5908 *J. Phys. Chem. A* **2008,** *112,* 5908–5916

Dimethylselenide as a Probe for Reactions of Halogenated Alkoxyl Radicals in Aqueous Solution. Degradation of Dichloro- and Dibromomethane

Oksana Makogon,[†] Roman Flyunt,*[,†,‡] Thomas Tobien,[§] Sergej Naumov,[‡] and Marija Bonifačić[||]

Institute of Physico-Chemistry, National Academy of Science of the Ukraine, Naukova Street 3a, UA-79053 L'viv, Ukraine, Leibniz-Institut für Oberflächenmodifizierung (IOM), Permoserstrasse 15, D-04303 Leipzig, Germany, LEAP Technologies, P.O. Box 969, 610 Jones Ferry Road, Carrboro, North Carolina 27510, and Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička c. 54, HR-10000 Zagreb, Croatia

Received: December 19, 2007; Revised Manuscript Received: March 27, 2008

Using pulse radiolysis and steady-state γ-radiolysis techniques, it has been established that, in air-saturated aqueous solutions, peroxyl radicals $CH_2HalOO^\bullet$ (Hal = halogen) derived from CH_2Cl_2 and CH_2Br_2 react with dimethyl selenide (Me_2Se), with k on the order of 7×10^7 M^{-1} s^{-1}, to form HCO_2H, CH_2O, CO_2, and CO as final products. An overall two-electron oxidation process leads directly to dimethyl selenoxide (Me_2SeO), along with oxyl radical $CH_2HalO^\bullet$. The latter subsequently oxidizes another Me_2Se molecule by a much faster one-electron transfer mechanism, leading to the formation of equal yields of CH_2O and the dimer radical cation $(Me_2Se)_2^{\bullet+}$. In absolute terms, these yields amount to 18% and 28% of the $CH_2ClO^\bullet$ and $CH_2BrO^\bullet$ yields, respectively, at 1 mM Me_2Se. In competition, $CH_2HalO^\bullet$ rearranges into $^\bullet CH(OH)Hal$. These C-centered radicals react further via two pathways: (a) Addition of an oxygen molecule leads to the corresponding peroxyl radicals, that is, species prone to decomposition into $H^+/O_2^{\bullet-}$ and formylhalide, HC(O)Hal, which further degrades mostly to H^+/Hal^- and CO. (b) Elimination of HHal yields the formyl radical $H{-}C^\bullet{=}O$ with a rate constant of about 6×10^5 s^{-1} for Hal = Cl. In an air-saturated solution, the predominant reaction pathway of the $H{-}C^\bullet{=}O$ radical is addition of oxygen. The formylperoxyl radical $HC(O)OO^\bullet$ thus formed reacts with Me_2Se via an overall two-electron transfer mechanism, giving additional Me_2SeO and formyloxyl radicals $HC(O)O^\bullet$. The latter rearrange via a 1,2 H-atom shift into $^\bullet C(O)OH$, which reacts with O_2 to give CO_2 and $O_2^{\bullet-}$. The minor fraction of $H{-}C^\bullet{=}O$ undergoes hydration, with an estimated rate constant of $k \approx 2 \times 10^5$ s^{-1}. The resulting $HC^\bullet(OH)_2$ radical, upon reaction with O_2, yields HCO_2H and $H^+/O_2^{\bullet-}$. Some of the conclusions about the reactions of halogenated alkoxyl radicals are supported by quantum chemical calculations [B3LYP/6-31G(d,p)] taking into account the influence of water as a dielectric continuum [by the self-consistent reaction field polarized continuum model (SCRF=PCM) technique]. Based on detailed product studies, mechanisms are proposed for the free-radical degradation of CH_2Cl_2 and CH_2Br_2 in the presence of oxygen and an electron donor (namely, Me_2Se in this study), and properties of the reactive intermediates are discussed.

Introduction

Halogenated organic compounds are known to be potent toxins. Nevertheless, they are still in widespread use in various industrial applications. To a great extent, their toxic action, such as in the livers of animals and humans, involves free radicals.[1] However, even for halogenated methanes, despite the general simplicity of C-1 chemistry, the detailed degradation mechanisms are not known. The reason for this lack of understanding is that no suitable model systems have been proposed to study the independent reactive fates of the most important intermediates, namely, halogenated peroxyl and alkoxyl radicals and hydroperoxides. Recently, it has been shown that the chemistry of halogenated alkoxyl radicals can be conveniently studied through the reaction of halogenated alkylperoxyl radicals with organic sulfides[2–5] or iodide,[6,7] via an effective multielectron oxidation mechanism.

In this work, we explore another model system for the study of $RHalO^\bullet$-induced (Hal = halogen) reaction mechanisms, employing the interaction of peroxyl radicals derived from CH_2Cl_2 and CH_2Br_2 with Me_2Se, a compound known to be a good electron donor. We show that the use of such well-defined model systems allows for progress to be made in both the qualitative and quantitative understanding of the degradation processes.

For this study, we selected CH_2Cl_2 as one of the most widely used halogenated solvent (and chose CH_2Br_2 for comparative purposes). CH_2Cl_2 does not occur naturally but is produced in large amounts: its world production in 1980 was estimated to be 570 000 tonnes/year, and a similar amount was produced in 1992.[8] About 80% of the world production of CH_2Cl_2 is emitted into the atmosphere during its use as a solvent and in paint removers, aerosols, solvent degreasers, and fumigants. The major sources of CH_2Cl_2 emission are the wood pulp and paper industry, water treatment facilities, and the chemical and pharmaceutical industries.[9] The atmospheric lifetime of CH_2Cl_2 is 5–6 months.[10] CH_2Br_2 finds limited use in chemical synthesis, as a solvent, and as a gage fluid.[11] Natural production by marine algae also adds to its environmental input. The estimated half-

---

* To whom correspondence should be addressed. E-mail: roman.flyunt@iom-leipzig.de.

[†] On leave from National Academy of Science of the Ukraine.

[‡] Leibniz-Institut für Oberflächenmodifizierung (IOM).

[§] LEAP Technologies.

[||] Ruđer Bošković Institute.

10.1021/jp711894k CCC: $40.75

TABLE 1: Yields, Expressed as *G*, of Me_2SeO and $(Me_2Se)_2^{\bullet +}$ Formed in the Reaction of Me_2Se with Different Oxidants and Rate Constants for Me_2Se Oxidation

system	$G(Me_2SeO)^a$	$G(Me_2Se)_2^{\bullet + b}$	G (10^{-7} mol J^{-1}) (oxidant)	rate constant for Me_2Se oxidation (M^{-1} s^{-1})
1 mM Me_2Se,N_2O-saturated	1.2	4.4	5.5 ($^{\bullet}OH$)	7.7×10^9
10 mM CH_2Cl_2,1 mM Me_2Se, 1 vol % 2-propanol,air-saturated	3.4	0.48	2.3 ($CH_2ClOO^{\bullet}$)	7.5×10^7
10 mM CH_2Br_2,1 mM Me_2Se, 1 vol % 2-propanol,air-saturated	4.5	0.98	3.2 ($CH_2BrOO^{\bullet}$)	6.0×10^7

[a] γ-Radiolysis (dose rate, 0.37 Gy s^{-1}). [b] Pulse radiolysis.

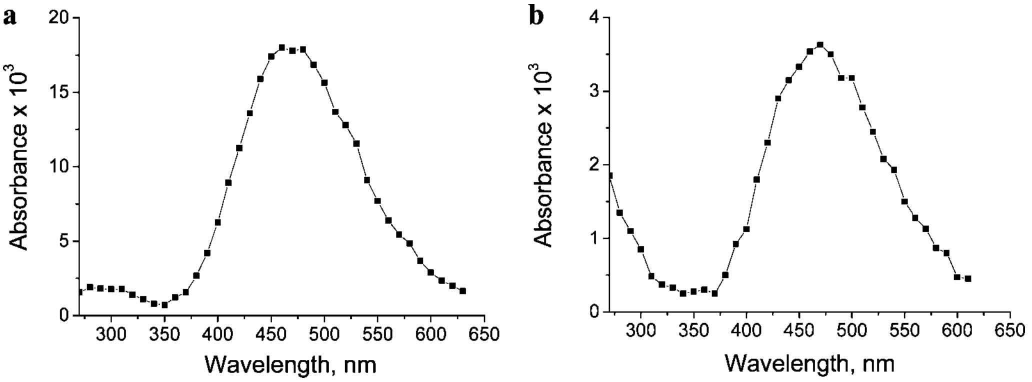

Figure 1. Optical spectra of $(Me_2Se)_2^{\bullet +}$ obtained by pulse radiolysis (dose per pulse, 3.6 Gy; path length, 1 cm) for aqueous solutions containing 1 mM Me_2Se at pH 6 in (a) N_2O-saturated solution, with the oxidizing radical $^{\bullet}OH$ (spectrum taken 3.5 μs after the pulse), and (b) air-saturated solution also containing 1 vol % 2-propanol and 10 mM CH_2Br_2, with the oxidizing radical $CH_2BrOO^{\bullet}$ (spectrum taken 50 μs after the pulse).

life for the atmospheric reaction of CH_2Br_2 with hydroxyl radicals is 213 days.[11]

The U.S. Environmental Protective Agency (EPA) has classified CH_2Cl_2 and CH_2Br_2 as group B2, probable human carcinogens, clearly indicating both the medical and environmental relevance of any studies on these halogenated alkanes.

