

Kinetic and mechanistic study of the X and XO (X = Cl, Br) reactions with dimethyl sulfoxide

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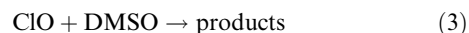
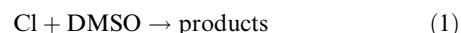
The kinetics and mechanism of the reactions of dimethyl sulfoxide (DMSO) with Cl, Br, ClO and BrO have been studied by the mass spectrometric discharge-flow method at 298 K and at a total pressure of 1 Torr of helium. The rate coefficient of the reaction $\text{Cl} + \text{DMSO} \rightarrow \text{products}$ (1) was measured under pseudo-first-order conditions either in excess of DMSO or in excess of Cl atoms: $k_1 = (2.05 \pm 0.35) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (quoted uncertainty includes estimated systematic errors). Both HCl and CH_3 were detected as products of reaction (1) and the branching ratios 0.91 ± 0.15 and 0.10 ± 0.02 , respectively, were found for the channels forming these species. For the reaction $\text{Br} + \text{DMSO} \rightarrow \text{products}$ (2) the rate constants for the HBr and CH_3 forming channels (2a and 2b, respectively) were determined from the kinetics of formation of these products: $k_{2a} = (1.1 \pm 0.3) \times 10^{-14}$ and $k_{2b} = (1.2 \pm 0.3) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For the reactions $\text{ClO} + \text{DMSO} \rightarrow \text{products}$ (3) and $\text{BrO} + \text{DMSO} \rightarrow \text{products}$ (4), only upper limits, $k_3 < 1.6 \times 10^{-14}$ and $k_4 < 4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, could be determined.

Introduction

Largely emitted by oceans, dimethyl sulfide (DMS) has been postulated to be involved in global climate system through the formation of aerosols and clouds influencing in this way the Earth radiation budget.¹ Dimethyl sulfoxide (DMSO) is an intermediate species of the addition route of the OH-initiated oxidation of dimethyl sulfide.^{2,3} Laboratory studies have shown that DMSO is also formed in reactions of DMS with BrO.^{4,5} DMSO has been observed in the marine atmosphere.^{6–8} Although the OH reaction is the major gas phase oxidation process for DMSO in the atmosphere, reactions with halogen atoms and radicals (Cl, Br, ClO, BrO), for which tropospheric concentrations (except Cl) are much higher than those of OH,^{9–13} may also play some role.

The kinetic and mechanistic information available for these reactions is rather limited. The reaction of Cl atoms with DMSO has been investigated in three previous works.^{14–16} The values of the reaction rate constant obtained in two smog chamber studies^{14,15} at one atmosphere pressure of air are in good agreement, whereas a value lower by a factor four at $P = 0.5\text{--}3.0$ Torr was recently reported by Martínez *et al.*¹⁶ Barnes *et al.*¹⁴ and Falbe-Hansen *et al.*¹⁵ have quantified the final reaction products, SO_2 and DMSO_2 , while Martínez *et al.*¹⁶ report qualitative detection of the reaction adduct $\text{CH}_3\text{SO}(\text{Cl})\text{CH}_3$ and the absence of HCl among the reaction products. The reactions of Br atoms and BrO radicals with DMSO have been investigated only in one work,¹⁷ where the rate constants have been determined at $P = 740$ Torr by the relative rate method. For the reaction of ClO radicals with DMSO the only study¹⁶ reports an upper limit of $6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The kinetic and mechanistic data available for the title reactions are therefore scarce and uncertain, and additional studies are needed.

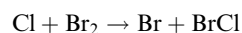
The present paper reports the results of the experimental study of the kinetics and products of reactions (1)–(4) at $T = 298$ K and 1 Torr total pressure of helium:



Experimental section

Experiments were carried out in a discharge flow reactor using a modulated molecular beam mass spectrometer as the detection method. The main reactor, shown in Fig. 1 along with the movable injector for the reactants, consisted of a Pyrex tube (45 cm length and 2.4 cm id). The walls of the reactor as well as of the injector were coated with halocarbon wax (Halocarbon products corporation, series 1500) in order to minimize the heterogeneous loss of active species. All experiments were conducted at $T = 298$ K and 1 Torr total pressure, Helium being used as the carrier gas. Under these conditions the laminar flow is established in the reactor.

Chlorine atoms were generated from microwave discharge in Cl_2/He mixtures. Two detection methods of Cl atoms were used. At high concentrations, Cl was detected at its parent peak as Cl^+ ($m/z = 35$). The absolute concentrations of Cl atoms were determined in this case from the fraction of Cl_2 dissociated in the microwave discharge ($\Delta[\text{Cl}_2] = 2[\text{Cl}]$). At low concentrations of chlorine atoms, Br_2 was added at the end of the reactor through inlet 5 (located 5 cm upstream of the sampling cone) in order to scavenge Cl:



$$k_5 = (1.45 \pm 0.20) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{18,19} \quad (5)$$

(all rate constants are given at $T = 298$ K).

