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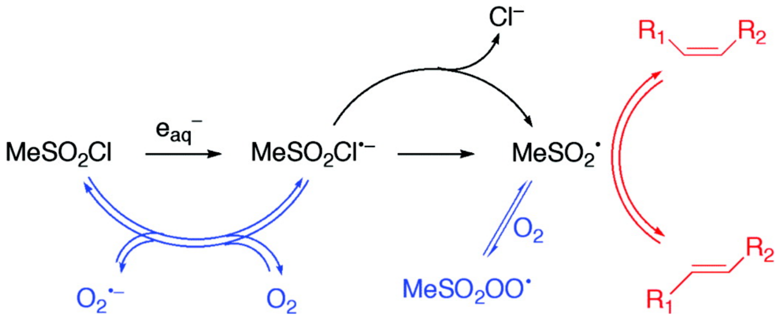

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One-Electron Reduction of Methanesulfonyl Chloride. The Fate of $MeSO_2Cl^{\bullet -}$ and $MeSO_2^{\bullet}$ Intermediates in Oxygenated Solutions and Their Role in the Cis−Trans Isomerization of Mono-unsaturated Fatty Acids

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Abstract: The one-electron reduction of methanesulfonyl chloride ($MeSO_2Cl$) leads, in the first instance, to an electron adduct $MeSO_2Cl^{\bullet -}$ which lives long enough for direct detection and decays into sulfonyl radicals $MeSO_2^{\bullet}$ and Cl^-, with $k = 1.5 \times 10^6$ s^{-1}. Both, $MeSO_2Cl^{\bullet -}$ and $MeSO_2^{\bullet}$ showed a similar absorption in the UV with λ_{max} of 320 nm. In the presence of oxygen, $MeSO_2Cl^{\bullet -}$ transfers an electron to O_2 and establishes an equilibrium with superoxide. The rate constant for the forward reaction was measured to 4.1×10^9 M^{-1} s^{-1}, while for the back reaction only an interval of 1.7×10^5 to 1.7×10^6 M^{-1} s^{-1} could be estimated, with a somewhat higher degree of confidence for the lower value. This corresponds to an equilibrium constant in the range of 2.4×10^3 to 2.4×10^4. With reference to $E°$ ($O_2/O_2^{\bullet -}$) = −155 mV, the redox potential of the sulfonyl chloride couple, $E°$($MeSO_2Cl/MeSO_2Cl^{\bullet -}$), thus results between being equal to −355 and −414 mV (vs NHE). $MeSO_2Cl^{\bullet -}$ reduces (besides O_2) 4-nitroacetophenone. The underlying electron transfer took place with $k = 1.5 \times 10^9$ M^{-1} s^{-1}, corroborating an $E°$ for the sulfonyl chloride couple significantly exceeding the above listed lower value. The $MeSO_2^{\bullet}$ radical added to oxygen with a rate constant of 1.1×10^9 M^{-1} s^{-1}. Re-dissociation of O_2 from $MeSO_2OO^{\bullet}$ occurred only very slowly, if at all, that is, with $k \ll 10^5$ s^{-1}. $MeSO_2^{\bullet}$ radicals can act as the catalyst for the cis−trans isomerization of several *Z*- and *E*-mono-unsaturated fatty acid methyl esters in homogeneous solution. The effectiveness of the isomerization processes has been addressed, and in the presence of oxygen the isomerization is completely suppressed.

Introduction

Sulfur-centered and sulfur-containing organic free radicals have received increasing attention in biological and biochemical mechanisms. The species of main interest in this context are thiyl radicals, $RS^{\bullet}$. In many studies this radical has been characterized as a very versatile species engaged in a variety of redox, addition, and abstraction reactions. $RS^{\bullet}$ have been identified as, for example, moderately good oxidants with $E°$ typically in the 1.0−1.4 V range. Their oxidative power is thus sufficient to oxidize, for example, Vit C, various phenothiazine drugs, or NADH.[1−4] Thiyl radicals are also readily engaged in addition processes that are usually reversible. The most relevant examples from the biological point of view are formulated in eqs 1−3. The equilibrium constant of the oxygen addition (eq 1/-1) is about 3000, meaning that in air saturated aqueous systems ($[O_2] = 2.4 \times 10^{-4}$ M) both, $RS^{\bullet}$ and thiylperoxyl radical $RSOO^{\bullet}$ equilibrate at about equal concentrations, while under typical physiological conditions ($[O_2] \leq 10^{-5}$ M) the equilibrium remains overwhelmingly at the thiyl radical side.[5] Equilibrium 2/-2 has an important impact on the redox capacity of a thiyl/thiol containing system. While $RS^{\bullet}$ is an oxidant, the conjugated form with a thiolate (i.e., $RSSR^{\bullet -}$) is a reductant.[6] The latter readily transfers an electron to, for example, molecular oxygen yielding superoxide. Finally, the occurrence of the reaction 3/-3 has a significant biological consequence for the integrity of membranes, because it converts cis-unsaturated fatty acid residues to corresponding trans isomers. Many important studies have exclusively been devoted to this topic recently.[7]

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(1) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(2) *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K.-D., Eds.; Plenum Press: New York, 1990.

(3) Asmus, K.-D.; M. Bonifačić, M. In *S-Centered Radicals*; Alfassi, Z. B., Ed.; Wiley: Chichester, U.K. 1999; pp 141−191. Asmus, K.-D. In *Radiation Chemistry: Present Status and Future Prospects*; Jonah, C. D., Rao, B. M. S., Eds.; Elsevier: Amsterdam, The Netherlands, 2001, 341.

(4) Tamba, M.; O'Neill, P. *J. Chem. Soc., Perkin Trans.* **1991**, *2*, 1681.

(5) Tamba, M.; Simone, G.; Quintiliani, M. *Int. J. Radiat. Biol.* **1986**, *50*, 595. Zhang, X.; Zhang, N.; Schuchmann, H.-P.; von Sonntag, C. *J. Phys. Chem.* **1994**, *98*, 6541.

(6) Wardman, P. In *Glutathione Conjugation-Mechanisms and Biological Significance*; Sies, H., Ketterer, B., Eds; Academic Press: London, 1988; pp 44−72. Wardman, P. In *S-Centered Radicals*; Alfassi, Z. B., Ed.; Wiley: Chichester, U.K. 1999; pp 289−309.

(7) Chatgilialoglu, C.; Ferreri, C. *Acc. Chem. Res.* **2005**, *36*, 441. Ferreri, C.; Chatgilialoglu, C. *ChemBioChem.* **2005**, *6*, 1722. Chatgilialoglu, C.; Ferreri, C. *Cis-Trans Isomerization in Biochemistry*; Dugave, C., Ed.; Wiley-VCH: Wenheim, Germany, **2006**, 95. Chatgilialoglu, C.; Ferreri, C.; Lykakis, I. N.; Wardman, P. *Bioorg. Med. Chem.* **2006**, *14*, 6144.