Despite their biological relevance,[12–14] the free-radical chemistry of selenium-containing compounds has been investigated relatively poorly.[15,16] This encouraged us to study the role of Me_2Se as a model electron-donating compound in reactions with the oxidizing free radicals $RHalOO^{\bullet}$ and $RHalO^{\bullet}$.

Experimental Section

All chemicals were of analytical grade and were used without further purification. They were supplied by Aldrich [NaCl, NaBr, HCOONa, Na_2CO_3, 2-propanol, acetone, formaldehyde, CH_2Cl_2, CH_2Br_2, and superoxide dismutase (SOD, from bovine liver, 2000−6000 units/mg of protein)] or by Strem Chemicals, Inc. (Me_2Se).

Solutions were always freshly prepared shortly before irradiation using Millipore-filtered water ($R > 18$ MΩ).

γ-Radiolysis was carried out in the field of a ^{60}Co γ-source. Total absorbed doses, as determined by Fricke dosimetry,[17] were in the range of 50−300 Gy. Pulse radiolysis experiments were performed using 50-ns pulses of 8 or 12 MeV electrons from a linear electron accelerator (Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, IN, or Institut für Oberflächenmodifizierung e.V., Leipzig, Germany, respectively). Time-resolved optical absorption spectrometry was used as the detection method. Other details about the equipment and the analysis of data have been described elsewhere.[18–20]

Ionic products HCO_2^-, Cl^-, and Br^- (including CO_2 analyzed in the form of HCO_3^- ions) were measured by high-performance ion chromatography (HPIC) on a Dionex 2010i machine. The yields of CO were analyzed by gas chromatography (GC), using a molecular sieve 5A column, helium as the carrier gas, a thermoconductivity detector, and the headspace technique.

Me_2SeO was determined by high-performance liquid chromatography (HPLC) using Millipore water as the eluent at 1 mL min^{-1} and UV detection at 205 nm. Reference Me_2SeO was prepared from a solution of 0.1 M Me_2Se and 1 mM H_2O_2 under stirring at room temperature within 24 h of analysis. A 100-fold excess of Me_2Se was taken in order to avoid further oxidation of Me_2SeO to Me_2SeO_2.

Formaldehyde and acetone were determined by HPLC as the corresponding 2,4-dinitrophenylhydrazones.[21]

All radiation chemical yields in this article are reported in units of 10^{-7} moles per joule of absorbed energy, denoted by *G*. The factor of 10^{-7} and the units, moles per joule, are not explicitly included throughout the text for the reason of simplicity. In the case of steady-state measurements of stable final product yields, the *G* values were determined by the standard procedure, that is, from the initial slopes of concentration−dose plots, typically covering four to five measurements. All experiments were performed at room temperature. Error limits of all radiation-based data are estimated to about ±10%.

Quantum-chemical calculations were carried out using the Gaussian 03 package.[22] For the systems under study, geometries were optimized by applying the density functional theory (DFT) approach with the B3LYP hybrid functional.[23,24] Using unscaled vibrations, frequency analyses were performed to characterize the stationary points on the potential surface and to obtain zero-point energies (ZPEs) and thermochemical properties, such as the enthalpy (*H*) and Gibbs energy (*G*) at standard temperature (298.15 K) and pressure (1 atm). For geometry optimizations, the standard 6-31G(d,p) basis sets[25] were used. To investigate the influence of a solvent on the molecular structure of the radicals, geometry optimizations were carried out using the self-consistent reaction field (SCRF) polarized continuum model (PCM) approach.[26,27] To validate the performance of the model used, the calculations on radical anions in water were done also with the 6-311+G(d,p) basis set and SCRF=CPCM.[28,29] However, the calculated reaction parameters differed by less than 1 kcal/mol from those calculated with the 6-31G(d,p) basis set and SCRF=PCM.

Results and Discussion

Primary Processes. Radiolysis of water leads to the formation of three highly reactive radical species: hydrated electrons (e_{aq}^-), hydroxyl radicals ($^{\bullet}OH$), and hydrogen atoms ($H^{\bullet}$).[30] In addition, some hydrogen peroxide, protons, and molecular hydrogen are also formed, as summarized in eq 1.

$$H_2O \xrightarrow{\text{high energy radiation}} e_{aq}^-, {}^{\bullet}OH, H^{\bullet}, H_2O_2, H_{aq}^+, H_2 \quad (1)$$

In dilute aqueous solutions, the radiation chemical yield of these species are $G = 2.9$ for e_{aq}^- and $^{\bullet}OH$ and $G = 0.6$ for $H^{\bullet}$.

All γ-radiolysis and most of the pulse-radiolysis experiments in the present work were carried on air-saturated aqueous solutions containing 1 vol % 2-propanol (0.13 M), 10 mM CH_2Cl_2 or CH_2Br_2, and 1 mM Me_2Se at natural pH of about 6. In such systems, hydrated electrons react mainly with CH_2Cl_2 (CH_2Br_2) giving halogenated alkyl radicals ($k_2 = 6.3 \times 10^9$ and 2.0×10^{10} M^{-1} s^{-1} for CH_2Cl_2 and CH_2Br_2, respectively)[30]

$$e_{aq}^- + CH_2Hal_2 \rightarrow Hal^- + {}^{\bullet}CH_2Hal \quad (2)$$

In air-saturated solution, $^{\bullet}CH_2Hal$ radicals are quantitatively transformed into the corresponding peroxyl radicals through the fast addition of molecular oxygen ($k_3 \approx 2.0 \times 10^9$ M^{-1} s^{-1} for both chloro- and bromomethyl radicals[30]).

$${}^{\bullet}CH_2Hal + O_2 \rightarrow CH_2HalOO^{\bullet} \quad (3)$$

Another possible reaction of hydrated electrons is an interaction with dissolved oxygen, reaction 4, contributing somewhat to the scavenging of e_{aq}^-, although to a minor extent ($[O_2] = 2.8 \times 10^{-4}$ M in air-saturated solution, $k_4 = 2.2 \times 10^{10}$ M^{-1} s^{-1}).[30]

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet -} \quad (4)$$

Reaction of Me_2Se with e_{aq}^- was of no importance in any of the systems studied, because of its comparatively low rate constant (2×10^8 M^{-1} s^{-1}).[15]

In the studied systems, hydrogen atoms reacted mainly with 2-propanol, generating $(CH_3)_2C^{\bullet}OH$ ($k = 7.4 \times 10^7$ M^{-1} s^{-1}).[30] The reaction of $H^{\bullet}$ with CH_2Cl_2 is too slow ($k = 4 \times 10^6$ M^{-1} s^{-1})[30] to make any contribution. The corresponding reaction with CH_2Br_2, however, is 2 orders of magnitude faster ($k = 4.1 \times 10^8$ M^{-1} s^{-1}),[30] causing a small extra degradation of CH_2Br_2 (reduction to $Br^- + H^+ + {}^{\bullet}CH_2Br$ with $G \approx 0.1$). Other reactions, namely, addition to Me_2Se ($k = 4.1 \times 10^9$ M^{-1} s^{-1})[15] and O_2 ($k = 1.2 \times 10^{10}$ M^{-1} s^{-1}),[30] contributed negligibly to $H^{\bullet}$ scavenging.

Hydroxyl radicals were almost exclusively (96%) scavenged by 2-propanol in the systems considered here ($k_5 = 1.6 \times 10^9$ M^{-1} s^{-1}),[30] whereas the remaining 4% reacted with Me_2Se. The main product of reaction 5 is the reducing $(CH_3)_2C^{\bullet}OH$ radical ($G = 2.5$).[31,32] The minor product, $CH_3CH(OH)CH_2^{\bullet}$ radical ($G = 0.4$), is redox-inert.[32]

$${}^{\bullet}OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2C^{\bullet}OH/{}^{\bullet}CH_2CH(CH_3)OH \quad (5)$$

In the presence of O_2, the C-centered radicals derived from 2-propanol are quantitatively transformed into the corresponding peroxyl radicals ($k_{6a} = 4.2 \times 10^9$ M^{-1} s^{-1}).[30]

$$(CH_3)_2C^{\bullet}OH + O_2 \rightarrow (CH_3)_2C(OH)OO^{\bullet} \rightarrow (CH_3)_2C{=}O + HO_2^{\bullet} \quad (6a,b)$$

The latter species undergo first-order decomposition with $k_{6b} = 665$ s^{-1}.[33] Under the applied conditions (low radical concentration, particularly in the γ-radiolysis experiments), reaction 6b dominates over possible bimolecular disappearance and thus is responsible for the generation of high yields of $HO_2^{\bullet}/O_2^{\bullet -}$.

