCN[a]

			products after 10 min of irradiation (μmol)[b]		
entry	substrate (M)	additive (M)	sulfoxide	sulfone	disulfide
1	PhSMe (0.01)		6.8	c	c
2	PhSMe (0.01)	BQ (2.5×10^{-3})	c	c	c
3	Bu_2S (0.01)[d]	BP (0.5)	20[e]	c	1.6
4	Bu_2S (0.01)	BQ (2.5×10^{-3})	21	0.5	2.0
5	Bu_2S (0.1)	BQ (2.5×10^{-3})	6.4	0.12	0.7
6	Bu_2S (0.01)		18	0.95	2.5
7	Bu_2S (0.02)		13	0.4	1.8
8	Bu_2S (0.03)		9.1	0.4	1.2
9	Bu_2S (0.06)		8.2	0.25	0.9
10	Bu_2S (0.1)		8.9	0.25	0.8

[a] Volume: 4 mL. In all cases, the sensitizer concentration was 0.2 mM. [b] Determined by GC analysis. [c] Not detected ($<5 \times 10^{-3}$ μmol). [d] Irradiation time: 5 min. [e] Determined by ^{1}NMR analysis.

Figure 5. Sulfoxide (μmol) formed after 10 min of irradiation of solutions vs the initial concentration (M) of Bu_2S (●) or PhSMe (○).

Accordingly, two absorptions were detected in the 400–750 nm range. The short-lived transient, which absorbs in the 600–750 nm region and decays within 100 ns after the laser pulse, is assigned to $BP^{+\bullet}$, while the broad band centered at 510 nm, present at longer delay times, is assigned to the $(Bu_2S)_2^{+\bullet}$ dimer.[35] The longer component of the decay kinetics recorded in the 450–650 nm range was well fitted by second-order laws (see Table 1 for the k_2/ϵ values recorded at 510 nm).

With PhSMe, the absorption spectra recorded after the decay of $BP^{+\bullet}$ exhibited the same bands for the monomer and dimer radical cations observed in the absence of BP (Figure S5, Supporting Information). These transients decayed by second-order kinetics and rate parameters that do not change with the wavelength of analysis. The k_2/ϵ value recorded at 520 nm (Table 1) was practically the same as in the absence of BP.

Quenching of Fluorescence. The fluorescence of $^1NMQ^{+*}$ was quenched in deareated MeCN by both Bu_2S and PhSMe. The quenching rate constants were determined by the Stern–Volmer plots with the lifetime of $^1NMQ^{+*}$ of 20 ns.[40] The values are 1.8×10^{10} M^{-1} s^{-1} (Bu_2S) and 2.4×10^{10} M^{-1} s^{-1} (PhSMe). Quenching of $^1NMQ^{+*}$ by O_2 was also very efficient occurring with a rate constant of 5.9×10^9 M^{-1} s^{-1}. The Stern–Volmer plots provided quenching rate constants of 8.9×10^9 M^{-1} s^{-1} with PhSMe and 1.7×10^{10} M^{-1} s^{-1} with Bu_2S, taking 15.3 ns as the lifetime of $^1DCA^{*}$.[17] Quenching of $^1DCA^{*}$ with $^3O_2$ was also measured. The quenching rate constant was 6.8×10^9 M^{-1} s^{-1}.
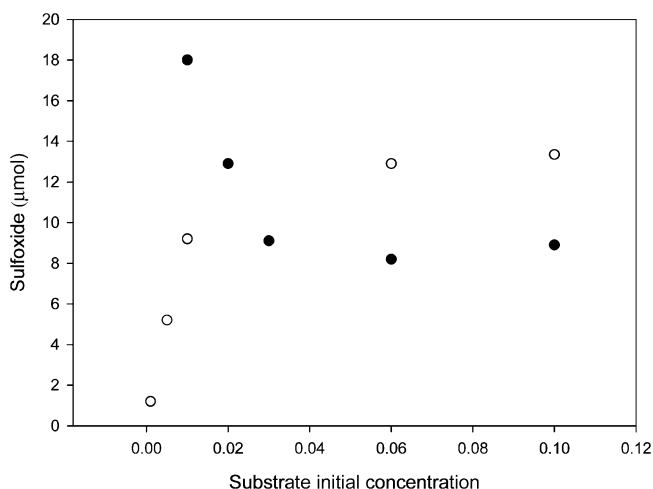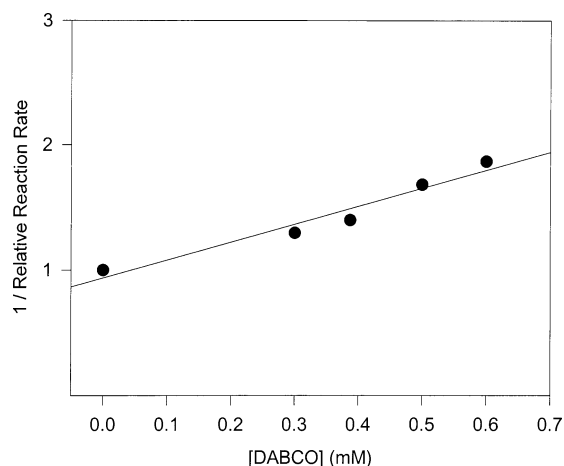
Steady-State Photolysis. Steady-state photolysis of Bu_2S and PhSMe, sensitized by NMQ^+ or DCA in oxygen-saturated MeCN, was carried out as described in the Experimental Section. The sensitizer was used in catalytic amounts (0.2–2%) with respect to the substrate (0.01–0.1M) and was not consumed during the run. No reaction was observed in the absence of sensitizer. Generally, short (10 min) reaction times were used in order to minimize any possible overoxidation. In all cases, the reaction products (comparison with authentic specimens) were determined and quantitated by GC, HPLC, and GC-MS. The results for the reactions with NMQ^+ are reported in Table 2, and those for the reactions with DCA are reported in Table 3.