Cl was detected as BrCl^+ ($m/z = 116$). This method of Cl detection was preferred to the direct detection at

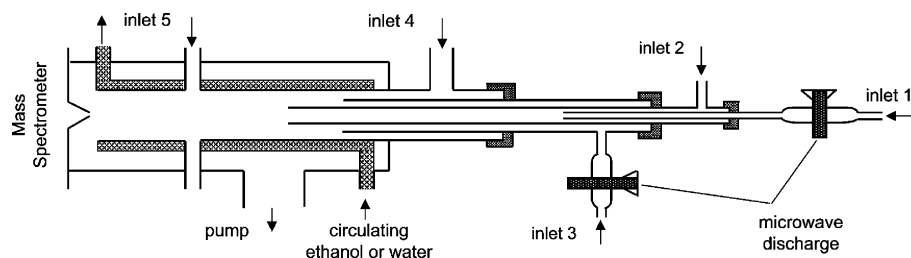
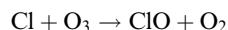


Fig. 1 Diagram of the apparatus used.

$m/z = 35/37$ (Cl^+), since complications may arise from the contribution of Cl_2 (precursor of Cl atoms) and Cl containing products of reaction (1) at these peaks due to the fragmentation of these species in the ion source of the mass spectrometer (operating at *ca.* 30 eV). The absolute concentrations of Cl atoms (*i.e.* BrCl) in this case were measured using titration reaction (5) in excess of Br_2 : $[\text{Cl}] = \Delta[\text{Br}_2] = [\text{BrCl}]$.

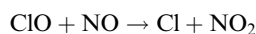
Bromine atoms were generated from microwave discharge in Br_2/He mixtures and were detected at their parent peaks at $m/z = 79/81$ (Br^+). Their absolute concentrations were measured from the fraction of Br_2 dissociated in the microwave discharge ($\Delta[\text{Br}_2] = 2[\text{Br}]$).

In kinetic experiments ClO radicals were generated through the fast reaction of Cl atoms with ozone in excess of O_3 :



$$k_6 = (1.2 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{20} \quad (6)$$

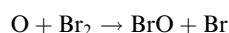
ClO radicals were detected at their parent peak (ClO^+ , $m/z = 51$). Reaction (7), converting ClO into the NO_2 stable species, was used for the determination of the absolute concentrations of these radicals:



$$k_7 = (1.7 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{20} \quad (7)$$

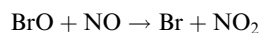
ClO radicals, needed for these calibration experiments, were produced through reaction (6) in excess of Cl atoms.

Reaction (8) was used as a source of BrO radicals:



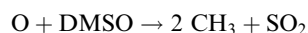
$$k_8 = (1.4 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{18} \quad (8)$$

The O atoms were generated from microwave discharge in O_2/He mixtures. BrO radicals were detected at their parent peaks at $m/z = 95/97$ as BrO^+ . Absolute BrO concentrations were determined by titration with NO and subsequent detection of NO_2 formed ($[\text{BrO}] = [\text{NO}_2]$):



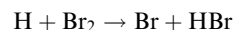
$$k_9 = (2.1 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (9)$$

DMSO was injected into the reactor through a continuous flow of He in DMSO and was detected at its parent peak as DMSO^+ ($m/z = 78$). The measurement of the absolute concentrations of DMSO in the flow reactor represents a significant experimental challenge due to the low vapour pressure of DMSO (near 0.6 Torr at 298 K) and its sticky behaviour. In this study, a new method to determine DMSO concentrations proposed in a recent work from this group²¹ was employed. This direct calibration method uses the reaction of oxygen atoms with DMSO and consists of the chemical conversion of DMSO to SO_2 which can be easily calibrated ($\Delta[\text{DMSO}] = \Delta[\text{SO}_2]$):



$$k_{10} = (1.0 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{21} \quad (10)$$

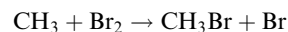
The measurement of the absolute concentrations of HBr (detected as a product of reaction (2)) consisted of the chemical conversion of H atom to HBr by excess Br_2 :



$$k_{11} = (7.4 \pm 2.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{22} \quad (11)$$

In this case, the concentration of HBr formed was determined from the fraction of Br_2 consumed.

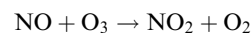
CH_3 radicals observed as products of DMSO reactions with Cl and Br atoms were detected as CH_3Br^+ at $m/z = 94/96$, after scavenging by an excess of Br_2 (added at the end of the reactor through inlet 5). Thus, CH_3 was converted into CH_3Br via reaction (12):



$$k_{12} = (3.9 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{23} \quad (12)$$

This method of CH_3 detection was preferred to the direct monitoring at $m/z = 15$ (CH_3^+) because of the significant contribution of DMSO at this mass. The absolute concentrations of CH_3Br and of all the stable species of this study were determined directly from their flow rates, obtained from measurements of the pressure drop in calibrated volume flasks containing mixtures of the species with helium.