The other peroxyl radical, $CH_3CH(OH)CH_2OO^{\bullet}$, formed from 2-propanol disappears mostly by cross-termination with superoxide, giving organic hydroperoxide[34]

$$CH_3CH(OH)CH_2OO^{\bullet} + O_2^{\bullet -} + H^+ \rightarrow O_2 + CH_3CH(OH)CH_2OOH \quad (7)$$

Indeed, some organic peroxide has been detected in γ-irradiated air-saturated aqueous solutions of 2-propanol in the absence of CH_2Cl_2/CH_2Br_2 and Me_2Se, with an approximate yield of $G = 0.3$.[34]

Nonhalogenated peroxyl radicals, like those derived from 2-propanol, are only weakly oxidizing agents[30] and are assumed not to react with the Me_2Se present in our systems, or in any case, such a reaction is most probably too slow to compete with other processes mentioned (reactions 6b and 7).

The reaction of $(CH_3)_2C^{\bullet}OH$ with CH_2Cl_2 is relatively slow ($k = 1 \times 10^6$ M^{-1} s^{-1})[30] and is completely suppressed by reaction 6a. In the systems with CH_2Br_2, some minor fraction of $(CH_3)_2C^{\bullet}OH$ radicals reduces this halogenated methane via reaction 8

$$(CH_3)_2C^{\bullet}OH + CH_2Br_2 \rightarrow (CH_3)_2CO + H^+ + Br^- + {}^{\bullet}CH_2Br \quad (8)$$

The yield of this reaction, $G \approx 0.32$, was obtained from the difference between the experimentally determined value of $G(-CH_2Br_2)_{total} = 3.2$ (see below) and $G(-CH_2Br_2) = 2.88$ calculated for the reaction of CH_2Br_2 with hydrated electrons and hydrogen atoms ($G = 2.75$ and 0.13, respectively). An overall yield of $(CH_3)_2C^{\bullet}OH$ radicals formed via reactions with $^{\bullet}OH$ and $H^{\bullet}$ should be equal to 2.84 in CH_2Br_2-containing systems. Using these data and the known value of k_{6a}, the value of the rate constant $k_8 \approx 1.6 \times 10^7$ M^{-1} s^{-1} can be now estimated. This value is in good agreement with rate constants reported for bromide elimination from some other organic bromides (e.g., halothane, bromouracil) with $(CH_3)_2C^{\bullet}OH$.[35]

Determination of $CH_2ClOO^{\bullet}$ and $CH_2BrOO^{\bullet}$ Yields. The yields of peroxyl radicals $CH_2ClOO^{\bullet}$ and $CH_2BrOO^{\bullet}$ studied here should be equal to the yields of $^{\bullet}CH_2Cl$ and $^{\bullet}CH_2Br$ produced upon one-electron reduction of CH_2Cl_2 and CH_2Br_2, respectively, by e_{aq}^-, $H^{\bullet}$, and $(CH_3)_2C^{\bullet}OH$. Because none of these reactions proceeded quantitatively under the applied conditions, the actual yields were determined experimentally. This was done by measuring the yields of the corresponding halides, Cl^- and Br^-, in γ-irradiated systems. They amounted to $G(Cl^-) = 4.6$ for the CH_2Cl_2-containing system and $G(Br^-) = 6.4$ for the CH_2Br_2-containing system. Because one halide ion is freed per each $CH_2ClOO^{\bullet}/CH_2BrOO^{\bullet}$ radical formed and because further reactions of these peroxyl radicals are assumed to lead to their complete dehalogenation and liberation of the second halide ion, the corresponding yields were calculated to be $G(CH_2ClOO^{\bullet}) = 2.3$ and $G(CH_2BrOO^{\bullet}) = 3.2$. These values are listed in Table 1.

TABLE 2: Products, Yields (in Terms of G), and Selectivities of Formation for the γ-Radiolysis of Air-Saturated Aqueous Solutions of 10 mM CH_2Cl_2 or CH_2Br_2 in the Presence of 1 vol % 2-Propanol and 1 mM Me_2Se[a]

product	CH_2Cl_2 G (10^{-7} mol J^{-1})	selectivity (%)[d]	CH_2Br_2 G (10^{-7} mol J^{-1})	selectivity (%)[d]
Hal^-	4.6	200	6.4	200
HCO_2H	0.3	13	0.3	9.5
CH_2O	0.4	18	0.9	28
CO_2	0.7	30	0.8	25.0
CO	0.9	39	1.2	37.5
Me_2SeO[b]	3.0	130	4.0	125
$(Me_2Se)_2^{+•}$	0.4[e]	17.5[f]	0.9[e]	28[f]
$CH_2HalOO•/CH_2HalO^•$	2.3[g]	100[h]	3.2[g]	100[h]
total carbon[c]	2.3	100	3.2	100

[a] pH 6; dose rate, 0.37 Gy s^{-1}. [b] Yields corrected for the formation of Me_2SeO in the system without RHal and for disproportionation of $(Me_2Se)_2^{+•}$ species (reactions 11 and 12). [c] Total carbon yield calculated as the sum of the radiation yields of HCO_2H, CH_2O, CO_2, and CO. [d] Calculated as 100 × [G(product)/G(total C)]. [e] Yields corrected for $(Me_2Se)_2^{+•}$ formation in the system without RHal. [f] Calculated as 100 × [$G(Me_2Se)_2^{+•}/G(CH_2HalOO^•)$]. [g] Calculated as $G(CH_2HalOO^•) = G(CH_2HalO^•) = G(Hal^-)/2$. [h] Assumed quantitative transformation of $^•CH_2Hal$ into $CH_2HalOO^•$ and of $CH_2HalOO^•$ into $CH_2HalO^•$.

Oxidation Mechanism of Me_2Se. ***Reactions Induced by $^•OH$.*** In aqueous solution, $^•OH$ radicals react with Me_2Se with the overall rate constant of $k_9 = 7.7 \times 10^9$ M^{-1} s^{-1},[15] mostly via an addition mechanism (79%), the minor route being a H-atom abstraction reaction from the methyl group (21%)

$$^•OH + Me_2Se \rightarrow Me_2Se^•{-}OH/CH_3SeCH_2^• + H_2O \quad (9)$$

The adduct $Me_2Se^•{-}OH$ has an optical absorption maximum at 330 nm with $\varepsilon = 4.6 \times 10^3$ M^{-1} cm^{-1}.[15] Radical $CH_3SeCH_2^•$ has an optical absorption maximum at 290 nm. No direct evidence was found for the possible formation of the monomer radical cation $Me_2Se^{•+}$ from $HO{-}Me_2Se^•$ via OH^- elimination. Instead, the radical adduct appears to react rapidly with a second Me_2Se molecule to establish equilibrium 10 ($k_{forward} = 1.4 \times 10^9$ M^{-1} s^{-1})[15] and produce $(Me_2Se)_2^{•+}$, showing an optical absorption maximum at 470 nm (Figure 1a) with $\varepsilon_{470} = 1.1 \times 10^4$ M^{-1} cm^{-1}.[15] In a N_2O-saturated aqueous solution containing 1 mM Me_2Se, a value of $G(Me_2Se)_2^{•+} = 4.4$ was measured.[15]

$$Me_2Se^•{-}OH + Me_2Se \rightleftharpoons OH^- + (Me_2Se)_2^{•+} \quad (10)$$

The decay of $(Me_2Se)_2^{•+}$ in N_2O- or N_2O/O_2(4:1)-saturated aqueous solutions visibly includes second-order kinetics in the sense that the measured half-lives decreased with increasing dose (radical concentration).[15] In analogy to the established fate of the corresponding sulfur radical cation $(Me_2S)_2^{•+}$,[36] this radical−radical termination mechanism of $(Me_2Se)_2^{•+}$ is assumed to include disproportionation via formation of a dimer dication (reaction 11). The latter should instantly react with water to give 1 equiv of Me_2SeO (reaction 12).[15]

$$2(Me_2Se)_2^{•+} \rightarrow 2Me_2Se + (Me_2Se)_2^{2+} \quad (11)$$

$$(Me_2Se)_2^{2+} + H_2O \rightarrow 2H^+ + Me_2SeO + Me_2Se \quad (12)$$

Reactions with some other radicals (for example, $CH_3SeCH_2^•$ or $H^•$ adduct to Me_2Se) could also contribute to the overall termination of $(Me_2Se)_2^{•+}$. Such reactions do not necessarily lead to Me_2SeO as the final product. Indeed, in our steady-state γ-radiolysis experiment carried out with 1 mM Me_2Se in N_2O-saturated aqueous solution, the yield of Me_2SeO amounted to $G = 1.2$ or only 27% of the yield of $(Me_2Se)_2^{•+}$ ($G = 4.4$). An even lower relative yield of dimethyl sulfoxide was detected in a corresponding dimethyl sulfide-containing system under similar conditions.[37]