Looking first at the data in Table 2, we find that the NMQ^+-sensitized photooxygenation of PhSMe leads exclusively to the

(40) Fukuzumi, S.; Fujita, M.; Noura, S.; Ohkubo, K.; Suenobu, T. Araki, Y.; Ito, O. *J. Phys. Chem. A* **2001**, *105*, 1857–1868.

corresponding sulfoxide, even when irradiation times as long as 60 min were used (entries 1 and 2 in Table 2). With Bu_2S, however, formation of Bu_2SO was accompanied by that of small amounts of Bu_2S_2 (Table 2, entries 4 and 5). When toluene 1 M was added as cosensitizer the reaction increased in efficiency (compare entry 4 with entry 6 in Table 2, taking the different reaction times into account). Photosulfoxidation was suppressed in the presence of benzoquinone (BQ), as shown by entries 3 and 7 in Table 2.

More peculiar results were obtained with DCA as the sensitizer (Table 3). With PhSMe, exclusive formation of PhS(O)Me is again observed, but with Bu_2S, the formation of Bu_2SO and Bu_2S_2 is accompanied by that of Bu_2SO_2 (Table 3, entries 4–10). Interestingly, Figure 5 also shows that PhSMe and Bu_2S exhibit opposite behaviors with respect to the effect of sulfide initial concentration. The relative rate of product formation increases by increasing the concentration of PhSMe but decreases with increasing concentration of Bu_2S (Figure 5). Thus, at 0.06 M concentration of sulfide, the photosulfoxidation of PhSMe is more efficient than that of Bu_2S; the reverse occurs when the sulfide concentration is 0.01 M (compare entries 1 and 6 in Table 3). Likewise, the products quantum yields (Φ) increased from 0.051 to 0.065 with the increase of the concentration of PhSMe from 0.01 to 0.05 M, whereas, with Bu_2S, Φ decreased from 0.11 to 0.057 for the same variation in sulfide concentration.

Figure 6. Reciprocal of the relative rate of dibutyl sulfoxide formation vs DABCO concentration ($r^2 = 0.95$) in the DCA-sensitized photooxidation of Bu$_2$S in oxygen-saturated MeCN at 25 °C.

Table 4. Photooxygenation of PhSMe and Bu$_2$S in the Presence of Ph$_2$SO[a]

entry	substrate (M)	sensitizer	[Ph$_2$SO] (M)	[sulfoxide]/[Ph$_2$SO$_2$][b]
1	PhSMe (0.01)	NMQ$^+$	0.05	c
2	Bu$_2$S (0.01)	NMQ$^+$	0.05	c
3	PhSMe (0.01)	DCA	0.05	c
4	Bu$_2$S (0.01)	DCA	0.05	8.3
5	Bu$_2$S (0.01) + BP[d]	DCA	0.05	66
6	Bu$_2$S (0.01)	DCA	0.1	5.1
7	Bu$_2$S (0.01)	DCA	0.02	17.6
8	Bu$_2$S (0.05)	DCA	0.05	8.5

[a] Irradiation time was 10 min if not otherwise indicated. Volume: 4 mL. In all cases, the sensitizer concentration was 0.2 mM. [b] Molar ratio between the sulfoxide of the substrate and Ph$_2$SO$_2$. [c] Ph$_2$SO$_2$ was not detected. [d] BP 0.5 M, irradiation time: 5 min.

Some experiments were carried out in the presence of benzoquinone (BQ). Under these conditions, the PhSMe sulfoxidation was completely suppressed (Table 3, entry 2), while that of Bu$_2$S was hardly affected when the concentration of the substrate was 0.01 M and underwent a small decrease in the product yield at [Bu$_2$S] = 0.1M (Table 3, entries 4 and 5). The photooxygenation of Bu$_2$S was also studied in the presence of DABCO, a well-known trap of ^{1}O$_2$.[16] It was found that the yield in Bu$_2$SO decreased by increasing the DABCO concentration. A linear plot was obtained between the reciprocal of the relative rate of sulfoxidation and the DABCO concentration, which is displayed in Figure 6.

With both NMQ$^+$ and DCA, some experiments were carried out in the presence of Ph$_2$SO as a cosubstrate. The results reported in Table 4 indicate that cooxidation of Ph$_2$SO with formation of Ph$_2$SO$_2$ takes place only in the DCA-sensitized photooxygenation of Bu$_2$S.