Ozone was produced by an ozonizer (Trailigaz) and was collected and stored in a trap containing silica gel at $T = 195 \text{ K}$. The trap was pumped before use in order to reduce the O_2 concentration. The resulting oxygen concentration was always less than 20% of the ozone concentration introduced into the reactor. The absolute concentration of O_3 was determined by titration with NO with simultaneous detection of ozone consumed and NO_2 formed ($\Delta[\text{O}_3] = \Delta[\text{NO}_2]$):



$$k_{13} = (1.8 \pm 0.2) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{20} \quad (13)$$

The purities of the gases used were as follows: He > 99.9995% (Alphagaz), was passed through liquid nitrogen traps; DMSO > 99.9% (Aldrich); Br_2 > 99.99% (Aldrich); CH_3Br > 99.5% (UCAR); Cl_2 > 99% (UCAR); HCl – 5% mixture in He (Praxair); O_2 > 99.995% (Alphagaz); NO_2 > 99% (Alphagaz); NO > 99% (Alphagaz), purified by trap-to trap distillation in order to remove NO_2 traces.

Results

Reaction Cl + DMSO (1): rate constant measurements

Two series of experiments were performed in order to measure the rate constant of the reaction Cl + DMSO: one by monitoring DMSO kinetic decays in excess of Cl atoms and the other one by monitoring Cl decays in excess of DMSO.

DMSO kinetics in excess of Cl atoms. DMSO was injected into the reactor through the central tube of the sliding injector

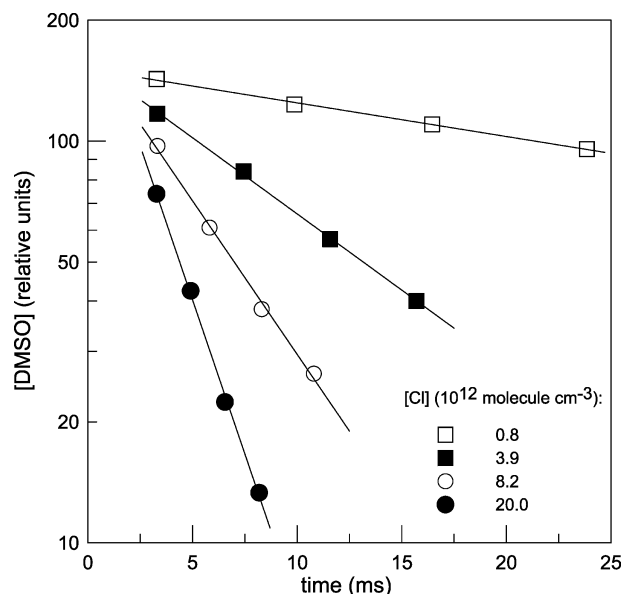


Fig. 2 Reaction $\text{Cl} + \text{DMSO} \rightarrow \text{products}$ (1): example of kinetic runs of DMSO consumption in reaction with excess Cl atoms.

(inlet 2). Cl atoms were produced in the microwave discharge of Cl_2 and introduced in the reactor through inlet 3. They were detected at $m/z = 35$ (as Cl^+). Initial concentrations of the species were in the following ranges: $[\text{DMSO}]_0 = (1.7\text{--}2.7) \times 10^{11} \text{ molecule cm}^{-3}$ and $[\text{Cl}]_0 = (0.8\text{--}2.0) \times 10^{13} \text{ molecule cm}^{-3}$. Flow velocities in the reactor were near 1200 cm s^{-1} . The experiments were carried out under pseudo-first-order conditions and the consumption of the excess Cl was observed to be negligible. Fig. 2 shows examples of exponential decays of DMSO concentration for various concentrations of chlorine atoms. The pseudo-first-order rate constants, $k'_1 = -d(\ln[\text{DMSO}])/dt$, were corrected for the axial and radial diffusion of DMSO.²⁴ The diffusion coefficient of DMSO in He was calculated from that of Kr in He.²⁵ These corrections on the measured values of k'_1 were generally less than 10%. The pseudo-first-order plot resulting from the DMSO decay kinetics in excess of Cl atoms is shown in Fig. 3. The linear least-squares fit to these experimental data provides the follow-