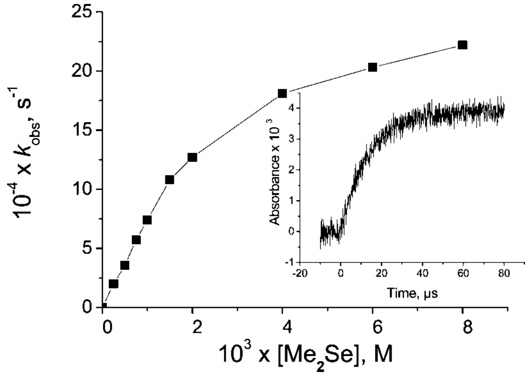

Figure 2. Dependence of k_{obs} for the buildup kinetics of the $(Me_2Se)_2^{•+}$ absorbance at 470 nm on Me_2Se concentration for the reaction of Me_2Se with $CH_2ClOO^•$ in the pulse irradiated air-saturated aqueous solution containing 1 vol % 2-propanol, 10 mM CH_2Cl_2, and different concentrations of Me_2Se. Inset: Buildup kinetics of the $(Me_2Se)_2^{•+}$ absorbance at 470 nm obtained in the solution with 1 mM Me_2Se (dose per pulse, 7 Gy; path length, 1 cm).

Reactions Induced by $CH_2HalOO^•$: Yields and Formation Rate Constants of $(Me_2Se)_2^{•+}$. Pulse radiolysis experiments showed that $(Me_2Se)_2^{•+}$ radical cations are produced as intermediates in the reactions of $CH_2ClOO^•$ and $CH_2BrOO^•$ with Me_2Se. This is demonstrated in Figure 1b for $CH_2BrOO^•$ radicals as reactants. The obtained optical spectrum is identical to the spectrum of $(Me_2Se)_2^{•+}$ shown in Figure 1a. From the known molar extinction coefficient, the yield was calculated to be $G[(Me_2Se)_2^{•+}] = 0.48$ for $CH_2ClOO^•$ and $G[(Me_2Se)_2^{•+}] = 0.98$ for $CH_2BrOO^•$ (Table 1). These values were corrected to 0.40 and 0.90 (see Table 2), because some small amount of $(Me_2Se)_2^{•+}$ ($G = 0.08$) was also formed by the direct reaction of Me_2Se with $^•OH$, as already mentioned.

A typical time versus absorbance trace of $(Me_2Se)_2^{•+}$ formation at 470 nm is displayed in Figure 2 (inset). The kinetics of such traces was always exponential, with the individual k_{obs} values (in s^{-1}) being dependent on the Me_2Se concentration in the manner shown in Figure 2. From the slope of the initial linear part of this plot and a very similar one obtained for $CH_2BrOO^•$, the absolute second-order rate constants for the reactions of $CH_2HalOO^•$ with Me_2Se were determined and are presented in Table 1. The rate constants for both $CH_2ClOO^•$ and $CH_2BrOO^•$ are in the range of 7×10^7 M^{-1} s^{-1}. Similar findings (no difference in reactivity) were reported for the reaction of these radicals with ascorbate and tyrosine anions.[30]

At higher Me_2Se concentrations, the correlation between k_{obs} and Me_2Se concentration deviates from linearity (Figure 2). This is to be expected and, in fact, is typical for most reaction kinetics of halogenated peroxyl radicals[38] due to the fact that reaction 3, that is, the addition of oxygen to alkyl radicals, becomes the rate-limiting step for the Me_2Se oxidation.

From the limiting value of $k_{obs} \geq 22 \times 10^4$ s^{-1} measured for $CH_2ClOO^{\bullet}$ at the highest Me_2Se concentration used, the bimolecular rate constant for the O_2 addition to $^{\bullet}CH_2Cl$, k_3, was evaluated to be on the order of 1×10^9 M^{-1} s^{-1}. This rate constant is in good agreement with previously determined values for other halogenated alkyl radicals.[38]

Me_2SeO Yields. The experimentally determined selenoxide yields of $G(Me_2SeO) = 3.4$ and 4.5, respectively, in CH_2Cl_2- and CH_2Br_2-containing systems (Table 1) are much higher than $G(Me_2Se)_2^{\bullet+}$ and even exceed the yields of the initial oxidants $CH_2HalOO^{\bullet}$. The necessity of the presence of molecular oxygen for Me_2SeO formation was demonstrated in a control system consisting of 10 mM RHal, 1 vol % 2-propanol, and 1 mM Me_2Se in O_2-free, N_2-saturated aqueous solution. The selenoxide yield measured in this solution after γ-irradiation was negligibly small, $G = 0.02$, and can be attributed to the slow reaction of Me_2Se with radiolytically formed H_2O_2. The yield of Me_2SeO in the same system without RHal but in air-saturated solution was $G = 0.3$, as determined immediately after irradiation. Again, this is a considerably smaller yield than that observed in the presence of both RHal and oxygen (see Table 1). In addition to the mentioned reaction of Me_2Se with H_2O_2, some minor radical-induced transformation of Me_2Se by reaction with $^{\bullet}OOCH_2C(CH_3)OH$ and/or $HO_2^{\bullet}/O_2^{\bullet-}$ might contribute here as well. This small blank yield, together with the amount arising from the $(Me_2Se)_2^{\bullet+}$ decay, was subtracted from the measured yields. The resulting corrected yields are listed in Table 2 as $G(Me_2SeO)$.

It is important to point out that the observed $(Me_2Se)_2^{\bullet+}$ yields are relatively low, amounting to only 17.5% and 28% of the yields of the initial reactants $CH_2ClOO^{\bullet}$ and $CH_2BrOO^{\bullet}$, respectively. Taking into account the fact that only 27% of the $(Me_2Se)_2^{\bullet+}$ radical ions lead to Me_2SeO, the maximum possible contribution of $(Me_2Se)_2^{\bullet+}$ as a precursor of Me_2SeO is of only minor significance [$G(Me_2SeO) \approx 0.1$ and 0.2 from this route for the CH_2Cl_2 and CH_2Br_2 systems, respectively].

The above blank experiments indicate that neither the peroxyl radicals derived from 2-propanol or $HO_2^{\bullet}/O_2^{\bullet-}$ nor H_2O_2 can be responsible for the high Me_2SeO yields that are observed only in the systems containing RHal and oxygen.

It should be mentioned at this point that postirradiation effects were observed in both systems regarding the yield of Me_2SeO. For example, a value of $G(Me_2SeO) = 3.4$ was measured in the CH_2Cl_2-containing system (Table 2) directly after γ-irradiation. This value increased to $G = 4.1$ during the postirradiation time (3.5 h at room temperature in the dark). Because the chloride yield did not change ($G = 4.6$), the increase of $G(Me_2SeO)$ can be attributed only to the slow reaction of Me_2Se with H_2O_2. Taking into account the fact that the time of irradiation and the postirradiation period before Me_2SeO analysis were always minimized (<20 min), the postirradiation effects in the studied systems could be neglected.