Discussion

Laser Photolysis Experiments. The LFP experiments clearly showed that, in agreement with previous results,[18] NMQ$^+$ is an excellent ET sensitizer, capable of efficiently promoting the formation of radical ions from aliphatic and aromatic sulfides even in the absence of a cosensitizer. Such a high efficiency is certainly related to the high reduction potential of ^{1}NMQ^{+*} as well as to the already mentioned fact that excited NMQ$^+$ reacts with the substrate to produce a neutral radical/radical cation

pair whose separation is facilitated by the lack of any electrostatic barrier.[18]

DCA is less efficient than NMQ$^+$ in promoting formation of radical ions from sulfides, although the DCA fluorescence, as that of NMQ$^+$, is quenched by both PhSMe and Bu$_2$S at a diffusion-controlled rate. ^{1}DCA* induced radical ion formation only with PhSMe. With Bu$_2$S, radical ions were observed only in the presence of BP as the cosensitizer.

Interestingly, when radical cations were formed, their decay was found to follow strict second-order kinetics in the presence of oxygen, which is a strong indication of a reaction of the radical cation with O$_2^{-\bullet}$, formed by the very fast reaction of NMQ$^\bullet$ or DCA$^{-\bullet}$ with O$_2$ (eq 5).[18,41] The reduction potential of DCA ($E°_{DCA/DCA^{-\bullet}} = -0.98$ V vs SCE)[14] is slightly more negative than that of O$_2$ ($E°_{O_2/O_2^{-\bullet}} = -0.87$ V vs SCE).[42] The reduction potential (vs SCE) of NMQ$^+$ is -0.85 V,[19] but the reaction with O$_2$ is still slightly exergonic after correction for the electrostatic factor (0.06 eV).[43]

$$NMQ^\bullet(DCA^{-\bullet}) + O_2 \rightarrow NMQ^+(DCA) + O_2^{-\bullet} \quad (5)$$

In view of the relatively small quantum yield observed (for PhSMe, Φ is 0.15 with NMQ$^+$ and 0.06 with DCA), it seems that back electron transfer is a major process with both sensitizers but, as expected, more with DCA than with NMQ$^+$. However, it should be considered that the relatively low quantum yields may also be due to an electron-transfer process between the sulfide radical cation and O$_2^{-\bullet}$, which competes with radical coupling.

Photooxygenation Reactions: Reactions with NMQ$^+$. An ET mechanism (Scheme 2) seems very likely for the photooxygenation of PhSMe and Bu$_2$S sensitized by NMQ$^+$ on the basis of the LFP experiments that have indicated formation of radical ions both in the presence and in the absence of a cosensitizer. The fact that only catalytic amounts of sensitizer (0.2–2% with respect to the substrate) were necessary is further support for the occurrence of reaction 5, a key step in this mechanism (Scheme 2). However, the previously unreported observation that NMQ$^+$ is also efficiently quenched by oxygen, producing ^{1}O$_2$ with a high quantum yield, makes it necessary to assess if and to what extent ^{1}O$_2$ might contribute to the sulfoxidation of our substrates. Reasonably, a contribution of ^{1}O$_2$ in the photosulfoxidation of PhSMe can be considered negligible in view of the very low efficiency of ^{1}O$_2$-promoted sulfoxidation of this substrate (several hours are required to form few percent of sulfoxide).[10,44] Moreover, at variance with our results (exclusive formation of sulfoxide), significant formation of the sulfone was observed in authentic ^{1}O$_2$ photooxygenation of PhSMe.[10] Additional strong support for the conclusion that the ET mechanism is operating in the NMQ$^+$-sensitized photosulfoxidation of PhSMe was obtained by carrying out the photolysis in the presence of benzoquinone (BQ, $E_{red} = -0.51$ V vs SCE),[45] which has been reported to be a very efficient

(41) Actually, in some experiments with air-saturated solutions, i.e., with a smaller oxygen concentration, it was possible to detect a very fast component (lifetime about 150 ns) in the early portion of the decay of the absorption at 550 nm, attributable to reaction 5.
(42) Sawyer, D. T.; Chiericato, G., Jr.; Angelis, C. T.; Nanni, E. J., Jr.; Tsuchiya, T. *Anal. Chem.* **1982**, *54*, 1720–1724.
(43) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.
(44) PhSMe (0.01 M) showed to be unreactive after 10 min of irradiation in the presence of rose bengal (0.2 mM) at 400–600 nm.

trap for $O_2^{-\bullet}$ and should also trap $NMQ^{\bullet}$.[46] As shown in Table 2, entry 3, the formation of sulfoxide was completely suppressed.

An ET mechanism can also be safely assigned to the NMQ^+-sensitized photooxygenation of Bu_2S, although this sulfide undergoes a very fast sulfoxidation by $^1O_2$ (20% of sulfoxide after 1 min of irradiation!). Again, this conclusion is supported by the fact that no photosulfoxidation of Bu_2S took place when the photolysis was run in the presence of BQ (Table 2, entry 7). Moreover, when the photolysis was carried out in the presence of 1 M toluene (T) as a cosensitizer, that is, under conditions where the possibility of an intervention of $^1O_2$ should be excluded and an ET mechanism should certainly hold, only Bu_2SO was formed, accompanied by very small amounts of Bu_2S_2. No formation of the sulfone Bu_2SO_2 was observed. The outcome was therefore the same as that of the photolysis performed in the absence of toluene (however, the latter process was less efficient, as already mentioned) and somewhat different from that found in $^1O_2$ photooxygenations, where formation of Bu_2SO_2 always accompanies that of Bu_2SO and Bu_2S_2 either with rose bengal[47] or with tetraphenylporphyrin[13] as the sensitizer.