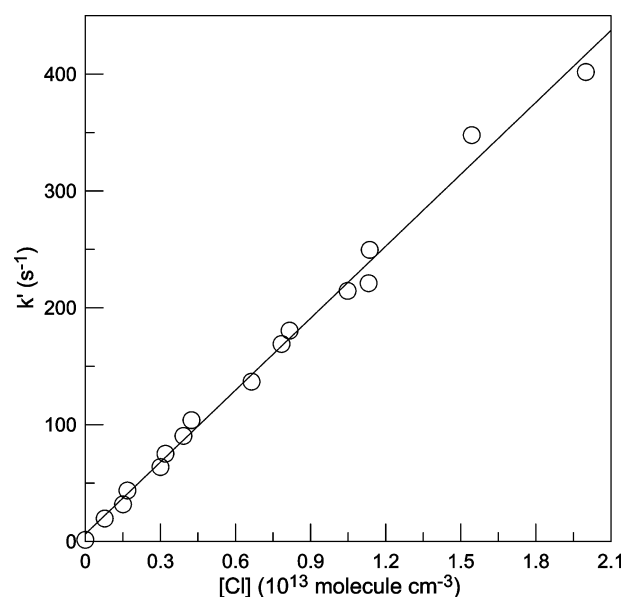


Fig. 3 Reaction $\text{Cl} + \text{DMSO} \rightarrow \text{products}$ (1): pseudo-first-order plot obtained from DMSO decay kinetics in excess of Cl atoms.

ing value for the rate coefficient of reaction (1):

$$k_1 = (2.05 \pm 0.05) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(where the uncertainty represents 1σ). The zero-intercept ($6.4 \pm 4.3 \text{ s}^{-1}$), is in agreement with the rate of DMSO decay of $(1.4 \pm 1.4) \text{ s}^{-1}$ measured in the absence of Cl atoms (discharge of Cl_2 turned off).

Cl kinetics in excess of DMSO. Cl atom decays were monitored under pseudo first order conditions. Cl atoms produced in the microwave discharge (inlet 1) were introduced into the reactor through the central tube of the movable injector and DMSO through the reactor side-arm (inlet 4). Cl atoms were detected as BrCl (see Experimental section). Br_2 molecules, added at the end of the reactor (inlet 5), were always present at concentrations near $5 \times 10^{13} \text{ molecule cm}^{-3}$. The initial concentrations of chlorine atoms were in the range: $[\text{Cl}]_0 = (0.6\text{--}1.1) \times 10^{11} \text{ molecule cm}^{-3}$. Flow velocities in the reactor were around 1150 cm s^{-1} . The concentration of DMSO was varied between 1.1×10^{12} and $1.2 \times 10^{13} \text{ molecule cm}^{-3}$. Under these experimental conditions, DMSO consumption was observed to be negligible. Examples of observed kinetic runs for Cl atoms are presented in Fig. 4. The pseudo first order rate constants, $k'_1 = -d(\ln[\text{Cl}])/dt$, obtained from the Cl kinetics, were corrected for axial and radial diffusion of Cl atoms. The diffusion coefficient of Cl in He, $0.75 \text{ atm cm}^2 \text{ s}^{-1}$, used in these calculations was determined from that of Ar in He.²⁵ The diffusion corrections on the k'_1 were within 10%. Fig. 5 shows the dependence of the pseudo-first-order rate constant of Cl consumption as a function of excess DMSO concentration. The slope of the linear fit to the experimental points in Fig. 4 provides the value of the rate constant for reaction (1):

$$k_1 = (2.06 \pm 0.09) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(with 1σ statistical uncertainty). The intercept ($5.9 \pm 5.3 \text{ s}^{-1}$) is in agreement with the negligible decay of Cl atoms observed in the absence of DMSO.

As noted above, Cl atoms were scavenged by Br_2 at the end of the reaction zone to be detected as BrCl molecules. This led to a simultaneous production of Br atoms. The important point is that possible reactions of these Br atoms could not lead to BrCl production or consumption, therefore, they had no impact on the observed kinetics of Cl. First, the concentrations of these Br atoms were low: $[\text{Br}] = [\text{Cl}] = [\text{BrCl}]$.

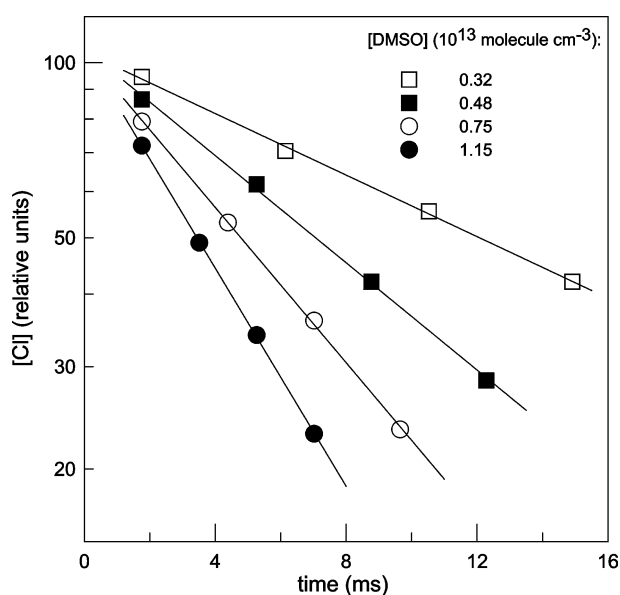


Fig. 4 Reaction $\text{Cl} + \text{DMSO} \rightarrow \text{products}$ (1): example of kinetic runs of Cl consumption in reaction with excess DMSO.