SOD Experiments. To establish a possible role of superoxide, $O_2^{\bullet-}$, in the overall reaction mechanism, especially considering Me_2SeO formation, an experiment was conducted in the presence of 25 mg/L superoxide dismutase (SOD). Under such conditions, $O_2^{\bullet-}$ reacts exclusively with SOD (reported rate constants are in the range from 1×10^8 to 1×10^9 M^{-1} s^{-1} [39]). In our experiments $O_2^{\bullet-}$ was formed in a high yield of $G \approx 5$ via reactions 4, 6b, 23, 29b, and 34. No difference was found, however, for the Me_2SeO yields in CH_2Cl_2-containing systems with or without SOD. These results suggest that, in the studied systems, $O_2^{\bullet-}$ does not contribute to the formation of Me_2SeO and disappears mostly via dismutation.[39]

Mechanism of $CH_2HalOO^{\bullet}$ Oxidation of Me_2Se. In analogy with the mechanism proposed for Me_2S,[2] the interaction of $RHalOO^{\bullet}$ with Me_2Se most probably proceeds via formation of the transient adduct (reaction 13), which could further transform via three alternative pathways, eqs 14–16

$$\mathrm{RHalOO^{\bullet} + Me_2Se \rightarrow RHalOO{-}Se^{\bullet}(Me)_2} \qquad (13)$$

$$\mathrm{RHalOO{-}Se^{\bullet}(Me)_2 \rightarrow RHalOO^{-} + Me_2Se^{\bullet+}} \qquad (14)$$

$$\mathrm{RHalOO{-}Se^{\bullet}(Me)_2 + Me_2Se \rightarrow RHalOO^{-} + (Me_2Se)_2^{\bullet+}} \qquad (15)$$

$$\mathrm{RHalOO{-}Se^{\bullet}(Me)_2 \xrightarrow{H_2O} RHalO^{\bullet} + Me_2SeO} \qquad (16)$$

$$\mathrm{RHalO^{\bullet} + Me_2Se \rightarrow RHalO^{-} + Me_2Se^{\bullet+}} \qquad (17)$$

$$\mathrm{Me_2Se^{\bullet+} + Me_2Se \rightleftharpoons (Me_2Se)_2^{\bullet+}} \qquad (18)$$

Heterolytic dissociation of the adduct radical formed in reaction 13 leads to a halogenated hydroperoxide anion and the monomer radical cation $Me_2Se^{\bullet+}$ (eq 14), which, in a fast forward reaction of equilibrium 18, gives $(Me_2Se)_2^{\bullet+}$. Reaction 15 leads to the same products but predicts an interaction of $RHalOO{-}Se^{\bullet}(Me)_2$ with a second Me_2Se molecule. Both reactions 14 and 15 should give high yields of $(Me_2Se)_2^{\bullet+}$, and 27% of this species can lead to Me_2SeO formation (reactions 11 and 12). Experimentally observed low yields of $(Me_2Se)_2^{\bullet+}$ and high yields of Me_2SeO are not compatible with any significance of reactions 14 and 15. Therefore, the third route seems to be the predominant, if not the only one occurring. This is reaction 16, in which the adduct $RHalOO{-}Se^{\bullet}(Me)_2$ undergoes homolytic cleavage, which formally constitutes an oxygen transfer but, in fact, is a two-electron transfer process with the assistance of a water molecule.[2,5] Reaction 16 leads to the formation of a halogenated alkoxyl radical and a Me_2SeO molecule. Alkoxyl radicals are known as strong one-electron oxidants,[40] more powerful than the corresponding peroxyl radicals. For example, a reduction potential of $E° = 2.3 \pm 0.3$ V has been reported for the half-reaction $CCl_3O^{\bullet} + e^{-} \rightarrow CCl_3O^{-}$, whereas for the corresponding $CCl_3OO^{\bullet} + e^{-} \rightarrow CCl_3OO^{-}$ half-reaction, the reduction potential amounts to only $E° = 1.15 \pm 0.16$ V.[40] It is, therefore, reasonable to assume that $CH_2HalO^{\bullet}$ radicals would undergo reaction 17, thereby producing $Me_2Se^{\bullet+}$. The latter leads to $(Me_2Se)_2^{\bullet+}$ via equilibrium 18. Thus, it is the $CH_2HalO^{\bullet}$ alkoxyl radical rather than its precursor $CH_2HalOO^{\bullet}$ that oxidizes Me_2Se into $(Me_2Se)_2^{\bullet+}$.

If one assumes that reactions 13 and 16 occur quantitatively, the yields of both $CH_2HalO^{\bullet}$ and Me_2SeO should be equal to the yield of their precursor $CH_2HalOO^{\bullet}$. The Me_2SeO yields even exceed this amount (Table 1), indicating formation of the same product by still another process. $(Me_2Se)_2^{\bullet+}$, a direct successor of $CH_2HalO^{\bullet}$, was formed, but in yields much below the expected values. This suggests that $CH_2HalO^{\bullet}$ radicals undergo some additional reaction(s) in competition with reaction 17. These additional reactions of $CH_2HalO^{\bullet}$ radicals are analyzed in the next section. For now, this finding can be used to assign the reactions to which the measured second-order rate constants for $(Me_2Se)_2^{\bullet+}$ formation (Table 1) belong. Specifically, at lower Me_2Se concentrations, where k_{obs} increases linearly with Me_2Se conccentration (Figure 2), either reaction 13 or 17 could be

TABLE 3: Activation Energies (E_a), Reaction Enthalpies (ΔH), and Gibbs Free Energies (ΔG) Calculated with B3LYP/6-31G(d,p)/SCRF=PCM for the Reactions of Halogenated Methyloxyl Radicals in Water

alkoxyl radical	reaction	products	E_a (kcal/mol)	ΔH (kcal/mol)	ΔG (kcal/mol)
$CH_2ClO^•$	1,2 H-atom shift	$•CHClOH$	32.8	−8.9	−8.5
$CH_2ClO^•$	X-elimination	$Cl^• + CH_2O$	–	+11.0	+3.8
$CH_2BrO^•$	1,2 H-atom shift	$•CHBrOH$	34.9	−8.8	−8.2
$CH_2BrO^•$	X-elimination	$Br^• + CH_2O$	–	+3.1	−3.9

responsible for the observed rate of $(Me_2Se)_2^{•+}$ formation. [The dimerization of $Me_2Se^{•+}$ into $(Me_2Se)_2^{•+}$, equilibrium 18, is too fast to have any influence.] However, if the observed kinetics is defined by the rate of $CH_2HalO^•$ decay, then the initial straight part of the line in Figure 2 should show a considerable intercept on the *y* axis belonging to the reaction in competition with reaction 17. However, practically no intercept is observed, strongly indicating that reaction 13 [i.e., formation of the adduct $RHalOO{-}Se^•(Me)_2$] is slower and, therefore, the rate-limiting step for all other reactions occurring subsequently. This allows the conclusion that reaction 17 occurs with a rate constant well above 7×10^7 M^{-1} s^{-1} and also places the rate of the reaction occurring in competition with reaction 17 in the range of $>10^5$ s^{-1}.

Degradation of $CH_2HalO^•$ Radicals. ***Material Balance.*** The yields of carbon-containing products originating from CH_2Cl_2 or CH_2Br_2 are listed in Table 2. These products are HCO_2H, CH_2O, CO_2, and CO. A total material balance was obtained in accordance with the condition that $G(Cl^-)$ and $G(Br^-)$ amount to twice the value of *G*(total C). The latter was calculated as the sum of $G(HCO_2H) + G(CH_2O) + G(CO_2) + G(CO)$. The results reflect the respective 2:1 composition in CH_2Cl_2 and CH_2Br_2.

In the following sections, various reaction routes and their associated stoichiometries are presented and discussed, taking CH_2Cl_2 as an example.

Mechanism of $CH_2ClO^•$ Formation. It was assumed that, in the investigated systems, the oxidation of Me_2Se is the only reaction that $CH_2ClOO^•$ radicals undergo and that this reaction occurs exclusively by the two-electron transfer mechanism, reactions 13 and 16. The process leads to the formation of 1 equiv of Me_2SeO and alkoxyl radical per each $CH_2ClOO^•$ radical. Therefore, all of the carbon-containing products derived from CH_2Cl_2 must be due to further reactions of $CH_2ClO^•$.

Reactions of $CH_2ClO^•$ Radicals. In principle, three reactions are possible: one-electron oxidation of Me_2Se, chlorine-atom elimination, and isomerization via 1,2 H-atom shift (see eqs 17, 19, and 22, respectively).

First, a possible chlorine-atom elimination (β-scission) from $CH_2ClO^•$ (reaction 19)

$$CH_2ClO^• \rightarrow CH_2O + Cl^• \qquad (19)$$

$$Cl^• + (CH_3)_2CHOH \rightarrow HCl + (CH_3)_2C^•OH/{}^•CH_2CH(CH_3)OH \qquad (20)$$

is neglected for the following reasons: (a) There is no extra yield of acetone (an ultimate product from the reaction of Cl atoms and 2-propanol, reaction 20, $k = 6 \times 10^9$ M^{-1} s^{-1} [41]) compared to the blank system without CH_2Cl_2 and Me_2Se, where acetone is formed through $^•OH$ scavenging by 2-propanol (reactions 5 and 6a,b). (b) As shown by quantum-chemical calculations, reaction 19 is endothermic ($\Delta H = 11.0$ kcal/mol and $\Delta G = 3.8$ kcal/mol), whereas the 1,2 H-atom shift is exothermic ($\Delta H = -8.9$ kcal/mol and $\Delta G = -8.5$ kcal/mol; see Table 3), making the latter much more probable. (c) Reaction 19 was found to be unimportant in the gas phase.[42] Although these three arguments clearly eliminate chlorine-atom cleavage, the other two reactions and the subsequent chemical transformations of their products by routes 1−4 are shown in the following sections to be responsible for the observed results.