Thus, there is little doubt that the ET mechanism is operating also in the NMQ^+-sensitized photosulfoxidation of Bu_2S in MeCN, at least in the 0.01–0.1 M substrate concentration range. The small amounts of disulfide observed in this process might reasonably derive from a partial α-CH deprotonation of the intermediate sulfide radical cation, a well-known reaction of these species.[48]

Reactions with DCA. The DCA-sensitizited photosulfoxidation of PhSMe is also occurring by an ET mechanism, as shown by the fact that this reaction is also completely suppressed in the presence of BQ (Table 3, entry 2), a well recognized trap also for $DCA^{-\bullet}$.[46] This conclusion is in line with the LFP results showing that DCA can produce PhSMe radical cations even in the absence of a cosensitizer.

A drastically different situation, however, holds in the photooxidation of Bu_2S, where instead a fundamental role of $^1O_2$ is clearly indicated by a number of results. First, the rate of Bu_2SO formation decreases by increasing the concentration of Bu_2S, as clearly shown by the plot in Figure 5. A reasonable explanation is possible if the sulfoxide mainly comes from the reaction of Bu_2S with $^1O_2$. Accordingly, by increasing Bu_2S concentration, more $^1DCA^*$ is quenched by the sulfide ($k_q = 1.7 \times 10^{10}$ M^{-1} s^{-1}) than by O_2 so that less $^1O_2$ is formed. Implicitly, this observation also indicates that the quenching of $^1DCA^*$ by Bu_2S does not lead to significant products formation, at least at concentrations of Bu_2S < 0.1 M. This is in agreement with LFP experiments that demonstrated no appreciable radical ion formation in the $DCA-Bu_2S$ system, in the absence of a cosensitizer.[49] On the contrary, with PhSMe, the relative sulfoxidation rate was found to increase by increasing the

concentration of the substrate (Figure 5), thus clearly suggesting that the two sulfides react by different mechanisms: ET with PhSMe and singlet oxygen with Bu_2S.

Further, albeit indirect, proof in favor of the role of $^1O_2$ in the DCA-sensitized photooxygenation of Bu_2S is that addition of BQ (a trap for both $DCA^{-\bullet}$ and $O_2^{-\bullet}$)[46] does not substantially modify the sulfoxide yield for $[Bu_2S] = 0.01$ M (in fact, a slight increase is observed) and only decreases the yield slightly for $[Bu_2S] = 0.1$ M. Again, these findings have to be compared with the already mentioned complete suppression of photosulfoxidation for the case of PhSMe.

Finally, addition of DABCO, which is a very effective trap for $^1O_2$,[16] decreases the photosulfoxidation rate of Bu_2S (Figure 6). From the linear plot between the reciprocal of the photosulfoxidation rate and DABCO concentration, it is possible to calculate the rate of $^1O_2$ quenching by DABCO in MeCN by taking 2.9×10^7 M^{-1} s^{-1} as the rate constant for the reaction of $^1O_2$ with Bu_2S.[16] A value of 4.2×10^8 M^{-1} s^{-1} was obtained, very close to the values (from 4.0 to 5.5×10^8 M^{-1} s^{-1}) reported in the literature.[16,37]

The observation that the behaviors of DCA are different from those of NMQ^+ with respect to the mechanism of the photooxygenation of Bu_2S (singlet oxygen with the former and ET with the second), whereas the fluorescence of both sensitizers is quenched by Bu_2S at a diffusion-controlled rate and by O_2 (with production of $^1O_2$), at a rate that is not much slower, deserves some comment. A possible explanation is certainly that the ET process is more efficient with NMQ^+ than with DCA (with the former sensitizer the ET is much more exergonic [by ca. 0.8 V], and moreover, back-electron transfer is less competitive, as also clearly shown by LFP experiments.[18,19] Thus, with NMQ^+, Bu_2S is probably oxidized by ET more rapidly than it reacts with $^1O_2$, whereas the reverse may hold for DCA. In addition, sulfides have the capacity to promote $^1DCA^* \rightarrow {}^3DCA^*$ intersystem crossing (isc), presumably through a CT complex.[50] This means that quenching of $^1DCA^*$ by Bu_2S may only partially suppress the production of $^1O_2$, in view of the high efficiency of reaction 2. With $^1NMQ^{+*}$, Bu_2S-enhanced isc might be relatively less important than with DCA due to the much larger exergonicity of the ET process with the former sensitizer. Thus, the $Bu_2S/^1NMQ^{+*}$ CT complex, once formed, might have a much larger tendency than the $Bu_2S/^1DCA^*$ complex to evolve into a radical couple rather than undergoing isc.