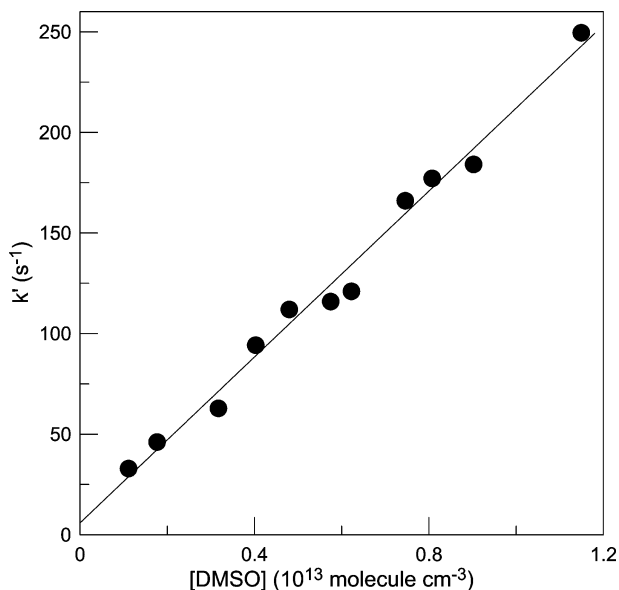
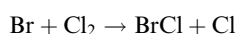


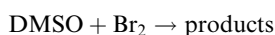
Fig. 5 Reaction $\text{Cl} + \text{DMSO} \rightarrow \text{products}$ (1): pseudo-first-order plot obtained from Cl decay kinetics in excess of DMSO.

Further, the reactions of Br with chlorine containing species present in the reactor, Cl_2 (precursor of Cl atoms) and HCl (main product of reaction (1), see below) are very slow:



$$k_{14} = (1.1 \pm 0.3) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{26} \quad (14)$$

The formation of BrCl in the reaction of Br with HCl (endothermic by $\approx 51 \text{ kcal mol}^{-1}$) can be also excluded. In addition, the concentration of DMSO was not affected by the presence of Br_2 and Br in the reactor. This could be expected considering the kinetic data for the reactions of DMSO with Br (this work, see below) and Br_2 :



$$k_{15} < 5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},^{21} \quad (15)$$

The possible interference of the secondary reactions of Cl atoms with the products of reaction (1) can also be excluded considering the low initial concentrations of the Cl atoms used.

The value of k_1 determined in this series of experiments is in good agreement with that reported above from DMSO kinetics in excess of Cl atoms. The final value of k_1 at $T = 298 \text{ K}$, which can be recommended from this work, is:

$$k_1 = (2.05 \pm 0.35) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The uncertainty on k_1 represents a combination of statistical and estimated systematic errors. The estimated systematic uncertainties include $\pm 5\%$ for flow meter calibrations, $\pm 3\%$ for pressure measurements and $\pm 10\%$ for the procedure of measurements of the absolute concentrations of the species involved. The overall uncertainty represents the combination of these uncertainties in quadrature with the addition of 1σ statistical error.

Reaction $\text{Cl} + \text{DMSO}$ (1): product study

The mechanistic study of reaction (1) was carried out in excess of DMSO over Cl atoms and consisted of concentrations measurements of the reaction products as a function of the consumed concentration of chlorine atoms. In order to minimize the influence of the possible secondary reactions short reaction times ($\approx 2.5 \text{ ms}$), relatively high DMSO concentrations ($\approx 2 \times 10^{13} \text{ molecule cm}^{-3}$) and low Cl concentrations

($5 \times 10^{10} - 2.1 \times 10^{12} \text{ molecule cm}^{-3}$) were used. Under these experimental conditions around half of the initial Cl concentration was consumed in the reaction with DMSO. HCl has been found to be the major reaction product. The addition of Br_2 ($\approx 7 \times 10^{13} \text{ cm}^{-3}$) at the end of the reaction zone allowed for the detection of small concentrations of CH_3 (as CH_3Br^+ at $m/z = 94/96$) which was also formed in reaction (1). For a reaction time and an initial DMSO concentration fixed, $[\text{Cl}]_0$ was varied and its consumption was measured, as well as the concentration of both products formed. The observed concentrations of HCl and CH_3 are plotted in Fig. 6 as a function of the consumed concentration of Cl atoms. The linear fit to the presented results provides the branching ratios for the HCl and CH_3 forming pathways of reaction (1):

$$[\text{HCl}]_{\text{formed}}/[\text{Cl}]_{\text{consumed}} = 0.91 \pm 0.15$$

$$[\text{CH}_3]_{\text{formed}}/[\text{Cl}]_{\text{consumed}} = 0.10 \pm 0.02$$

(the quoted uncertainties include statistical and estimated systematic errors).