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$$RS^{\bullet} + O_2 \rightleftharpoons RSOO^{\bullet} \qquad (1/\text{-}1)$$

$$RS^{\bullet} + RS^{-} \rightleftharpoons RSSR^{\bullet -} \qquad (2/\text{-}2)$$

$$RS^{\bullet} + -CH{=}CH- \rightleftharpoons -C^{\bullet}H-CH(SR)- \qquad (3/\text{-}3)$$

The reversible oxygen addition to thiyl radicals (eq 1/-1) becomes significant also because of the known reactions: (i) a rearrangement of the thiylperoxyl radical $RSOO^{\bullet}$ to the sulfonyl radical $RSO_2^{\bullet}$ (eq 4)[8] and (ii) a further oxygen addition leading to the sulfonylperoxyl radical $RSO_2OO^{\bullet}$ (eq 5).[9] All these sulfur-oxygen radicals must, therefore, be considered as potential participants in thiol/thiyl based systems exposed to oxygen. For instance, they are likely to act as oxidants. The question is also to what extent they may undergo addition and abstraction reactions like the $RS^{\bullet}$ radicals.

$$RSOO^{\bullet} \rightarrow RSO_2^{\bullet} \qquad (4)$$

$$RSO_2^{\bullet} + O_2 \rightarrow RSO_2OO^{\bullet} \qquad (5)$$

ESR and optical absorption spectra of sulfonyl radicals indicated that they are σ-type species with similar spin density of the unpaired electron on sulfur and oxygen atoms at the SO_2 moiety.[10−12] Theoretical calculation supported these findings and showed that the spin distribution for the unpaired electron in $MeSO_2^{\bullet}$ is 42% on sulfur and 44% on the oxygen atoms. For $PhSO_2^{\bullet}$ the corresponding values are 43% and 39%.[12] Moreover, the $\Delta H_{298}(RSO_2-Cl)$ were measured for R = Me or Ph by photoacoustic calorimetry and found to be equal (295 kJ mol^{-1}), indicating that the radical chemistry of $RSO_2^{\bullet}$ should be independent of the R group.[13]

The main synthetic applications of $RSO_2^{\bullet}$ radicals are based on their ability to add to carbon−carbon double bonds.[10,14] There is also a clear evidence that the addition of a sulfonyl radical to an olefin is a reversible reaction.[15] Although the absolute rate constants for the addition of $RSO_2^{\bullet}$ radicals to double bonds are absent from the literature, rate constants for the β-elimination of a p-$CH_3C_6H_4SO_2^{\bullet}$ radical from a variety of carbon-centered radicals have been measured.[16]

In radiation chemical studies, $MeSO_2^{\bullet}$ radicals have been generated by dissociative electron capture using sulfonyl chloride (eq 6)[17] or by oxidation of sulfinic acid (eq 7).[9] The present study focuses especially on the former reaction in an aqueous environment in the absence or in the presence of oxygen and on the ability of $MeSO_2^{\bullet}$ radical to act as oxidant and as catalyst in the cis−trans isomerization of unsaturated fatty acids.

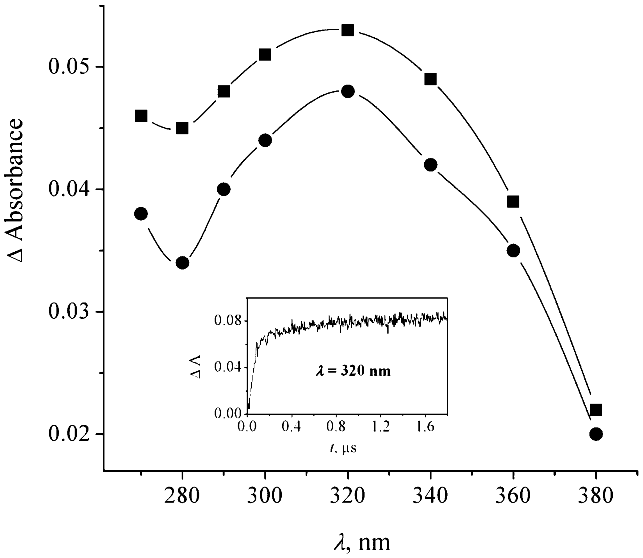

Figure 1. Absorption spectra obtained from the pulse radiolysis of Ar-purged aqueous solutions containing 5 mM $MeSO_2Cl$ and 0.5 M CH_3OH: (●) 0.1 μs after the pulse; (■) 1.0 μs after the pulse. Inset shows the absorption-time trace at 320 nm. Optical path = 5.0 cm; dose per pulse = 39 Gy.

$$e_{aq}^{-} + MeSO_2Cl \rightarrow MeSO_2^{\bullet} + Cl^{-} \qquad (6)$$

$$HO^{\bullet} + MeSO_2^{-} \rightarrow MeSO_2^{\bullet} + HO^{-} \qquad (7)$$

Results and Discussion

Reduction of Sulfonyl Chloride in the Absence of Oxygen. Until now the generation of the sulfonyl radical, as formulated in eq 6, has been considered a one-step dissociative electron attachment reaction. As shown below, the formation of $MeSO_2^{\bullet}$ involves, however, an intermediate sulfonyl chloride radical anion. The bimolecular rate constant $k_6 = (3.3 \pm 0.3) \times 10^{10}$ $M^{-1}\,s^{-1}$, evaluated for the reduction of $MeSO_2Cl$ from the decay of the e_{aq}^{-} absorption (e.g., at its maximum at 720 nm at three different sulfonyl chloride concentrations), thus refers only to the initial electron attachment. This step is clearly controlled only by the diffusion of the reactants.

Tracing the sulfonyl chloride reduction at 320 nm, that is, at the maximum of the $MeSO_2^{\bullet}$ radical absorption, revealed the above indicated, more complex situation. This can be realized by inspection of the inset in Figure 1, which specifically pertains to an argon-saturated aqueous solution containing 50 mM $MeSO_2Cl$ and 0.5 M methanol.[18] Two distinct processes are apparent. An initial fast rise occurred practically within the duration of the pulse and accounted for almost two-thirds of the final absorption. The second, considerably slower step, made up for the remaining third.

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(8) Sevilla, M. D.; Yan, M.; Becker, D. *Biochem. Biophys. Res. Commun.* **1988**, *155*, 405. Sevilla, M. D.; Becker, D.; Yan, M. *Int. J. Radiat. Biol.* **1990**, *57*, 65. Razskazovskii, Y.; Colason, A.-O.; Sevilla, M. D. *J. Phys. Chem.* **1995**, *99*, 7993.

(9) Sehested, K.; Holcman, J. J. *Radiat. Phys. Chem.* **1996**, *47*, 357. Razskazovskii, Y.; Sevilla, M. D. *J. Phys. Chem.* **1996**, *100*, 4090. Flyunt, R.; Makogon, O.; Schuchmann, M. N.; Asmus, K.-D.; von Sonntag, C. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 787.

(10) Chatgilialoglu, C. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: Chichester, U.K. 1988; pp 1089−1113.

(11) Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc. Perkin Trans.* **1979**, *2*, 770. Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans.* **1980**, *2*, 1429.

(12) Chatgilialoglu, C.; Griller, D.; Guerra, M. *J. Phys. Chem.* **1987**, *91*, 3747. Alberti, A.; Chatgilialoglu, C.; Guerra, M. *J. Chem. Soc., Perkin Trans.* **1986**, *2*, 1179.

(13) Chatgilialoglu, C.; Griller, D.; Kanabus-Kaminska, J. M.; Lossing, F. P. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 357. See also: Laarhoven, L. J. J.; Mulder, P.; Wayner, D. D. M. *Acc. Chem. Res.* **1999**, *32*, 342.

(14) Chatgilialoglu, C.; Bertrand, M. P.; Ferreri, C. In *S-Centered Radicals*; Alfassi, Z. B., Ed.; Wiley: Chichester, U.K. 1999; pp 312−354. Bertrand, M. P.; Ferreri, C. In *Radical in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 2, pp 485−503.

(15) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964**, 4962.

(16) Timokhin, V. I.; Gastaldi, S.; Bertrand, M. P.; Chatgilialoglu, C. *J. Org. Chem.* **2003**, *68*, 3532.