Is a Persulfoxide Involved in ET Photooxygenations? The results discussed above allowed us to conclude with reasonable certainty that the NMQ^+- and DCA-sensitized photosulfoxidations of PhSMe occur by an ET mechanism. With Bu_2S, instead the two sensitizers behave very differently: NMQ^+ promotes an ET photooxygenation, whereas DCA promotes a singlet oxygen photooxygenation. In addition, these results also showed that photooxidation sensitized by NMQ^+ and $^1O_2$ photooxidations led to somewhat different product distributions; in particular, the formation of sulfone appears to be a peculiar outcome of singlet oxygen photooxidation, while it is never observed in ET photosulfoxidations. Such an observation is not in line with the mechanisms illustrated in Schemes 1 and 2, which contemplate the same key reaction intermediate, namely,

(45) Fox, M. A., Chanon, M., Eds. *Photoinduced Electron Transfer*; Elsevier: 1988; Part A, p 475.

(46) Manring, L. E.; Kramer, M. K.; Foote, C. S. *Tetrahedron Lett.* **1984**, *25*, 2523–2526.

(47) Photooxygenation of 4 mL of a solution of 0.01 M Bu_2S in the presence of rose bengal at 400–600 nm led to the formation of Bu_2SO (6.3 μmol), Bu_2S_2 (0.22 μmol), and Bu_2SO_2 (0.09 μmol).

(48) Asmus, K.-D. In *Sulfur Centered Intermediates in Chemistry and Biology*; Chatgilialoglu, C. K.-D., Asmus, K.-D., Eds.; Plenum Press: New York, 1990; Nato Asi Series, pp 155–172.

(49) Quenching is probably related to the formation of a CT complex that does not proceed further towards radical ion formation.

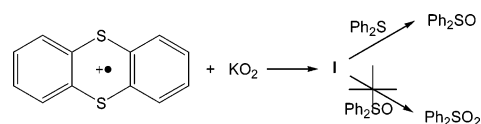(50) Manring, L. E.; Gu, C.-L.; Foote, C. S. *J. Phys. Chem.* **1983**, *87*, 40–44.

the persulfoxide **1**. Thus, the same products should be expected in $^1O_2$ and ET sulfoxidations.

In $^1O_2$ photooxidations, important evidence in favor of the intermediacy of **1** has come from trapping experiments with diphenyl sulfoxide (Ph$_2$SO);[2,4,9,51] namely, when a dialkyl sulfide is photooxidized in the presence of diphenyl sulfoxide (Ph$_2$SO) in aprotic solvents, the formation of diphenyl sulfone (Ph$_2$SO$_2$) is observed. Since Ph$_2$SO does not react with singlet oxygen, the formation of the sulfone is reasonably attributed to the reaction with **1**. Interestingly, **1** is not trapped by the sulfide in agreement with its expected nucleophilic behavior. Convincing experimental evidence supporting the nucleophilicity of **1** is also available.[52,53] Thus, we felt it appropriate to test our photooxygenations also with respect to trapping experiments with Ph$_2$SO.

First, the DCA-sensitized photoreaction of Bu$_2$S was studied in order to check if this reaction exhibits the same behavior of bona fide singlet oxygen photooxygenations with respect to the cooxidation of Ph$_2$SO. The results, reported in Table 4, clearly indicate that this is actually the case, as significant amounts of Ph$_2$SO$_2$ were formed (no Ph$_2$SO$_2$ is formed in the absence of Bu$_2$S). Moreover, we found that the product ratio Bu$_2$SO/Ph$_2$SO$_2$ was almost the same at different sulfide initial concentrations (compare entries 4 and 8), which indicates that, as expected, the reaction intermediate is trapped by Ph$_2$SO but not by Bu$_2$S.[9] Clearly, in this respect, the behaviors of the DCA-sensitized photosulfoxidation of Bu$_2$S fully conform to those expected for a singlet oxygen photooxygenation. However, as shown by the results in Table 4 (entries 1 and 2), cooxidation of Ph$_2$SO was never observed in the ET photooxidation of either PhSMe or Bu$_2$S with NMQ$^+$, or of PhSMe with DCA (Table 4, entry 3). Clearly, at variance with what was observed in $^1O_2$ photooxidations. Consequently, it does not seem that a nucleophilic species capable of capture by Ph$_2$SO is formed in ET photooxygenations. A very nice confirmation of this conclusion comes from the observation that the cooxidation of Ph$_2$SO in the DCA-sensitized photooxygenation of Bu$_2$S is drastically reduced when the photolysis is performed in the presence of 0.5 M BP, that is, under conditions where, as also shown by LFP experiments, an (indirect) ET mechanism should operate (Table 4, entry 5). The fact that Ph$_2$SO is cooxidized with Bu$_2$S in the absence of BP, but not in its presence, is a very important result since it clearly demonstrates that the intermediate formed in the ET process (Scheme 2) *cannot* have the same structure as that formed in the singlet oxygen photooxygenation. Accordingly, the latter is able to oxidize Ph$_2$SO, whereas the former is not.