One can note the non-zero intercept for the dependence of $[\text{CH}_3]_{\text{formed}}$ on $[\text{Cl}]_{\text{consumed}}$ in Fig. 6. The reason for this is the presence of low concentrations of oxygen atoms in the reactor coming from the microwave discharge of He. In the presence of Br_2 in the reactor these trace O atoms were converted to BrO via reaction (8) and could be detected at $m/z = 95/97$ as BrO^+ . Their initial concentration was found to be $\leq 10^{11} \text{ molecule cm}^{-3}$. It was observed also that around 30% of these O atoms was consumed in reaction (10) with DMSO under the experimental conditions of the study leading to an additional formation of CH_3 radicals. The concentration of the CH_3 radicals thus formed was measured in the absence of Cl atoms in the reactor and is shown in Fig. 6 as a point corresponding to $[\text{Cl}]_{\text{consumed}} = 0$. It is important to note that no changes in this trace concentration of O atoms was observed when Cl_2 was added in the discharge and this concentration was constant when $[\text{Cl}_2]$, hence $[\text{Cl}]$, was varied. Thus, the contribution of the $\text{O} + \text{DMSO}$ reaction to the observed concentration of CH_3 radicals could be considered identical for all the experiments with different initial concentrations of Cl atoms.

The possible impact of secondary chemistry on the obtained results can be considered. The concentrations of CH_3 radicals

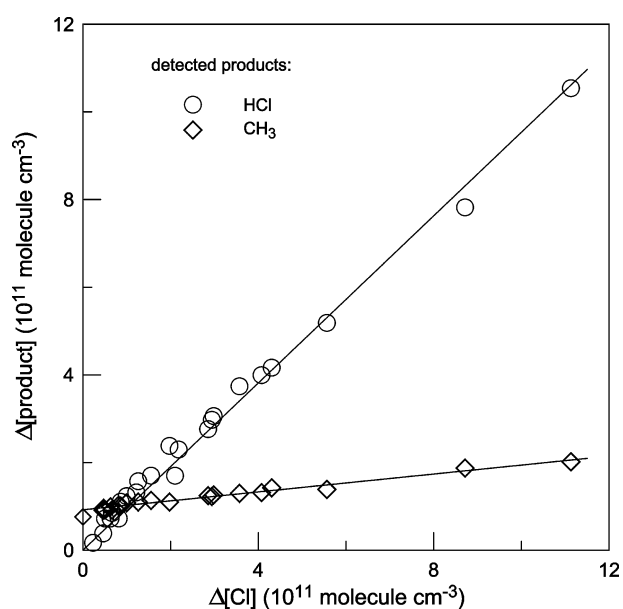
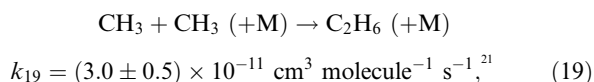
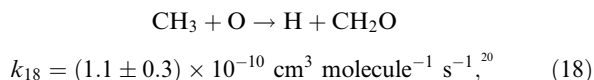
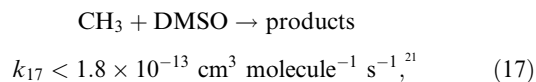
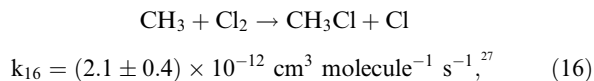


Fig. 6 Reaction $\text{Cl} + \text{DMSO} \rightarrow \text{products}$ (1): concentrations of HCl and CH_3 formed in reaction (1) as a function of consumed concentration of Cl atoms.

could be influenced mainly by the reactions of CH₃ with DMSO, Cl₂ (precursor of Cl atoms), trace O atoms and by recombination reaction (19):



However, considering the rate constant data of these reactions in combination with the concentrations of the respective species ($[\text{Cl}_2] \leq 6 \times 10^{12}$, $[\text{DMSO}] \leq 2 \times 10^{13}$, $[\text{O}] < 10^{11}$, $[\text{CH}_3] \leq 2 \times 10^{11} \text{ molecule cm}^{-3}$) and the relatively short reaction time, their impact on the observed concentrations of methyl radicals can be considered as negligible. Other possible secondary reactions are those of Cl atoms with CH₃ and the co-product of HCl in reaction (1), CH₃S(O)CH₂. To our knowledge no kinetic data for these reactions are available in the literature. However, their impact on the measured concentrations of CH₃ and HCl seems to be negligible, considering the good linearity of the plots of Fig. 6, initial concentrations of Cl being changed by a factor of 40.