(17) Eriksen, T. E.; Lind, L. *Radiochem. Radioanal. Lett.* **1976**, *25*, 11.

(18) Radiolysis of neutral water leads to e_{aq}^{-} (0.27), $HO^{\bullet}$ (0.28), and $H^{\bullet}$ (0.062); the values in parentheses represent the radiation yields in units of μmol J^{-1}. In the presence of 0.5 M CH_3OH, both $HO^{\bullet}$ ($k = 9.7 \times 10^{8}$ $M^{-1}\,s^{-1}$) and $H^{\bullet}$ ($k = 2.6 \times 10^{6}$ $M^{-1}\,s^{-1}$) are scavenged efficiently.[19]

The same picture was observed when methanol is replaced by *tert*-butanol. Neither $^{\bullet}CH_2OH$ (as abstracting or reducing species) nor $^{\bullet}CH_2C(CH_3)_2OH$ (as abstracting species) contributed to the observed effects on this early time scale reported in the figure.[20] The absorption spectrum of the slowly formed species, recorded at times ≥ 1 μs, is identical to that of the $MeSO_2^{\bullet}$ radical. Qualitatively the same spectrum was obtained for the transient formed in the much faster initial process. This was recorded at 100 ns, that is, practically immediately after the pulse. It also exhibited a maximum at around 320 nm but differed from that of the sulfonyl radical by a generally lower absorptivity. This difference was slightly more pronounced at the high-energy side than at the low-energy side, indicating an apparent slight red-shift relative to $MeSO_2^{\bullet}$ radical. For comparison, both spectra are shown in Figure 1.

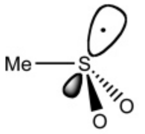
Kinetically, the slow step can be fitted by an exponential. The first-order rate constant corresponded to $k = (1.5 \pm 0.5) \times 10^6$ s^{-1}. The same value was obtained at any other, for example, a ten times lower (5 mM), sulfonyl chloride concentration, identifying this step as a true first-order process. This, together with the slight difference in absorption characteristics, suggests that we are dealing with two different, although spectroscopically similar species, namely, a transient immediately formed in the $e_{aq}^- + MeSO_2Cl$ reaction, which subsequently decays into the sulfonyl radical. The intermediate is considered to be the electron adduct, that is, the sulfonyl chloride radical anion. Mechanistically, both species are linked through the reaction sequence formulated in eqs 8 and 9

$$MeSO_2Cl + e_{aq}^- \rightarrow MeSO_2Cl^{\bullet -} \tag{8}$$

$$MeSO_2Cl^{\bullet -} \rightarrow MeSO_2^{\bullet} + Cl^- \tag{9}$$

The reaction of hydrated electrons with the 5 mM $MeSO_2Cl$ occurs with $t_{1/2} = 4.2$ ns and is completed within a few nanoseconds. For such fast reactions the yield of scavengable electrons is expected to increase noticeably with the scavenger concentration in the upper mM range, because of an increased probability to intercept the radiation chemical geminate recombination process. In accordance with corresponding findings in other systems with efficient electron scavengers,[21] the measured yield of $MeSO_2Cl^{\bullet -}$ (initial absorption) increased by about 10–15% when the $MeSO_2Cl$ concentration was increased from 5 to 50 mM.

The optical absorption spectra of $MeSO_2^{\bullet}$ and other substituted sulfonyl radicals have been the subject of a detailed study.[12] The maximum around 325 nm ($\epsilon \approx 800$ M^{-1} cm^{-1}) in water was assigned by multiple scattering X_α calculations to valence transitions involving transfer of electrons from the lone pair orbitals of the oxygen atoms to the SOMO (**1**), which is in accord with a red shift observed in going from water to hydrocarbon solvents, owing to stabilization of the ground state by hydrogen bonds. Regarding the transient radical anion of sulfonyl chlorides, evidence for its existence came from the ESR studies of radiolysis of a solid sample of piperidine-1-sulfonyl chloride.[22] Its radical anion is believed to possess the σ^*-type rather than the π-type quasi-trigonal bipyramidal structure, on the basis of the spectral parameters, that is, the incoming electron is accommodated in an antibonding orbital of the sulfur-chlorine bond, yielding a $2\sigma/1\sigma^*$ three-electron bonded species (**2**). The fact that both radicals show similar optical absorptions in the UV (with λ_{max} at around 320 nm) with relatively low extinction coefficient, suggests that in the radical anion **2** the valence transitions also involves transfer of electrons from the lone pair orbitals of the oxygen atoms to the SOMO σ^*.



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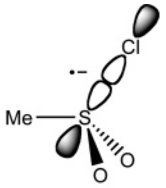

2

Reduction of Sulfonyl Chloride in the Presence of Oxygen. In the presence of oxygen a two-step absorption increase was also observed in the UV, which qualitatively resembles that displayed in the inset of Figure 1. With respect to yields and kinetics certain differences were noted. Based on current knowledge, at least two features can be anticipated, namely, (i) competition between $MeSO_2Cl$ and O_2 for the hydrated electron and (ii) reaction of the $MeSO_2^{\bullet}$ radical with O_2. Concerning the first aspect, the rate constant for the sulfonyl chloride reduction (eq 8) is almost 50% higher than that for the oxygen reduction (eq 10, $k_{10} = 2.1 \times 10^{10}$ M^{-1} s^{-1}).[19] In 5 mM $MeSO_2Cl$ solution, for example, which contains also 1×10^{-4}, 2.4×10^{-4} (air sat.) or 5×10^{-4} M oxygen, about 1.2, 3, and 6% of the hydrated electrons will be scavenged by O_2, respectively. Accordingly, the yields of the sulfonyl radical and its presumed radical anion precursor should be lowered by similar percentages. In the presence of the above listed oxygen concentrations the yields of $MeSO_2^{\bullet}$ (as measured at 320 nm) dropped, however, by 20 (24% according to averaged curve), 43%, and 56%, respectively (see Figure 2).

Raising the $MeSO_2Cl$ concentration to 50 mM (all other conditions unchanged) left even only a tenth of the above calculated yields for the direct contribution by reaction 8, that is, 0.6% at most. Yet, the $MeSO_2^{\bullet}$ radical yield was still reduced by the same percentages observed with the oxygen-free system as in the 5 mM $MeSO_2Cl$ system. This clearly hints at a reaction of $MeSO_2Cl^{\bullet -}$ (i.e., the precursor of $MeSO_2^{\bullet}$) with O_2 (eq 11) as a process that competes with eq 9.

$$O_2 + e_{aq}^- \rightarrow O_2^{\bullet -} \tag{10}$$

$$MeSO_2Cl^{\bullet -} + O_2 \rightarrow MeSO_2Cl + O_2^{\bullet -} \tag{11}$$

Kinetically this competition has been evaluated by measuring the decrease in sulfonyl radical yield (which equals the yield

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[19] Buxton, G. V.; Greenstock, C. L.; Helman, P. W.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

[20] A slow reaction of $HOCH_2^{\bullet}$ radical with $MeSO_2Cl$ is observed at longer time-scale. Detailed studies of a variety of α-hydroxyalkyl radicals with few sulfonyl chlorides are under investigation and will be published elsewhere. (Bobrowski, K.; Chatgilialoglu, C.; Tamba, M., et al. Unpublished results.)

[21] Asmus, K.-D.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1964**, *68*, 348.

[22] Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C.; Symons, M. C. R. *J. Chem. Res.* **1980**, *185*, 2610.