According to the mechanism of ET photooxygenation reported in Scheme 2, **1** should be formed by the reaction of the sulfide radical cation with O$_2$$^{-\bullet}$ (Scheme 2, step d); thus, further information in this respect can be provided from studies of the reactions of stable sulfur radical cations with O$_2$$^{-\bullet}$. It was therefore considered useful to reinvestigate the reaction of thianthrene radical cation (Th$^{+\bullet}$) and KO$_2$ already studied by Ando and his associates[54] in MeCN. In full agreement with Ando's study, it was found that this reaction forms thianthrene and thianthrene sulfoxide (ThO) and that, in the presence of

(51) Gu, C.-L.; Foote, C. S.; Kacher, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 5949–5951.
(52) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947–5948.
(53) Akasaka, T.; Haranaka, M.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 9898–9900.
(54) Ando, W.; Kabe, Y.; Kobayashi, S.; Takyu, C.; Yamagishi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4526–4528.

Scheme 3

Ph$_2$S, substantial formation of Ph$_2$SO is observed. Since Ph$_2$S does not react with KO$_2$, this result clearly indicates that an intermediate capable of oxidizing Ph$_2$S is formed. However, when we carried out the reaction between Th$^{+\bullet}$ and KO$_2$ in the presence of Ph$_2$SO or PhS(O)Me (both unreactive toward KO$_2$), no appreciable amounts of Ph$_2$SO$_2$ or PhS(O$_2$)Me, respectively, were formed.[55] Thus, the intermediate formed in the reaction of Th$^{+\bullet}$ with KO$_2$ is capable of oxidizing Ph$_2$S but *not* Ph$_2$SO (Scheme 3). It therefore seems unlikely that a nucleophilic persulfoxide is the species formed in this reaction and hence in step d of the ET mechanism (Scheme 2).

While the above results quite clearly indicate that a nucleophilic persulfoxide is an unlikely intermediate for ET sulfoxygenations of PhSMe and Bu$_2$S sensitized by NMQ$^+$, it is not simple to find a plausible alternative. At present, the only possible suggestion is that the intermediate in ET photosulfoxidations has the structure of a thiadioxirane (**3**) rather than of a persulfoxide. Accordingly, a thiadioxirane is a species with an electrophilic character and, therefore, with behavior consistent with the chemistry described above.

3
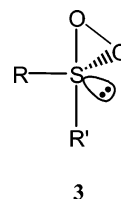
It should be noted, in this respect, that a thiadioxirane was also considered as a possible intermediate in $^1O_2$ photooxidations, but such a possibility was eventually discarded on the basis of calculations[11] showing that the kinetic barrier for the formation of thiadioxirane by reaction of singlet oxygen and sulfide is much higher than that for the formation of the persulfoxide and that the conversion of the latter into the former is also characterized by a high activation energy. However, a different situation might hold when we start from a radical cation or its dimer (species with much higher energy than the sulfide) and O$_2$$^{-\bullet}$; in this case, a thiadioxirane might become the species more easily formed. The results of theoretical calculations, presented below, provide a rationale for this hypothesis.

Theoretical Calculations. Theoretical calculations were performed to determine thermodynamics of the reaction of dimethyl sulfide radical cation, taken as a model system, with superoxide radical anion to form dimethyl persulfoxide **4** (path A in Scheme 4) and dimethyl thiadioxirane **5** (path B).

Table 5 shows that at the MP2/6-31+G(2d,p) level of theory, both the reactions are computed to be strongly exothermic ($\Delta H_{298}(A) = -156.9$ kcal/mol and $\Delta H_{298}(B) = -158.6$ kcal/

(55) Contrary to what was observed with Th$^{+\bullet}$, the reaction of dibenzodithiocin radical cation with KO$_2$ is reported to afford an intermediate that can oxidize PhS(O)Me. Akasaka, T.; Ando, W. *Terahedron Lett.* **1985**, *26*, 5049–5052. However, apart from the particular structure of this radical cation, it should be noted that in this reaction, $^1O_2$ should also form and some $^1O_2$ photooxidation could take place since dibenzodithiocin, differently than Th, is reactive towards $^1O_2$.

Table 5. Enthalpies^a (kcal/mol) for Formation of Dimethyl Persulfoxide **4** [ΔH_{298}(A)] and Dimethyl Thiadioxirane **5** [ΔH_{298}(B)] from Coupling of Me$_2$S$^{+\bullet}$ with O$_2^{-\bullet}$ along with the Activation Enthalpies [$\Delta H^{\#}_{298}$(DA) and $\Delta H^{\#}_{298}$(DB)] and Reaction Enthalpies [ΔH_{298} (DA) and ΔH_{298}(DB)] for Their Dissociation to Me$_2$S Plus ^{1}O$_2$ Computed at Different Levels of Theory

method	ΔH_{298}(A)	ΔH_{298}(B)	$\Delta H^{\#}_{298}$(DA)	$\Delta H^{\#}_{298}$(DB)	ΔH_{298}(DA)	ΔH_{298}(DB)
MP2/6-31+G(2d,p)	−156.9 (−47.8)	−158.6 (−48.7)	−0.5 (0.5)	9.9 (7.2)	−12.8 (−6.6)	−11.1 (−5.7)
QCISD/6-31+G(2d,p)	−153.5 (−43.9)	−151.2 (−44.9)	−0.7 (−0.2)	6.2 (6.2)	−12.8 (−7.3)	−15.1 (−6.3)
G3^b	−167.2	−167.6	−0.1	9.8	−3.0	−2.6

^{a} Enthalpies computed at the optimized structures taking into account the solvent effect (ϵ = MeCN) with the PCM method are reported in parentheses. Enthalpy corrections to the MP2 and QCISD total energies were estimated from frequency calculations at the MP2/6-31+G(d) level. ^{b} Geometries were optimized at the QCISD/6-31+G(2d,p) level and enthalpy corrections were estimated at the MP2/6-31+G(d) level (see Computational Details).