Reaction Br + DMSO (2): kinetics and products

In a first series of experiments the kinetics of DMSO consumption was monitored in excess of Br atoms. Br atoms formed in the microwave discharge of Br₂/He mixture were introduced into the reactor through inlet 3, and DMSO was injected through the central tube of the movable injector (inlet 2). For a Br concentration of $6.7 \times 10^{13} \text{ molecule cm}^{-3}$ and a reaction time of 35 ms, the rate of DMSO decay was less than 1 s^{-1} . This provides the upper limit for the total rate constant of reaction (2):

$$k_2 \leq 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

In a second series of experiments we have attempted to detect small concentrations of the possible reaction products, HBr and CH₃, as for reaction of Cl atoms with DMSO. Relatively high concentrations of both reactants were used in these experiments: $[\text{DMSO}]_0 = (0.7\text{--}2.2) \times 10^{13}$ and $[\text{Br}]_0 = (0.7\text{--}2.7) \times 10^{14} \text{ molecule cm}^{-3}$. Br₂ (precursor of Br atoms) was always present in the reactor at concentrations in the range $(0.3\text{--}1.5) \times 10^{14} \text{ molecule cm}^{-3}$. Under these conditions HBr and CH₃ (detected as CH₃Br) were identified to be the primary products of reaction (2). The kinetics of formation of these species could be observed under conditions when the concentrations of the reactants could be considered as constant: only slight (30% maximum) Br consumption mainly due to the recombination of the atoms on the wall of the reactor was observed. Under such conditions the formation rate of the products could be approximated by the expression:

$$\Delta[\text{product}]/\Delta t = k_{\text{product}}[\text{Br}][\text{DMSO}]$$

The formation rates of the products were measured for different concentrations of the reactants, Br (varied by a factor of four) and DMSO (varied by a factor of three). Mean concentrations of Br atoms when significant consumption was observed along the reaction zone were used in the calculations. Fig. 7 presents the rate of product formation as a function of $[\text{Br}] \times [\text{DMSO}]$. The slopes of the linear plots in Fig. 7 provide

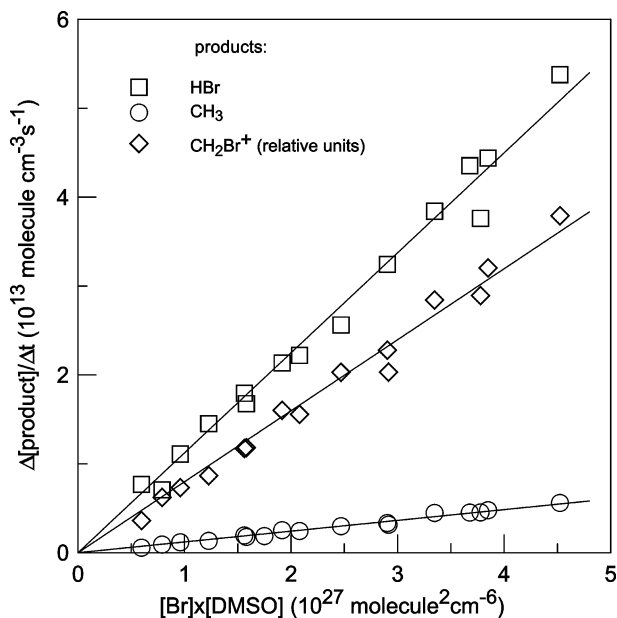
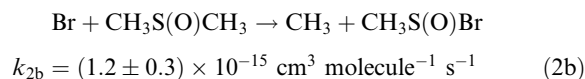
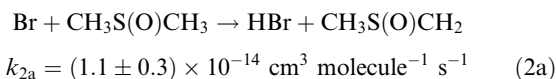


Fig. 7 Reaction Br + DMSO → products (2): rate of product formation in reaction (2) as a function of the product of the concentrations of the reactants, Br and DMSO.

the values of the rate constants for the HBr and CH₃ forming channels of reaction (2):



(the quoted uncertainties are combination of statistical and estimated systematic errors).

Concerning the possible influence of secondary chemistry, one can note that the kinetics of CH₃ was not affected by secondary reactions, since the methyl radicals, once formed in reaction (2), were rapidly converted to stable species CH₃Br through reaction with Br₂ (5). The secondary reaction of Br atoms with the co-product of HBr, CH₃S(O)CH₂, could be an additional source of HBr in the present experiments. Although this possibility can not be completely excluded, the Br-atom addition pathway seems to be the most probable channel of the Br reaction with CH₃S(O)CH₂. Moreover, the reaction of CH₃S(O)CH₂ with Br₂ is expected to rapidly scavenge and transform the radicals to the CH₃S(O)CH₂Br stable species. This latter was not found at its parent peak ($m/z = 156/158$, this mass range being perturbed by the presence of Br₂, $m/z = 158/160/162$). However the signal detected at $m/z = 93/95$ as a product of reaction (2) (see Fig. 7) can be attributed to the fragment CH₂Br from CH₃S(O)CH₂Br. We have also tried to detect the co-products of CH₃. No signal was detected at $m/z = 142/144$ (CH₃S(O)Br⁺), most probably due to the fragmentation of CH₃S(O)Br in the ion source of the mass spectrometer.