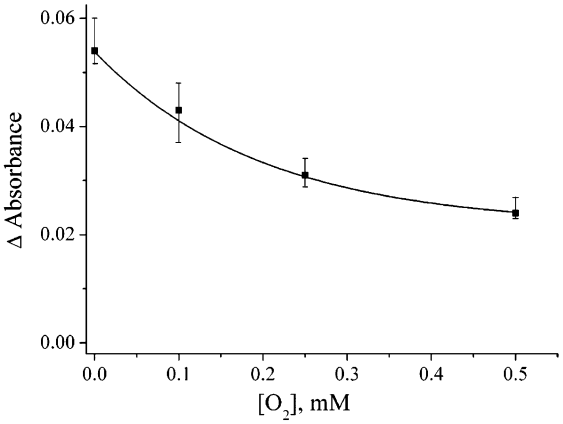

Figure 2. Optical density at 320 nm recorded 1 μs after the electron pulse from aqueous solutions containing 5 mM $MeSO_2Cl$, 0.5 M CH_3OH, and various O_2 concentrations. Optical path = 5.0 cm; dose per pulse = 39 Gy. Points represent the mean of at least three independent measurements. In the errors bars, the values of the low and high arguments are absolute values.

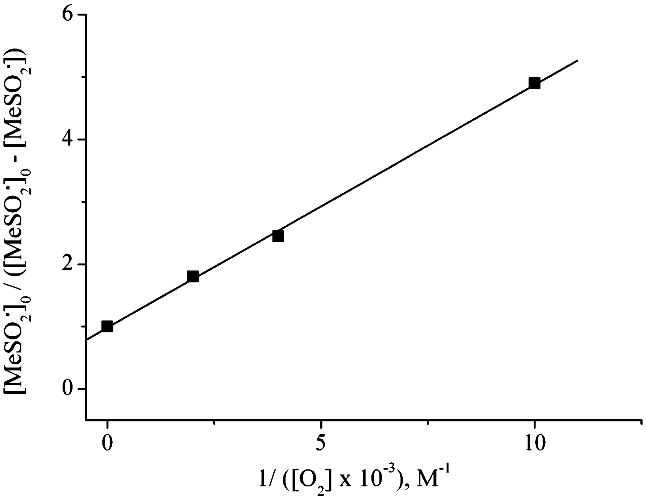

Figure 3. Evaluation of rate constant k_{11} according to eq 12.

of reaction 11) at the various oxygen concentrations. A plot of the appropriate relationship (eq 12), namely

$$[MeSO_2^{\bullet}]_0/([MeSO_2^{\bullet}]_0 - [MeSO_2^{\bullet}]) = 1 + (k_9/k_{11}) \times 1/[O_2] \quad (12)$$

is shown in Figure 3, with $[MeSO_2^{\bullet}]_0$ and $[MeSO_2^{\bullet}]$ referring to the measured absorptions at 320 nm in the absence and presence of oxygen, respectively. As can be appreciated upon inspection of the data, a good straight line can be drawn through the origin (infinite oxygen concentration) and the three experimental oxygen concentrations. From the slope of the straight line in Figure 3 and with the above evaluated $k_9 = 1.5 \times 10^6$ s^{-1}, a bimolecular rate constant for the electron transfer of $k_{11} = 4.1 \times 10^9$ M^{-1} s^{-1} is derived.

The yield of the initial $(MeSO_2Cl)^{\bullet-}$ absorption at 320 nm (recorded at 100 ns) was shown to decrease slightly with increasing $[O_2]$ and, at higher oxygen concentration, remained almost constant. An up to 6% decrease over the experimental $[O_2]$ range is due to the above-mentioned scavenging of hydrated electrons by O_2 (eq 10). The fact that the actual experimental readings are still somewhat lower (up to about 20% below the initial level) is plausibly explained by an increasingly faster reaction of $MeSO_2Cl^{\bullet-}$ with O_2. At 5×10^{-4} M O_2, reaction 9 occurred with $t_{1/2} \approx 0.5$ μs, that is, at 100 ns (the time of signal recording) ca. 13% of $MeSO_2Cl^{\bullet-}$ has already reacted. This, together with the 6% contribution of reaction 10, plausibly makes up for the observed overall 20% lower signal.

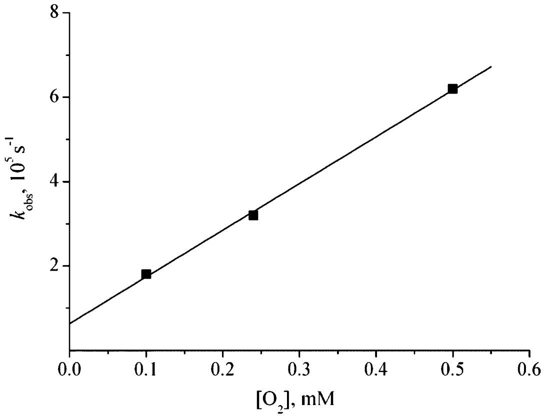

Figure 4. Plot of k_{obs} for decay of $MeSO_2^{\bullet}$ absorption at 320 nm as a function of O_2 concentration.

The fact that in oxygenated systems the absolute yields of $MeSO_2Cl^{\bullet-}$ and $MeSO_2^{\bullet}$ became about 15−20% higher, when the sulfonyl chloride concentration is increased from 5 to 50 mM, can be again reasonably explained by an increased efficiency of the e_{aq}^- and $H^{\bullet}$ scavenging (increased interference with the geminate recombination effect, see above).

Reaction of the Sulfonyl Radical with Oxygen. Our present results unambiguously confirm a reaction between the sulfonyl radical and oxygen (eq 13). This expresses itself in an increasingly faster decay of the $MeSO_2^{\bullet}$ radical absorption with increasing oxygen concentration. Figure 4 shows the plot of the observed first-order rate constants at various $[O_2]$. From the slope a rate constant of $k_{13} = (1.1 \pm 0.4) \times 10^9$ M^{-1} s^{-1} is derived for the oxygen addition. Our present measurement is in excellent agreement with earlier values around 1×10^9 M^{-1} s^{-1} and confirms that the underlying reaction is practically a diffusion-controlled process.[9]

$$MeSO_2^{\bullet} + O_2 \rightleftharpoons MeSO_2OO^{\bullet} \quad (13/-13)$$

Figure 4 shows an intercept of 6.3×10^4 s^{-1}. A smaller part of this reflects the decay of $MeSO_2^{\bullet}$ in the absence of O_2 (ca. 1×10^4 s^{-1} contribution based on the first half-life of the bimolecular termination). In addition, the intercept would also include the rate constant for a possible back reaction (eq -13). The assumption of such an oxygen addition equilibrium, in principle, is most reasonable in view of a corresponding equilibrium involving thiyl radicals (eq 1). For any quantitative assessment it must, in any case, be recognized that even small changes of the slope (remaining well within the above-mentioned error limits) strongly affect the absolute value of the intercept. The low rate constant $k_{-13} \leq 5 \times 10^4$ s^{-1} derived in this way is,[23] however, fully corroborated by the experimental results con-

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(23) An equilibrium may also be reflected in the incomplete decay of the absorption at 320 nm, which seems to remain at a finite level of about 15% of initial absorption (see Figure 5e). If all of this was due to the equilibrium concentration of $MeSO_2^{\bullet}$, K_{13} and k_{-13} could be evaluated more explicitly. However, because of other possible long-lived absorptions (sulfonyl peroxyl, final products), the values thus derived should again only be regarded as limiting values, that is, $K_{13} > 2.4 \times 10^4$ M^{-1} and $k_{-13} < 4.6 \times 10^4$ s^{-1}.