Route 1. As has already been discussed, $CH_2ClO^•$ radicals are assumed to oxidize Me_2Se by a 1e-transfer mechanism giving $(Me_2Se)_2^{•+}$ (reactions 17 and 18). The other complementary product, CH_2ClO^-, decomposes to give formaldehyde via Cl^- elimination (reaction 21), which in analogy with the decay of trichloromethanol ($CCl_3OH \rightarrow H^+ + Cl^- + COCl_2$, $k > 8 \times 10^4$ s^{-1} [43]) is expected to be fast.

$$CH_2ClO^- \rightarrow Cl^- + CH_2O \qquad (21)$$

This explains the formation of $(Me_2Se)_2^{•+}$ as an intermediate and formaldehyde as a final product, both with radiation yields of $G = 0.4$. From the relationship to $G(Cl^-)$, the contribution of this route is 18%.

$$\text{Overall stoichiometry for route 1:} \quad Cl^- + CH_2O + (Me_2Se)_2^{•+}$$

Routes 2a,b. We propose that reaction 22 occurs in competition with $CH_2ClO^•$ oxidation of Me_2Se (route 1). It represents a 1,2 H-atom shift in analogy to other alkoxyl radicals[44–48] with typical rate constants on the order of 10^5−10^6 s^{-1}. For halogenated methyl alkoxyl radicals, such a rearrangement was proposed in ref 49. The carbon-centered radicals produced in reaction 22 add oxygen and then eliminate $HO_2^•$ (reaction 23, well-known from α-hydroxylalkylperoxyl radicals studies[50]). The resulting formyl chloride mostly (94%) decomposes to carbon monoxide (route 2a; reaction 24, $k = 10^4$ s^{-1} [51]) and, to a minor extent, hydrolyzes to formic acid (route 2b; 6%, reaction 25).[51] Formyl bromide reacts similarly, giving CO and HCO_2H in 92% and 4% yields, respectively.[52]

$$CH_2ClO^• \rightarrow {}^•CHCl(OH) \qquad (22)$$

$${}^•CHCl(OH) + O_2 \rightarrow HO_2^• + HC(O)Cl \qquad (23)$$

$$HC(O)Cl \rightarrow HCl + CO \qquad (24)$$

$$HC(O)Cl + H_2O \rightarrow HCl + HCO_2H \qquad (25)$$

$$\text{Overall stoichiometry for route 2a:} \quad Cl^- + CO$$

$$\text{Overall stoichiometry for route 2b:} \quad Cl^- + HCO_2H$$

Based on the CO yield, the contribution of route 2a (the only possible source of CO in the present system) in the overall degradation of CH_2Cl_2 was calculated to be 39%. Because CO and formic acid arise from a common precursor, namely, HC(O)Cl, only up to $G(HCO_2H) = 0.05$ (or only about 2% of the overall CH_2Cl_2 degradation) could be assigned to route 2b. The remaining $G(HCO_2H) = 0.25$ must be formed via another route.

Route 3. A reasonable alternative to oxygen addition to $^•CHCl(OH)$ might be a fast HCl elimination (reaction 26) and generation of formyl radicals, $H{-}C^•{=}O$

$$^{\bullet}\mathrm{CHCl(OH)} \rightarrow \mathrm{HCl} + \mathrm{H{-}C^{\bullet}{=}O} \tag{26}$$

In the gas phase, HCl elimination from $CH_2ClO^{\bullet}$ is known to occur from a three-centered transition state with a rate constant of $k_{27} = 1.3 \times 10^{4}\ \mathrm{s^{-1}}$ [42]

$$\mathrm{CH_2ClO^{\bullet}} \rightarrow \mathrm{HCl} + \mathrm{H{-}C^{\bullet}{=}O} \tag{27}$$

Reaction 27 is stoichiometrically equivalent to the combination of reactions 22 and 26. Because reaction 22 could be significantly accelerated through the assistance of water and deprotonation of the rearranged radical $^{\bullet}CHCl(OH)$ with a subsequent rapid chloride elimination, any contribution of reaction 27 in aqueous solutions can be neglected. A fast elimination of HCl from geminal chlorohydrines in water, for example, $^{\bullet}CCl_2{-}CCl_2OH \rightarrow H^+ + Cl^- + {}^{\bullet}CCl_2{-}C(O)Cl$, $k > 7 \times 10^{5}\ \mathrm{s^{-1}}$,[53] supports the conclusion that reaction 26 can effectively compete with oxygen addition to $^{\bullet}CHCl(OH)$ radicals.

$H{-}C^{\bullet}{=}O$, an acyl type of radical, can undergo hydration (reaction 28a), followed by a fast oxygen addition (reaction 29a). The dihydroxymethylperoxyl radicals thus formed suffer fast decomposition to form HCO_2H and $HO_2^{\bullet}$ ($k_{29b} > 10^{6}\ \mathrm{s^{-1}}$ [50])

$$\mathrm{H{-}C^{\bullet}{=}O} + \mathrm{H_2O} \rightleftharpoons \mathrm{HC^{\bullet}(OH)_2} \tag{28a,b}$$

$$\mathrm{HC^{\bullet}(OH)_2} + \mathrm{O_2} \rightarrow \mathrm{HC(OH)_2OO^{\bullet}} \rightarrow \mathrm{HO_2^{\bullet}} + \mathrm{HCO_2H} \tag{29a,b}$$

Overall stoichiometry for route 3: $Cl^- + HCO_2H$

Based on $G(HCO_2H) = 0.25$, the contribution of route 3 is about 11%.

Route 4. As an alternative to the hydration of formyl radicals (reaction 28a), oxygen addition (reaction 30a) should also be taken into consideration.

$$\mathrm{H{-}C^{\bullet}{=}O} + \mathrm{O_2} \rightarrow \mathrm{HC(O)OO^{\bullet}} \rightarrow \mathrm{HO_2^{\bullet}} + \mathrm{CO} \tag{30a,b}$$

Formylperoxyl radical $HC(O)OO^{\bullet}$ and its dimer $[HC(O)OO]_2$ were successfully matrix isolated in solid O_2 at 13−18 K from UV photooxidation of solid O_2/H_2CO and $O_2/\mathit{trans}\text{-}H_2C_2O_2$ samples, respectively.[54] In refs 55− 57, the assumption was made that $HC(O)OO^{\bullet}$ is probably an intermediate in the atmospheric process in which reaction 30a is followed by the cleavage reaction 30b (overall $k_{30a,b} = 6.2 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$).[56] Most likely, reaction 30b is the rate-determining step. However, an absolute conversion of rate constants might not be feasible because the chemistry of formylperoxyl radicals in aqueous solutions might be different from that in the gas phase. It should be pointed out that formylperoxyl radicals $HC(O)OO^{\bullet}$, in fact, represent the simplest of acylperoxyl radicals. It has been shown that the nearest analogue, the acetylperoxyl radical, $CH_3C(O)OO^{\bullet}$, is the most reactive peroxyl radical known.[58] Hence, the reactivity of formylperoxyl radicals toward Me_2Se is expected to be much higher than that of $CH_2ClOO^{\bullet}$, i.e., the pseudo-first-order rate constant for reaction 32 should be on the order of $>7.5 \times 10^{4}\ \mathrm{s^{-1}}$ at 1 mM Me_2Se based on the determined rate constant for the reaction of $CH_2ClOO^{\bullet}$ with Me_2Se, $7.5 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$.

Reference 59 is the only work in which indirect generation of formylperoxyl radicals in aqueous solution has been postulated. According to the authors,[59] $HC(O)OO^{\bullet}$ radicals undergo hydrolysis followed by $HO_2^{\bullet}$ elimination and HCO_2H formation (reactions 31a,b). No carbon monoxide formation was described.

$$\mathrm{HC(O)OO^{\bullet}} + \mathrm{H_2O} \rightarrow \mathrm{HC(OH)_2OO^{\bullet}} \rightarrow \mathrm{HO_2^{\bullet}} + \mathrm{HCO_2H} \tag{31a,b}$$

However, the reported overall rate constant, $k_{31a,b} = 2.5 \times 10^{3}\ \mathrm{s^{-1}}$,[59] is too low for this reaction to compete with a possible reaction of $HC(O)OO^{\bullet}$ with Me_2Se ($>7.5 \times 10^{4}\ \mathrm{s^{-1}}$ as stated above) and, therefore, was not considered as a possible source of HCO_2H in our systems.