Scheme 4
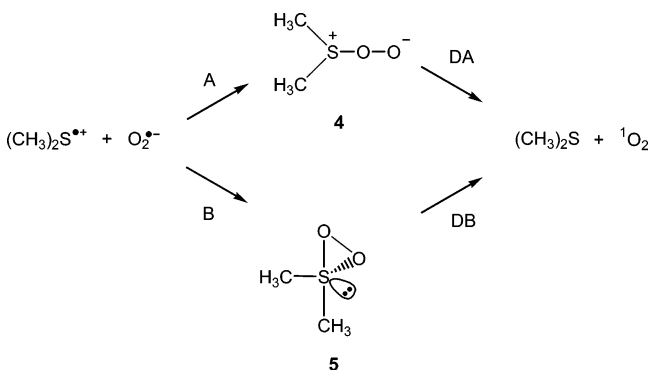
mol) in the gas phase. Exothermicity of both reactions does not change significantly by estimating electron correlation with the more reliable QCISD method and using a high accuracy energy method[56] such as G3.

Consequently, the reaction path for both reactions A and B cannot be computed since at any point of the energy surface an electron transfer from the superoxide radical anion to the sulfide cation occurs also using an unrestricted wave function. Spin-unrestricted calculations describe the reaction between the dimethyl sulfide and singlet oxygen previously studied at different level of theory with single-point spin-restricted calculations using MP2/6-31G(d)-optimized geometries.[11] Exothermicity decreases considerably if the effect of the solvent is taken into account in the calculations by means of the polarizable continuum model (PCM), being computed to be 47.8 and 48.7 kcal/mol for paths A and B, respectively, at the PCM(ϵ = MeCN)/MP2/6-31+G(2d,p)//MP2/6-31+G(2d,p) level. Exothermicity, however, remains large, so both coupling reactions should be controlled by diffusion. Indeed, a direct coupling between a radical cation and a radical anion, in the absence of steric effects, is expected to be a process without energy barrier so both intermediates should be formed.[57] Theoretical calculations performed on the dimethyl persulfoxide **4** and on the dimethyl thiadioxirane **5** at different levels of theory have provided contrasting results on their relative stability.[11,32,58] Preliminary calculations showed that the relative stability depends significantly on the equilibrium geometries. Hence the geometry of **4** and **5** were optimized with ab initio-correlated methods estimating electron correlation not only at the perturbative level (MP2) as in previous studies but also at the CI level (QCISD) and using a more flexible basis set (6-31+G(2d,p)).

(56) Other high-accuracy energy methods based on the Complete Basis Set model cannot be utilized since dimethyl persulfoxide was computed to be unstable (see Computational Details).
(57) A value of 2.3 × 10^{11} M^{-1} s^{-1} has been derived for the reaction of dimethyl sulfide radical cation with O$_2^{-\bullet}$ in H$_2$O. Miller, B. L.; Williams, T. D.; Schöneich *J. Am. Chem. Soc.* **1996**, *118*, 11014−11025.
(58) Shangguan, C.; McAllister, M. A. *THEOCHEM* **1998**, *422*, 123−132.

Table 5 shows that electron correlation improves the stability of **4**. In fact, **5** is more stable than **4** by 1.7 kcal/mol at the MP2/6-31+G(2d,p) level but less stable by 2.3 kcal/mol at the QCISD/6-31+G(2d,p) level, that is, using the same basis set. However, at a higher level of theory, **4** and **5** are nearly isoenergetic. G3 calculations predict **5** to be more stable than **4** by only 0.3 kcal/mol. Finally, **5** is predicted to be slightly more stable than **4** in solution. In conclusion, on the basis of these theoretical calculations, persulfoxide and thiadioxirane should be formed in approximately equal amounts in the coupling of the sulfide cation with the superoxide radical anion. However, the reactivity of these two intermediates could be influenced by their lifetime. In effect, the barrier to dissociation of **4** to form dimethyl sulfide plus singlet oxygen (reaction DA in Scheme 4) was previously computed to be very small (0.1 kcal/mol at the MP2/6-31G(d) level), whereas that of **5** was computed to be as large as 10.4 kcal/mol at the same level of theory.[11] Table 5 shows that this trend does not change optimizing geometries with MP2 and QCISD methods and a more flexible basis set as well as using the G3 model. Indeed, the transition-state structures resemble those previously obtained at the MP2/6-31G(d) level.[11] Importantly, the activation enthalpy for dissociation of **4** is very small and even slightly negative at the higher levels of theory (QCISD/6-31+G(2d,p) and G3). The solvent increases the activation enthalpy by about 1 kcal/mol, so the barrier to dissociation of **4** should be less than 1 kcal/mol. It was previously estimated, however, that **4** should be 16 kcal/mol more stable than Me$_2$S + ^{1}O$_2$ using MP2/6-31G(d) geometries, extrapolating energies to a complete basis set and taking into account solvent effects at the PCM(ϵ = acetone)/B3LYP/6-31G(d) level.[11] By contrast, Table 5 shows that **4** is less stable by about 6 kcal/mol in solution. This large discrepancy is due to the procedure in the energy extrapolation and to the use of a different solvent in the PCM calculations (about 5 kcal/mol). Furthermore, frequency calculations at the MP2/6-31+G(d) level show that the free energy contribution favors largely, as expected, the products (by 11.3 kcal/mol) and decreases slightly the barrier to dissociation (by 0.3 kcal/mol). Hence, **4** should dissociate in solution with a very small barrier. Thus, it is likely that the concentration of **4** is relatively small when formed by ^{1}O$_2$ and R$_2$S but sufficient to promote sulfoxidation. In contrast, reaction A is largely exothermic; hence, **4** is initially formed in vibrationally excited states, so it should immediately dissociate due to the very small vibrational frequency along the dissociation path. On the other hand, the barrier to dissociation of **5** is predicted to be about 7 kcal/mol larger than that of **4**, so its lifetime should be long enough to react with a sulfide as an electrophile, forming the corresponding sulfoxide.