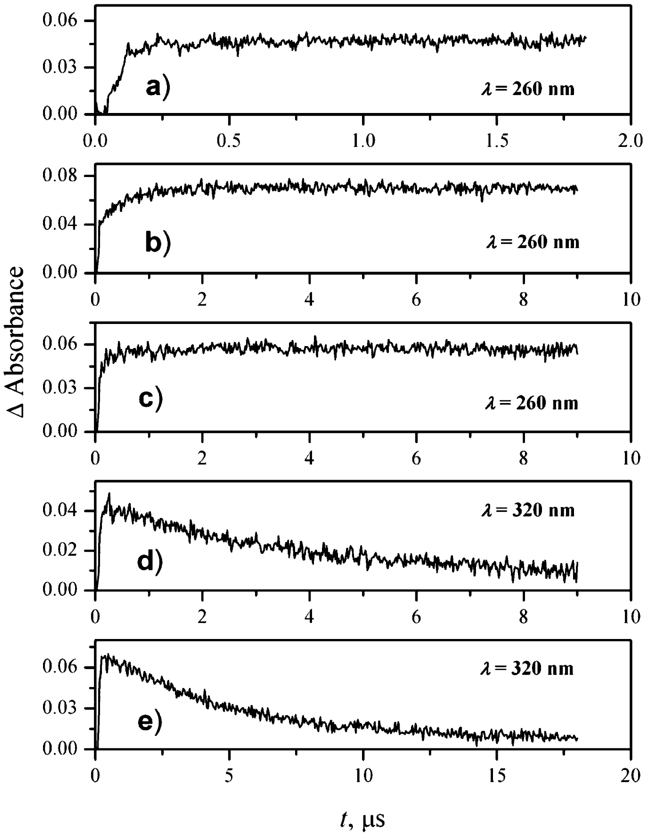

Figure 5. (a−c) Absorption-time traces at 260 nm obtained from pulsed aqueous radiolysis of 0.5 M CH_3OH, containing also (a) 5 mM $MeSO_2Cl$, no O_2 (Ar-saturated); (b) 5 mM $MeSO_2Cl$, air-saturated; and (c) 50 mM $MeSO_2Cl$, air-saturated. (d−e) Absorption-time traces at 320 nm obtained from pulsed aqueous of 0.5 M CH_3OH, containing also (d) 5 mM $MeSO_2$-Cl, air-saturated; (e) 50 mM $MeSO_2Cl$, air-saturated. Optical path cell = 5.0 cm; dose per pulse = 39 Gy.

cerning isomerization of double bonds in systems containing sulfonyl radicals and oxygen (see later).

Involvement of $O_2^{\bullet-}$. Direct observation of $O_2^{\bullet-}$, formed in reaction 11, is, in principle, possible through its optical absorption in the UV ($\lambda_{max} = 245$ nm, $\epsilon \approx 2350$ M^{-1} cm^{-1}).[24] Because of experimental limitations (e.g., self-absorption of solutes, other absorbing radicals, insufficient intensity of the analyzing light) meaningful measurements are often hampered at this low wavelength. This applied also to our sulfonyl chloride system, restricting us to the region ≥260 nm. The molar absorptivity of $O_2^{\bullet-}$ at this wavelength is, however, still high enough ($\epsilon \approx 1700$ M^{-1} cm^{-1}) for an identification of the superoxide anion.[24] Figure 5 displays three absorption-time traces recorded at this wavelength in pulse irradiated solutions containing 0.5 M CH_3OH and (a) 5 mM $MeSO_2Cl$, no O_2 (Argon-saturated), (b) 5 mM $MeSO_2Cl$, air-saturated, and (c) 50 mM $MeSO_2Cl$, air-saturated. Additionally shown are the traces of the latter two solutions at the wavelength of 320 nm (Figure 5d,e).

In the oxygen-free system (Figure 5a) the trace resembled the two-step features of the recording at 320 nm (Figure 1) and is, therefore, mainly attributed to the contributions of the $MeSO_2^{\bullet}$ radical and its $MeSO_2Cl^{\bullet-}$ precursor at this wavelength.

In an air-saturated solution of an otherwise identical system a significantly enhanced absorption signal was observed at 260 nm (Figure 5b). In particular, it is noted that the signal stays practically stable over a time range of 10 μs, while at 320 nm (Figure 5d) the signal (representing the forward reaction of equilibrium 10) decayed significantly within this period. Therefore, the long-term absorption at 260 nm cannot be attributed anymore to the $MeSO_2^{\bullet}$ radical but is, accordingly, assigned to the long-lived $O_2^{\bullet-}$. The possibility that the absorbing species may be the $MeSO_2OO^{\bullet}$ is discarded, because the rate of the oxygen addition to $MeSO_2^{\bullet}$ ($t_{1/2} = 2.6$ μs) is considerably slower than even the slowest step of the formation of the absorption at 260 nm ($t_{1/2} \approx 0.5$ μs).

A further piece of information concerns a reaction of $O_2^{\bullet-}$ with sulfonyl chloride. Occurrence of this process is concluded from an acceleration of the decay of the 260 nm absorption with increasing sulfonyl chloride concentration. The underlying reaction is considered to be an electron transfer by which a sulfonyl chloride radical anion is regenerated. The $O_2^{\bullet-}/MeSO_2Cl^{\bullet-}$ system thus constitutes an equilibrium, and eq 11 is, therefore, re-formulated as a reversible process.

$$MeSO_2Cl^{\bullet-} + O_2 \rightleftharpoons MeSO_2Cl + O_2^{\bullet-} \qquad (11/-11)$$

Further support for the equilibrium is provided by the slight drop in $O_2^{\bullet-}$ yield upon increasing the sulfonyl chloride concentration from 5 to 50 mM (in air-saturated solutions), as it can be seen from the long-term absorptions at 260 nm in Figure 5b,5c, respectively. This observation reflects the higher efficiency of the back reaction (eq -11) at the higher sulfonyl chloride concentration. The fact that simultaneously the $MeSO_2^{\bullet}$ yield increases (Figure 5e compared with Figure 5d) can, in part, also be interpreted along this line. For a quantitative assessment of k_{-11} several factors need to be taken into account. The observed decay rate at 260 nm thus reflects not only the inherent equilibrium kinetics and the various possible radical−radical termination reactions but also possible unknown contributions by other species (radicals and molecular products) to the absorption at this wavelength, as well as complications introduced by the chosen composition of the investigated systems. A desirable parameter is, for example, a sufficiently high $O_2^{\bullet-}$ concentration. This can be achieved by several means. The highest direct formation of this species via reaction 10 (and corresponding reaction of O_2 with $H^{\bullet}$ atoms) requires high O_2 concentration. This, in turn, accelerates the forward reaction in equilibrium 11/-11. As a consequence, any electron transfer from $O_2^{\bullet-}$ to $MeSO_2Cl$ will increasingly, and eventually much faster, be reversed than the irreversible removal of $MeSO_2Cl^{\bullet-}$ through chloride ion cleavage (eq 9). The apparent yield of $O_2^{\bullet-}$ decay thus becomes increasingly smaller. A higher yield of $O_2^{\bullet-}$ can alternatively (although indirectly) be generated by increasing the sulfonyl chloride concentration, namely, through the sequence of reactions 8 and 11. Addition of formate (instead of methanol) can potentially double the achievable $O_2^{\bullet-}$ yield via conversion of $^{\bullet}OH$ and $H^{\bullet}$ into superoxide.[18,24] Reactions contributing in such systems are formulated in eqs 14−16 and 11.