An overall two-electron oxidation of Me_2Se by means of formylperoxyl radicals would give Me_2SeO and formyloxyl radicals (reaction 32). The latter, as is typical for alkoxyl radicals, undergo a 1,2 H-atom shift (reaction 33a), followed by a prompt deprotonation (reaction 33b, $pK_a = 2.3$ [60]). A subsequent fast interaction with oxygen produces CO_2 and $O_2^{\bullet-}$ (reaction 34, $k = 2 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$ [61]).

$$\mathrm{HC(O)OO^{\bullet}} + \mathrm{Me_2Se} \rightarrow \mathrm{HC(O)O^{\bullet}} + \mathrm{Me_2SeO} \tag{32}$$

$$\mathrm{HC(O)O^{\bullet}} \rightarrow {}^{\bullet}\mathrm{C(O)OH} \rightleftharpoons \mathrm{H^+} + \mathrm{CO_2^{\bullet-}} \tag{33a,b}$$

$$\mathrm{CO_2^{\bullet-}} + \mathrm{O_2} \rightarrow \mathrm{O_2^{\bullet-}} + \mathrm{CO_2} \tag{34}$$

Overall stoichiometry for route 4: $Cl^- + CO_2 + Me_2SeO$

Route 4 is the only one able to explain the appearance of carbon dioxide among the products. This product is very informative because only alkoxyl radicals, which further suffer a 1,2 H-atom shift, could be its precursor. It should be noted that no carbon dioxide was found upon γ-radiolysis of the same system in the absence of Me_2Se. This demonstrates the essential role of an electron donor, such as Me_2Se in our systems, and formation of $CH_2ClO^{\bullet}$ for the overall degradation process. Based on a value of $G(CO_2) = 0.7$, the contribution of route 4 is 30%.

Mechanistic Considerations. Below is the list of routes necessary to explain the formation of all of the products determined. All of these routes originate from the reaction sequence 2 + 3 + 13/16, which gives 1 equiv each of Cl^- and Me_2SeO.

Route 1: $HCl + CH_2O + (Me_2Se)_2^{\bullet+}$

Route 2a: $HCl + CO$

Route 2b: $HCl + HCO_2H$

Route 3: $HCl + HCO_2H$

Route 4: $HCl + CO_2 + Me_2SeO$

Each route includes one characteristic product from CH_2Cl_2, together with some additional amount of Me_2SeO in route 4. This is in accordance with experimentally determined results for the yield of Me_2SeO exceeding the yield of $CH_2ClOO^{\bullet}$ radicals. Only route 1 explains the formation of $(Me_2Se)_2^{\bullet+}$ radical cations.

The proposed reaction mechanism for the $(Me_2Se)_2^{\bullet+}$ formation via reaction sequences 13, 16, and 17 followed by 18, now accommodates all of the experimental findings. It also allows for the assignment of the measured rate constants in Table 1 to reaction 13 as the slowest and thus the rate-determining step for the observed $(Me_2Se)_2^{\bullet+}$ formation kinetics.

Assuming that all $CH_2ClOO^{\bullet}$ radicals are quantitatively transformed into alkoxyl radicals $CH_2ClO^{\bullet}$, an 18% fraction of these oxyl radicals must react with Me_2Se via a one-electron oxidation (route 1). The remainder undergoes a 1,2 H-atom shift into $^{\bullet}CHCl(OH)$. Further reactions of the latter radical are able to accommodate all other observed products. All carbon-containing products from CH_2Cl_2 (HCO_2H, CO_2, and CO), except for CH_2O, originate from $^•CH(OH)Cl$ radicals, the yield of which can be calculated as the sum of $G(HCO_2H)$, $G(CO_2)$, and $G(CO)$, i.e., $0.3 + 0.7 + 0.9 = 1.9$. This accounts for 82% of all of the $CH_2ClO^•$ radicals taking $G = 2.3$ as their primary yield. Based on the obtained data and the proposed mechanism, it is now possible to estimate rate constants for some other key reactions.

By assuming $k_{23} = 2 \times 10^9$ M^{-1} s^{-1} and using the radiation yields of routes 3 and 4, the rate constant $k_{28a} \approx 2 \times 10^5$ s^{-1} for the hydration of the formyl radical was obtained. This value is 1 order of magnitude higher than that obtained for the hydration of the acetyl radical $CH_3C^•{=}O$.[58] The difference can be explained by the much stronger electron-donating influence of the methyl group compared to that of a H atom, resulting in a significantly lower positive charge on the carbonyl oxygen in $CH_3C^•{=}O$. Finally, $k_{26} \approx 6 \times 10^5$ s^{-1} for the HCl elimination from $^•CH(OH)Cl$ radical could be calculated based on the radiation yields of competing routes 2a,b versus routes 3 and 4. All of the estimated rate constants are in good accordance with the known values for analogous reactions (see above).

Dibromomethane System. In principle, the CH_2Br_2 system should exhibit the same results as the CH_2Cl_2-containing system. The same basic mechanism can be proposed for CH_2Br_2 degradation with somewhat different quantitative contributions of the various routes. It is important to emphasize that the rate constants for HBr elimination (analogous to reaction 26, $k \approx 5 \times 10^5$ s^{-1}) and hydration of $H{-}C^•{=}O$ radicals (reaction 28a, $k \approx 2 \times 10^5$ s^{-1}) calculated from the data obtained for the CH_2Br_2 system are in a very good agreement with those obtained for CH_2Cl_2. It should be pointed out that, in both the CH_2Cl_2 and CH_2Br_2 systems without Me_2Se, no CO_2 was found, clearly indicating that $HC(O)O^•$ radicals, necessary precursors for this product, are not formed. Hence, the mechanism of CH_2Cl_2 and CH_2Br_2 degradation is indeed significantly affected by the presence of an electron donor, such as Me_2Se in this study.

Quantum Chemical Calculations for the Reactions of the Studied Oxyl Radicals. To better understand the properties and reaction pathways of the discussed oxyl radicals, quantum chemical calculations were performed taking into account the influence of water as a dielectric continium. As reported in Table 3, cleavage of halogen atoms from $CH_2ClO^•$ and $CH_2BrO^•$ radicals is an endothermic process, especially for the first species ($\Delta H = 11.0$ kcal/mol and $\Delta G = 3.8$ kcal/mol). Even though the ΔG value for the $CH_2BrO^•$ radicals is slightly negative (-3.9 kcal/mol), cleavage of bromine atom should be less effective than the 1,2 H-atom shift ($\Delta G = -8.2$ kcal/mol, Table 3). In contrast, the 1,2 H-atom shift is an exothermic process for both radicals with $\Delta H = -8.9$ and -8.8 kcal/mol, respectively. Although these reactions exhibit high activation energies (E_a in the range of 33−35 kcal/mol), they are most likely strongly reduced by water assistance (in a five-membered ring transition state), which could not be fully estimated in our calculations.

The results strongly support the conclusion that the 1,2 H-atom shift, reaction 22, is a major process $CH_2ClO^•$ and $CH_2BrO^•$ radicals undergo. The rate constants k_{17} and k_{22} could not explicitly be determined or estimated. Based on the difference between the yields of $(Me_2Se)_2^{•+}$ in the two systems (CH_2Cl_2 and CH_2Br_2) at the same concentration of Me_2Se (1 mM, Table 2), one can conclude, however, that the rate constant for reaction 22 of the brominated species has to be lower than the corresponding rate constant for the chlorinated species. This is in accordance with the values shown in Table 3 and could be explained by the larger size of the bromine atom and, as a result, slower water entrance to the five-membered transition state. On the other hand, the lower rate constant increases the lifetime of the $CH_2BrO^•$ radicals and gives them more time for their reaction with Me_2Se, compared to $CH_2ClO^•$. Therefore, the yield of $(Me_2Se)_2^{•+}$ is more than twice as great in the CH_2Br_2 system.

Conclusions

It has been demonstrated that Me_2Se can be successfully used to generate halogenated alkoxyl radicals and study their chemistry. The latter are formed in a quantitative yield by the two-electron oxidation of Me_2Se by halogenated peroxyl radicals. Halogenated alkoxyl radicals derived from CH_2Cl_2 and CH_2Br_2 undergo either one-electron oxidation of Me_2Se (minor contribution under our conditions) or 1,2 H-atom shift. Further reactions of such isomerized alkoxyl radicals lead either to formyl halide (which ends up mostly as CO) or formyl radical $H{-}C^•{=}O$. It should be pointed out that the chemistry of $H{-}C^•{=}O$ is of considerable interest for atmospheric chemistry. Until now, the method of its generation in appreciable yields in aqueous solution has not been known. The systems proposed in this work allow for conclusions to be drawn on further reactions of formyl radicals such as hydration and oxygen addition en route to the final products HCO_2H and CO_2.

From the toxicological point of view, it is interesting to note that the presence of efficient electron donors leads to the transformation of oxidizing $RHalOO^•$ into the even stronger oxidants $RHalO^•$ and $HC(O)OO^•$ radicals.