Conclusion

NMQ$^+$ is a very efficient sensitizer in promoting the ET photooxygenation (Scheme 2) of aromatic (PhSMe) and aliphatic (Bu$_2$S) sulfides in MeCN, although excited NMQ$^+$ is capable of producing ^{1}O$_2$ in high yield. In the first place, laser photolysis experiments provided clear evidence that ^{1}NMQ^{+*} reacts with both substrates to form the sulfide radical cation and NMQ$^\bullet$. Additional support was provided by steady-state photooxygenations, showing that no sulfoxidation takes place in the presence of BQ, which is a trap for O$_2^{-\bullet}$ as well as for NMQ$^\bullet$. A different situation was found when DCA was the sensitizer, ET photooxygenation being observed only with PhSMe, but not with Bu$_2$S. Accordingly, whereas the former reaction was suppressed by BQ, the second was hardly affected. The involvement of ^{1}O$_2$ in the DCA-induced sulfoxygenation of Bu$_2$S was further supported by the finding that this reaction is slowed by DABCO (an efficient quencher of ^{1}O$_2$) and that the relative rate of formation of sulfoxide decreases by increasing the initial concentration of the sulfide. The DCA mechanistic dichotomy is in line with LFP experiments that showed that DCA can promote radical ion formation from PhSMe but not from Bu$_2$S. The present study has also allowed us to suggest that ET photosulfoxidations do not involve the same intermediate, a nucleophilic persulfoxide, proposed to be formed in ^{1}O$_2$ sulfoxidations in aprotic solvents. The first clue for this suggestion was the observation that the NMQ$^+$-sensitized photooxygenation of PhSMe and Bu$_2$S and the DCA-sensitized photooxygenation of PhSMe led to product distributions different from that found in ^{1}O$_2$ photooxygenations of the same substrates. In particular, formation of the sulfones is observed only in the reactions occurring by the latter mechanism. More important in this respect were the results of experiments, where Ph$_2$SO (a trap for the persulfoxide intermediate) was used as a cosubstrate. Formation of Ph$_2$SO$_2$ was observed, as expected, only in the DCA-sensitized photooxygenation of Bu$_2$S, that is, in a reaction suggested to be induced by ^{1}O$_2$. In the ET photooxygenations (NMQ$^+$ with Bu$_2$S and PhSMe and DCA with PhSMe), formation of Ph$_2$SO$_2$ was never observed.

Furthermore, the cooxidation of Ph$_2$SO observed in the DCA-sensitized photooxygenation of Bu$_2$S was almost suppressed when this reaction was carried out in the presence of BP, which induces an ET mechanism. Clearly, no nucleophilic character can be attributed to the intermediate formed in the ET photooxygenations. On the same line is the observation that the intermediate formed in the reaction of thianthrene radical cation with KO$_2$, a reaction that mimics step d of the ET mechanism of photooxygenation (Scheme 2), can oxidize Ph$_2$S but not Ph$_2$SO, that is, it shows electrophilic properties. Thus, for the intermediate involved in ET photooxygenations, a thiadioxirane (an electrophilic species) seems more in line with the observed chemistry. A rationale for this hypothesis has been provided by theoretical calculations that have shown that the reaction of a sulfide radical cation with O$_2^{-\bullet}$ is a strongly exergonic process with practically no activation energy. Thus, both the persulfoxide and the thiadioxirane might form in this process. However, the persulfoxide initially formed in vibrationally excited states should immediately dissociate due to the very small vibrational frequency along the dissociation path. On the other hand, the barrier to dissociation of the thiadioxirane is predicted to be about 7 kcal/mol larger, so the lifetime of this species should be long enough to allow it to react with a sulfide, forming the corresponding sulfoxide.

Supporting Information Available: Radical cation spectra obtained in laser photolysis experiments in the presence of cosensitizer, determination of singlet oxygen yields by ^{1}NMQ^{+*}, and total energies (MP2/6-31+G(2d,p), QCISD/6-31+G(2d,p), G3) and optimized geometries ((MP2/6-31+G(2d,p), QCISD/6-31+G(2d,p)) for the investigated species (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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