$$^{\bullet}OH/H^{\bullet} + HCO_2^{-} \rightarrow CO_2^{\bullet-} + H_2O/H_2 \qquad (14)$$

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[24] Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1987**, *14*, 1041. Bielski, B. H. J. *Photochem. Photobiol.* **1978**, *28*, 645.

$$CO_2^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + CO_2 \tag{15}$$

$$CO_2^{\bullet-} + MeSO_2Cl \rightarrow MeSO_2Cl^{\bullet-} + CO_2 \tag{16}$$

Considering all these aspects, we chose to conduct experiments with a system containing 1.25×10^{-3} M oxygen, 0.5 M HCO_2^-, and various concentrations of $MeSO_2Cl$. The observed first-order decay (k_{obs}) at 260 nm did not increase, however, linearly with sulfonyl chloride concentrations, but the plot of k_{obs} versus [$MeSO_2Cl$] showed a continuous curvature. Thus, it was not possible to extract an unambiguous value for k_{-11} from these data. The bimolecular rate constant evaluated from the lowest $MeSO_2Cl$ concentration (0.1 mM), under the assumption that eq -11 is the only process controlling the decay at 260 nm (1.7×10^6 M^{-1} s^{-1}), must be corrected at least for the mutual $O_2^{\bullet-}$ termination. Additionally, eq 17 may have to be considered owing to the reductive power of the $CO_2^{\bullet-}$ ($E^0 = -1.1$ V)[1] which should even reduce the superoxide to hydrogen peroxide ($E(O_2^{\bullet-}, 2H^+/H_2O_2) \approx 0.9$ V at pH 7).[1]

$$O_2^{\bullet-} + CO_2^{\bullet-} \xrightarrow{2H^+} H_2O_2 + CO_2 \tag{17}$$

With a $CO_2^{\bullet-}$ concentration of about 10^{-5} M in our experiment this electron-transfer reaction would become effective if k_{17} approaches or exceeds a value as low as 10^7 M^{-1} s^{-1}. Reaction 17 and the $O_2^{\bullet-}$ termination should have less, if any, of effect at the higher sulfonyl chloride concentrations. As mentioned above, these systems are affected by an almost complete and immediate back electron transfer (eq 11). The formally calculated k_{-11} values vary between 1.7×10^6 and 1.7×10^5 M^{-1} s^{-1} for the 0.1−5 mM $MeSO_2Cl$ range. Accordingly, the equilibrium constant K_{11} would range from 2.4×10^3 to 2.4×10^4. Because the k_{-11} and K_{11} values derived from the high concentration system lack the complication by reaction 17, they can probably be viewed with a comparatively higher degree of confidence. Irrespective of these uncertainties there seems to be no ambiguity though about the reversibility of eq 11. Knowing the equilibrium constant allowed us to calculate the difference in redox potentials between the $MeSO_2Cl/MeSO_2Cl^{\bullet-}$ and $O_2/O_2^{\bullet-}$ couples:

$$\Delta E° = E°(O_2/O_2^{\bullet-}) - E°(MeSO_2Cl/MeSO_2Cl^{\bullet-}) = RT \ln K/nF \approx 59.1 \log K$$

Our experimental limits for K_{11} translate into a $\Delta E° = 200$−259 mV range. With $E°(O_2/O_2^{\bullet-}) = -155$ mV[1] the redox potential range for the $MeSO_2Cl/MeSO_2Cl^{\bullet-}$ couple thus calculates to

$$E°(MeSO_2Cl/MeSO_2Cl^{\bullet-}) = E°(O_2/O_2^{\bullet-}) - \Delta E° = -355 \text{ to } -414 \text{ mV (vs NHE)}$$

The $MeSO_2Cl^{\bullet-}$ radical anion is, accordingly, a significantly better reductant than $O_2^{\bullet-}$, well in accord with our experimental finding. To further confirm this conclusion, we tested it with the $MeSO_2Cl^{\bullet-}$-induced reduction of 4-nitroacetophenone (PNAP):

$$MeSO_2Cl^{\bullet-} + PNAP \rightarrow MeSO_2Cl + PNAP^{\bullet-} \tag{18}$$

For a solution containing, for example, 5×10^{-5} M PNAP (besides 5 mM $MeSO_2Cl$ and 0.5 M CH_3OH) a first-order rate constant for the $PNAP^{\bullet-}$ formation was measured to be 7.5×10^4 s^{-1}. This is 20 times lower than the radical anion decay into sulfonyl radicals via eq 9 ($k_9 = 1.5 \times 10^6$ s^{-1}). Accordingly only about 5% of $MeSO_2Cl^{\bullet-}$ can react with PNAP in this system. This was fully corroborated by the absorptions measured after completion of reactions 9 and 18. On the basis of the known molar absorption coefficients of the reaction products $MeSO_2^{\bullet}$ ($\epsilon \approx 1000$ M^{-1} cm^{-1} at 320 nm) and $PNAP^{\bullet-}$ ($\epsilon \approx 18200$ M^{-1} cm^{-1} at 350 nm),[25] the PNAP reduction occurred with an efficiency of about 6%. The above first-order rate for the formation of $PNAP^{\bullet-}$ gives a bimolecular rate constant $k_{18} = 1.5(\pm0.2) \times 10^9$ M^{-1} s^{-1}. This efficient electron-transfer suggests that K_{11} must be high enough to yield a redox potential for the $MeSO_2Cl/MeSO_2Cl^{\bullet-}$ couple which is reasonably more negative than that of ($E° = -353$ mV)[1] for the $PNAP/PNAP^{\bullet-}$ couple, that is, $K_{11} > 2240$ in agreement with our above conclusion from the $O_2^{\bullet-}$ experiment.[26]

Cis−Trans Isomerization of Mono-unsaturated Fatty Acid Methyl Esters by Sulfonyl Radical. The γ-radiolysis of ethanol/water (2/1, v/v) in N_2 flushed solutions led to the transient species shown in eqs 19 and 20, where $R^{\bullet}$ represents the produced alcohol radicals (i.e., $^{\bullet}CH_2CH_2OH$, $CH_3{}^{\bullet}CHOH$, $CH_3CH_2O^{\bullet}$).[27] Hydrogen abstraction from ethanol by $HO^{\bullet}$ radical and $H^{\bullet}$ atoms increased the production of alkyl radical species (eq 21). Solvated electrons as well as possibly all $R^{\bullet}$ radicals reacted with methanesulfonyl chloride to give the corresponding sulfonyl radical (eqs 22 and 23).[28]

$$H_2O \xrightarrow{\gamma} e_{aq}^-, HO^{\bullet}, H^{\bullet} \tag{19}$$

$$CH_3CH_2OH \xrightarrow{\gamma} e_{sol}^-, R^{\bullet} \tag{20}$$

$$HO^{\bullet}/H^{\bullet} + CH_3CH_2OH \rightarrow H_2O/H_2 + R^{\bullet} \tag{21}$$

$$e_{aq}^-/e_{sol}^- + MeSO_2Cl \rightarrow MeSO_2^{\bullet} + Cl^- \tag{22}$$

$$R^{\bullet} + MeSO_2Cl \rightarrow MeSO_2^{\bullet} + RCl \tag{23}$$

A solution of 2.5 mM methyl palmitoleate (9c-C16:1) and 1.25 mM $MeSO_2Cl$ in ethanol/water (2/1, v/v) was deoxygenated by N_2 stream and then irradiated using a ^{60}Co-Gammacell (dose rate = 10 Gy min^{-1}) at 22 °C. The reaction was monitored by GC, and the dose profile of 9c-C16:1 disappearance (□) and methyl palmitelaidate (9t-C16:1) formation (■) is shown in Figure 6. The two geometrical isomers reached an equilibrium after 300 Gy, the cis/trans ratio being 18/82. Figure 6 (▲, △) shows also that the same equilibrium is reached in a practically equal time if one starts from the trans isomer 9t-C16:1.