Acknowledgment. The authors sincerely thank Prof. Dr. Klaus-Dieter Asmus for his continued interest in our work and appreciate many valuable and supportive discussions with him. Therefore, this paper is dedicated to Prof. Dr. Klaus-Dieter Asmus on the occasion of his 70th birthday. The authors are also thankful to Dr. J. von Sonntag and Dr. W. Knolle (IOM, Leipzig) for their help in some pulse radiolysis experiments and valuable discussions.

References and Notes

(1) Slater, T. F. In *Free Radical Mechanisms in Tissue Injury*; Pion Press: London, 1972; pp 85−170.

(2) Schöneich, C.; Aced, A.; Asmus, K.-D. *J. Am. Chem. Soc.* **1991**, *113*, 375–376.

(3) Flyunt, R.; Makogon, O.; Schöneich, C.; Asmus, K.-D. *Nukleonika* **2000**, *45*, 45–50.

(4) Flyunt, R.; Makogon, O.; Asmus, K.-D. *Radiat. Phys. Chem.* **2002**, *65*, 299–307.

(5) Flyunt, R.; Makogon, O.; Naumov, S.; Schöneich, C.; Asmus, K.-D. *J. Phys. Chem. A* **2007**, *111*, 11618–11625.

(6) Bonifačić, M.; Schöneich, C.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1991**, 1117–1119.

(7) Štefanić, I.; Asmus, K.-D.; Bonifačić, M. *J. Phys. Org. Chem.* **2005**, *18*, 408–416.

(8) From http://www.inchem.org/documents/ehc/ehc/ehc164.htm.

(9) *Toxicological Profile for Methylene Chloride (Update). Draft for Public Comment. Agency for Toxic Substances and Disease Registry (ATSDR)*; Public Health Service, U.S. Department of Health and Human Services: Atlanta, GA, 1998.

(10) Keene, W. C.; Khalil, M. A. K.; Erickson, D. J., III; McCulloch, A.; Graedel, T. E.; Lobert, J. M.; Aucott, M. L.; Gong, S. L.; Harper, D. B.; Kleiman, G.; Midgley, P.; Moore, R. M.; Seuzaret, C.; Sturges, W. T.; Benkovitz, C. M.; Koropalov, V.; Barrie, L. A.; Li, Y. F. *J. Geophys. Res.* **1999**, *104D*, 8429–8440.

(11) From http://www.speclab.com/compound/c74953.htm.

(12) Jacobs, M.; Frost, C. *J. Toxicol. Environ. Health* **1981**, *8*, 575–585.

(13) Clark, L. C.; Combs, G. F.; Turnbull, B. W.; Slate, E. H.; Chalker, D. K.; Chow, J.; Davis, L. S.; Glover, R. A.; Graham, G. F.; Gross, E. G.; Krongrad, A.; Lesher, J. L.; Park, K.; Sanders, B. B.; Smith, C. L.; Taylor, R. *J. Am. Med. Assoc.* **1996**, *276*, 1957–1985.

(14) Ip, C. *J. Nutr.* **1998**, *128*, 1845–1854.

(15) Tobien, T. Ph.D. Thesis, Untersuchungen zur Struktur ungeradzahliger Zwei-Zentren Bindungen. Technische Universität Berlin, Berlin, Germany, 1997.

(16) Assmann, A.; Bonifačić, M.; Brivida, K.; Sies, H.; Asmus, K.-D. *Free Radical Res.* **2000**, *32*, 371–376, and references therein.

(17) Fricke H.; Hart, E. J. *Radiation Chemistry*; Academic Press: New York, 1966; p 167.

(18) Asmus, K.-D. *Methods Enzymol.* **1984**, *105*, 167–178.

(19) Janata, E. *Radiat. Phys. Chem.* **1992**, *40*, 437–443.

(20) Knolle, W.; Müller, U.; Mehnert, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1425–1430.

(21) Lipari, F.; Swarin, S. J. *J. Chromatogr.* **1982**, *247*, 297–306.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian 03*, revision B.02; Gaussian, Inc.: Pittsburgh, PA, 2003.

(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(24) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040–1046.

(25) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998**, *18*, 404–417.

(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1987**, *37*, 785–789.

(27) Rega, N.; Cossi, M.; Barone, V. *J. Chem. Phys.* **1996**, *105*, 11060–11067.

(28) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995–2001.

(29) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669–681.

(30) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886.

(31) Ross, A. B.; Mallard, W. G.; Helman, W. P.; Buxton, G. V.; Huie, R. E.; Neta, P. NDRL−NIST Solution Kinetic Database; National Institute of Standards and Technology (NIST): Gaithersburg, MD, 1998.

(32) Asmus, K.-D.; Möckel, H.; Henglein, A. *J. Phys. Chem.* **1973**, *77*, 1218–1221.

(33) Bothe, E.; Behrens, G.; Schulte-Frohlinde, D. *Z. Naturforsch. B* **1977**, *32*, 886–889.

(34) Flyunt, R.; Leitzke, A.; von Sonntag, C. *Radiat. Phys. Chem.* **2003**, *67*, 469–473.

(35) Neta, P.; Grodkowski, J.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1996**, *25*, 709–1050.

(36) Bonifačić, M.; Möckel, H.; Bahnemann, D.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1975**, 675–685.

(37) Schöneich, C.; Aced, A.; Asmus, K.-D. *J. Am. Chem. Soc.* **1993**, *115*, 11376–11383.

(38) Lal, M.; Schöneich, C.; Mönig, J.; Asmus, K.-D. *Int. J. Radiat. Biol.* **1988**, *54*, 773–785.

(39) Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1041–1100.

(40) Merényi, G.; Lind, J.; Engman, L. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2551–2553.

(41) Mertens, R.; von Sonntag, C. *J. Photochem. Photobiol. A* **1995**, *85*, 1–9.

(42) Kaiser, T. J.; Wallington, T. *J. Phys. Chem.* **1994**, *98*, 5679–5685.

(43) Mertens, R. C.; von Sonntag, C.; Lind, J.; Merenyi, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1259–1961.

(44) Berdnikov, V. M.; Bazhin, N. M.; Fedorov, V. K.; Polyakov, O. V. *Kinet. Catal. (Engl.Transl.)* **1972**, *13*, 986–987.

(45) Gilbert, B. C.; Holmes, R. G. G.; Laue, H. A. H.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1047–1052.

(46) Gilbert, B. C.; Holmes, R. G. G.; Norman, R. O. C. *J. Chem. Res. S* **1977**, 1.

(47) Schuchmann, H.-P.; von Sonntag, C. *J. Photochem.* **1981**, *16*, 289–295.

(48) Schuchmann, M. N.; von Sonntag, C. *J. Phys. Chem.* **1982**, *86*, 1995–2000.

(49) Asmus, K.-D.; Bahnemann, D.; Krischer, K.; Lal, M.; Mönig, J. *Life Chem. Rep.* **1985**, *3*, 1–15.

(50) Bothe, E.; Schulte-Frohlinde, D. *Z. Naturforsch. B* **1980**, *35*, 1035–1039.

(51) Dowideit, P.; Mertens, R.; von Sonntag, C. *J. Am. Chem. Soc.* **1996**, *118*, 11288–11292.

(52) Leitzke, A.; Flyunt, R.; Theruvathu, J. A.; von Sonntag, C. *Org. Biomol. Chem.* **2003**, *1*, 1012–1019.

(53) Köster, R.; Asmus, K.-D. *Z. Naturforsch. B* **1971**, *26*, 1108–1116.

(54) Tso, T.-L.; Diem, M.; Lee, E. K. C. *Chem. Phys. Lett.* **1982**, *91*, 339–342.

(55) Washida, M.; Martinez, R. I.; Bayez, K. D. *Z. Naturforsch. A* **1974**, *29*, 251.

(56) Shibuya, K.; Ebata, T.; Obi, K.; Tanaka, I. *J. Phys. Chem.* **1977**, *81*, 2292–2294.

(57) Reilly, J. P.; Clark, J. H.; Moore, C. B.; Pimentel, G. C. *J. Chem. Phys.* **1978**, *69*, 4381–4394.

(58) Schuchmann, M. N.; von Sonntag, C. *J. Am. Chem. Soc.* **1988**, *110*, 5698–5701.

(59) Barlow, S.; Buxton, G. V.; Murray, S. A.; Salmon, G. A. *J. Chem. Soc., Faraday Trans.* **1997**, *93* (20), 3641–3645.

(60) Flyunt, R.; Schuchmann, M. N.; von Sonntag, C. *Chem. Eur. J.* **2001**, *7* (4), 796–799.

(61) Buxton, G. V.; Sellers, R. M.; McCracken, D. R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1464–1476.

JP711894K