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[25] Whillans, D. H. *Radiat. Phys. Chem.* **1977**, *10*, 335.

[26] In the interpretation of the above results, a possible reaction of PNAP with $^{\bullet}CH_2OH$ radicals should be considered. Having a rate constant as low as 8.6×10^6 M^{-1} s^{-1} (see: Jagannadham, V.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 2188) this reaction is, however, too slow to account for the observed $PNAP^{\bullet-}$ formation. Furthermore, this reaction is not an electron transfer but has been identified as an adduct formation. As in the $MeSO_2Cl/O_2$ system, the underlying electron transfer may also be reversible in the $MeSO_2Cl/PNAP$ system. Unambiguous proof of this reasonable assumption was, however, not anticipated in this study.

[27] Asmus, K.-D.; Möckel, H.; Henglein, A. *J. Phys. Chem.* **1973**, *77*, 1218.

[28] Primary and secondary alkyl radicals react with sulfonyl chlorides with rate constants in the range of 3×10^5 to 1.3×10^6 M^{-1} s^{-1} at 25 °C in organic solvents. See: Chatgilialoglu, C. *J. Org. Chem.* **1986**, *51*, 2871. Horowitz, A. *Int. J. Chem. Kinet.* **1976**, *8*, 709. The rate constants of the same reaction in water could be larger, because of the polar contributions that stabilize the transition state.

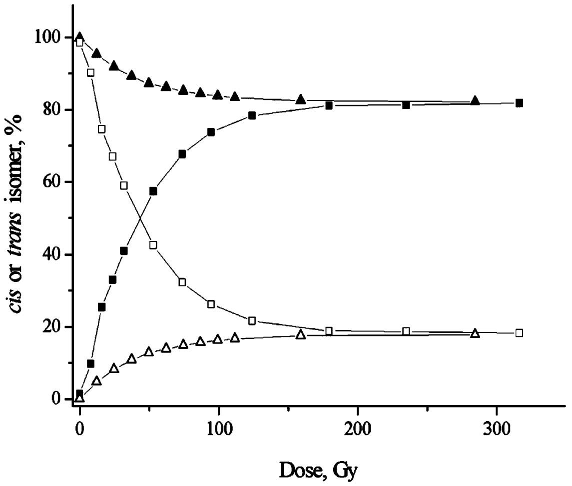

Figure 6. γ-Irradiation (dose rate = 10 Gy min^{-1}) of 2.5 mM methyl palmitoleate (9c-C16:1) or methyl palmitelaidate (9t-C16:1) with MeSO$_2$-Cl (1.25 mM) in N$_2$-fluxed ethanol/water (2/1, v/v) at 22 °C. Dose profiles of disappearance of 9c-C16:1 (□) and formation of 9t-C16:1 (■) starting from cis isomer or disappearance of 9t-C16:1 (▲) and formation of 9c-C16:1 (△) starting from trans isomer.

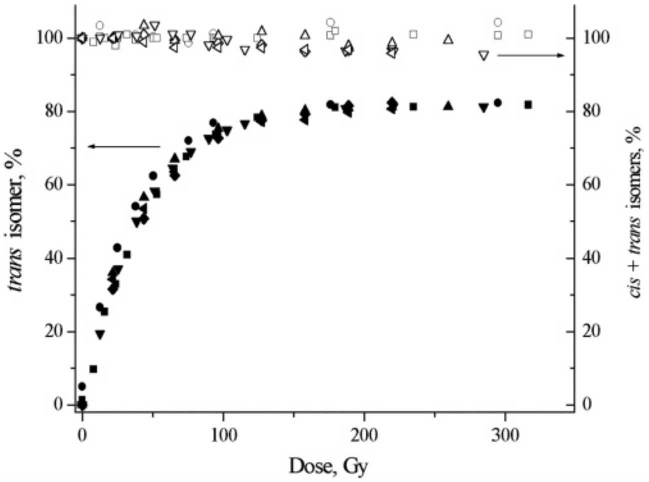

Figure 7. (left side) Formation of trans isomers from γ-irradiation (dose rate = 10 Gy min^{-1}) of different mono-unsaturated fatty acid methyl esters (2.5 mM) with MeSO$_2$Cl (1.25 mM) in N$_2$-fluxed ethanol/water (2/1, v/v) at 22 °C: (●) 9t-C14:1, (■) 9t-C16:1, (◆) 6t-C18:1, (▲) 9t-C18:1, (▼) 11t-C18:1, (left-pointing triangle) 11t-C20:1. (right side) Each point is the sum of cis and trans isomers.

We extended this approach to five other cis-mono-unsaturated fatty acid methyl esters, that is, myristoleate (9c-C14:1), petroselinate (6c-C18:1), oleate (9c-C18:1), vaccenate (11c-C18:1), and eicosenoate (11c-C20:1), and the results were very similar in all the experiments. Figure 7 (left side) shows the dose profile of the six trans isomer formations to be practically the same. These results also indicate that the position of unsaturation and the hydrocarbon chain length have no influence on the cis−trans isomerization process. Figure 7 (right side) shows no loss of unsaturated esters since the loss of cis isomer is exactly balanced by the formation of geometrical trans isomer.

The product yield (mol/kg) divided by the absorbed dose (1 Gy = 1 J kg^{-1}) gives the radiation chemical yield or G(isomerization). Plotting the G(isomerization) versus dose and extrapolating the curve to zero dose, a $G \cong 80$ μmol J^{-1} is obtained. Assuming that G(MeSO$_2^{\bullet}$) is 0.65 μmol J^{-1},[29] we calculated a catalytic cycle for the isomerization of ca. 120 at the initial phase. Scheme 1 shows the mechanism that we conceive for this process of cis−trans isomerization by the MeSO$_2^{\bullet}$ radical. The percentages of trans/cis isomers after completion are 82/18 at 22 °C for all compounds, corresponding to an equilibrium constant $K = 4.6$. The reported difference in the stability of the two isomers in 2-butenes, that is, $\Delta G°$(trans) − $\Delta G°$(cis) = −3.1 kJ mol^{-1}, corresponds to $K = 3.5$, since $\Delta G = -RT \ln K$. Therefore, in mono-unsaturated acid methyl esters the final isomeric composition should account for the difference in the stability of the two isomers and further support the role of MeSO$_2^{\bullet}$ radicals as an efficient catalyst in the cis−trans isomerization.[31]

We also tested the effect of molecular oxygen in the cis−trans isomerization. In particular, the isomerization of 9c-C14:1 was repeated under the above-described experimental conditions, without degassing and leaving the sample to the open air. After 400 Gy of irradiation dose, no isomerization was observed. A similar experiment was carried out with 6c-C18:1 and the sample was air-saturated prior to irradiation. After 300 Gy again no isomerization was observed. These results indicate an inhibitory effect of oxygen toward isomerization.[31] Although absolute rate constants for the addition of RSO$_2^{\bullet}$ radicals to double bonds are absent from the literature, rate constants for the β-elimination of p-CH$_3$C$_6$H$_4$SO$_2^{\bullet}$ from a variety of carbon-centered radicals have been measured.[16] Of interest to us is the rate constant of 1.5×10^6 s^{-1} (at 20 °C) obtained for PhCH$_2$CH($^{\bullet}$)CH$_2$SO$_2$Ts. This value is expected to be one or more orders of magnitude higher when a second β-substituent is attached to the carbon bearing the sulfonyl moiety and the efficiency of the alkyl radical trapping by oxygen should, accordingly, be very low (cf. Scheme 1).[32] Therefore, the observed inhibitory effect of oxygen could indeed plausibly be explained by the scavenging of the sulfonyl radicals.[33]

Conclusion

In the present study unambiguous evidence is provided for a relatively long-lived electron adduct to sulfonyl chlorides, RSO$_2$Cl$^{\bullet-}$. It acts as reductant and establishes an equilibrium with O$_2^{\bullet-}$. In the absence of a suitable redox partner, it decays under elimination of chloride into the RSO$_2^{\bullet}$ radical. Oxygen addition to RSO$_2^{\bullet}$ constitutes another likely equilibrium. The radical chemistry of sulfonyl chloride, particularly if occurring in an oxygenated environment, constitutes a complex system of several equilibria. Combined with or embedded into a thiol/oxygen containing system, which itself is characterized by redox and addition equilibria, as well as rearrangement reactions (e.g.,

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(29) On the basis of the total $G = 0.61$ μmol J^{-1} in water (eq 19) and the total $G = 0.67$ μmol J^{-1} in ethanol (eq 20),[30] the assumption of $G = 0.65$ μmol J^{-1} seems reasonable.

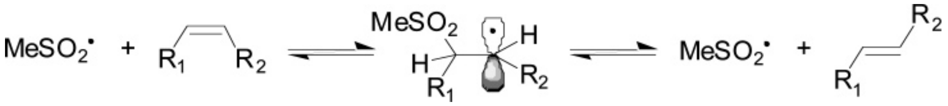
(30) Spinks, J. W. T.; Woods, R. J. *An Introduction to Radiation Chemistry*, 3rd Ed.; Wiley: New York, 1990.

(31) It is worth also recalling that the equilibrated cis/trans mixtures are similar to those reported for the isomerization of unsaturated fatty acid methyl esters by thiyl radicals, see: Chatgilialoglu, C.; Ferreri, C.; Mulazzani, Q. G.; Ballestri, M.; Landi, L. *J. Am. Chem. Soc.* **2000**, *122*, 4593. Chatgilialoglu, C.; Zambonin, L.; Altieri, A.; Ferreri, C.; Mulazzani, Q. G.; Landi, L. *Free Radical Biol. Med.* **2002**, *33*, 1681.

(32) Chatgilialoglu, C.; Altieri, A.; Fischer, H. *J. Am. Chem. Soc.* **2002**, *124*, 12816. Chatgilialoglu, C.; Samadi, A.; Guerra, M.; Fischer, H. *ChemPhysChem.* **2005**, *6*, 286.

(33) It is worth mentioning that the thiyl radical-catalysed isomerization process does not suffer from the presence of oxygen,[31] thus indicating that the equilibrium reaction of thiyl radical by oxygen is shifted to the left (see introduction).

Scheme 1. Reaction Mechanism for the Cis–Trans Isomerization



RSOO• → RSO2•) based on the RS• radical chemistry, the overall chemistry may thus assume a high degree of delicately balanced complexity. In the present study this was demonstrated, for example, with the cis–trans isomerization of mono-unsaturated fatty acid compounds.

Experimental Section

Materials. Methanesulfonyl chloride (Aldrich) was distilled before use under nitrogen. Sodium formate and *p*-nitroacetophenone (PNAP) from Merck and alcohols (HPLC grade) and mono-unsaturated fatty acid methyl esters from Sigma-Aldrich Co. were used without further purification. Solutions were freshly prepared using water purified with a Millipore (Milli-Q) system.

Pulse Radiolysis. All time-resolved investigations were conducted by means of the radiation chemistry technique of pulse radiolysis, using the 12 MeV LINAC (linear accelerator) CNR facility at the ISOF Institute in Bologna. Details of the optical detection system, methods, and computer treatment of data are described elsewhere.[34] Pulses from 50 to 200 ns were used according to the dose (10–40 Gy) to be delivered to the samples. The pulse irradiation was performed at room temperature (22 ± 2°) on samples contained in Spectrosil quartz cells of 5 cm optical path length. In the presence of oxygen, the investigated aqueous systems generally contained (5–50) mM $MeSO_2Cl$, 0.5 M CH_3OH, and various O_2 concentrations (5×10^{-5} to 1.2×10^{-3} M). Air- and oxygen-saturated solutions were directly used, other oxygen concentrations were attained by flushing solutions with varying percentages of Ar/O_2 or air/gas mixtures. Experimental error limits for individual radiation chemical experiments are typically 10%. Deviating figures are specifically noted.

Continuous Radiolyses. Continuous radiolyses were performed at room temperature (22 ± 2 °C) on 1 mL samples using a ^{60}Co-Gammacell at dose rate 10 Gy min^{-1}. The exact absorbed radiation dose was determined with the Fricke chemical dosimeter, by taking $G(Fe^{3+}) = 1.61$ μmol J^{-1}.[30]

GC Analyses. GC analyses for the determination of the isomeric ratio of the unsaturated fatty acids were performed using a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a Rtx-2330 column (90% biscyanopropyl–10% phenylcyanopropyl polysiloxane capillary column; 60 m, 0.25 mm i.d., 0.20 μm film thickness). Temperature started from 160 °C held for 55 min, followed by an increase of 5 °C/min up to 195 °C, held for 10 min, followed by a second increase of 10 °C/min up to 250 °C. The carrier gas pressure was helium at a constant pressure of 29 psi. Trans methyl esters were identified by comparison with the retention times of commercially available authentic samples.

Isomerization of Mono-unsaturated Fatty Acids Methyl Esters. A 2.5 mM solution of fatty acid methyl ester in ethanol/water (2/1, v/v) was placed in a 4 mL vial equipped with an open-top screw cap and a Teflon-faced septum and added with 1.25 mM methanesulfonyl chloride and methyl stearate (1 mM) as the internal standard. The mixture was flushed with N_2 for 15 min prior to γ-irradiation. To follow the reaction course by GC analysis, 100 μL aliquots were withdrawn at different times. The aliquots were processed by the addition of an aqueous saturated solution of $NaHCO_3$ and the evaporation of ethanol under vacuum. Then, *n*-hexane was added, and the organic phase, containing the methyl ester, was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under vacuum, the residue containing the fatty acid methyl esters was examined by GC for the determination of cis/trans isomeric ratio.

Isomerization of Mono-unsaturated Fatty Acids Methyl Esters in the Presence of Oxygen. The experiment reported above was repeated using methyl myristoleate as the substrate and avoiding the degassing procedure. After the above-reported workup of the reaction samples at different times reaching 400 Gy of total irradiation dose, GC analysis was carried out in comparison with an authentic commercially available sample of myristelaidic acid methyl ester. No traces of trans isomer were detected. Another experiment was carried out with methyl petroselinate under the same condition, except that the sample was air-saturated prior to irradiation. After the above-reported workup of the reaction samples at different times reaching 300 Gy of total irradiation dose, GC analysis was carried out in comparison with an authentic commercially available sample of petroselaidic acid methyl ester, showing the absence of trans isomer.

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(34) Emmi, S. S.; D'Angelantonio, M.; Poggi, G.; Beggiato, G.; Camaioni, N.; Geri, A.; Martelli, A.; Pietropaolo, D.; Zotti, G. *Res. Chem. Intermed.* **1998**, *24*, 1.