As noted above, Br-atom consumption (up to 30% in a few experiments) was observed and the mean concentrations of Br along the kinetic runs were used in the calculations of the rate constants. In order to verify the correctness of this procedure another approach was employed in a few experiments: the values of k_{2a} and k_{2b} were derived from the best fit to the kinetics of HBr and CH₃ formation using experimentally measured Br profiles (*i.e.* taking into account the Br consumption). An example of the experimental and simulated kinetics of HBr and CH₃ is shown in Fig. 8. The values obtained for k_{2a} and k_{2b} within the two approaches were consistent within 5%.

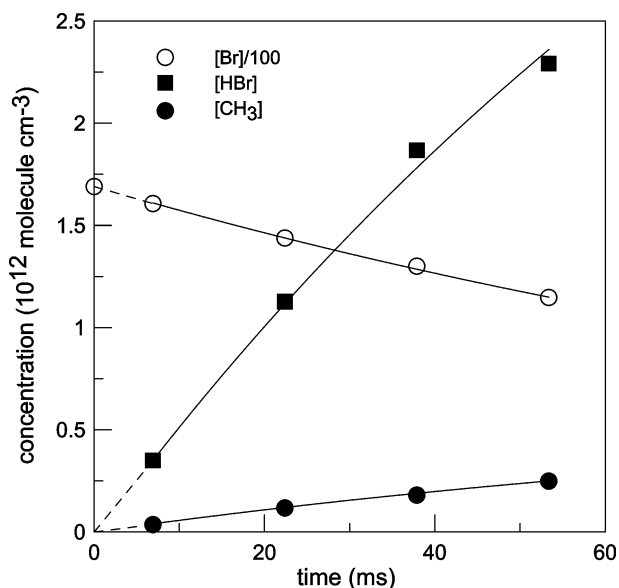


Fig. 8 Reaction $\text{Br} + \text{DMSO} \rightarrow \text{products}$ (2): example of experimental (points) and simulated (solid lines) kinetics for HBr and CH_3 ; initial concentrations of reactants: $[\text{Br}] = 1.7 \times 10^{14}$ and $[\text{DMSO}] = 2.8 \times 10^{13}$ molecule cm^{-3} ; best fit was obtained with $k_{2a} = (1.17 \pm 0.05) \times 10^{-14}$ and $k_{2b} = (1.23 \pm 0.05) \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$ (uncertainties represent 95% confidence limits of the simulation procedure).

Reactions $\text{ClO} + \text{DMSO}$ (3) and $\text{BrO} + \text{DMSO}$ (4)

The reaction of ClO radicals with DMSO was studied in excess of DMSO over ClO. ClO radicals were formed in the sliding injector *via* reaction of Cl atoms (discharge 1) with ozone ($[\text{O}_3] = 2 \times 10^{13}$ molecule cm^{-3} , inlet 2). DMSO was introduced through the reactor side-arm (inlet 4). In order to avoid the possible regeneration of ClO radicals in reaction (6), if Cl atoms are formed in reaction (3), Br_2 was added to the reaction zone together with DMSO ($[\text{Br}_2] \approx 10^{14}$ molecule cm^{-3} , inlet 3). Under these experimental conditions ($k_5[\text{Br}_2]/k_6[\text{O}_3] \sim 60$) if Cl atoms are formed, they are rapidly scavenged by Br_2 and do not regenerate ClO in the reaction with O_3 . First, the kinetics of ClO consumption ($[\text{ClO}]_0 \sim 10^{12}$ molecule cm^{-3}) was monitored. In the presence of 3.1×10^{13} molecule cm^{-3} of DMSO in the reactor the rate of ClO decay was less than 0.5 s $^{-1}$. From these data an upper limit for the total rate constant of reaction (3) can be derived:

$$k_3 \leq 1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Under the same experimental conditions (except higher concentrations of ClO, 4×10^{12} molecule cm^{-3}) we have tried to detect the possible reaction product, Cl atoms:



In the presence of Br_2 in the reactor, if formed Cl could be easily detected as BrCl^+ (at $m/z = 116$). With the above reactant concentrations no formation of measurable concentrations of Cl atoms was observed ($\Delta[\text{Cl}] \leq 1.0 \times 10^{10}$ molecule cm^{-3}) for a reaction time of 43 ms. These data allow for the determination of an upper limit of the rate constant for the Cl forming channel of reaction (3):

$$k_{3a} \leq \frac{1}{[\text{ClO}][\text{DMSO}]} \frac{\Delta[\text{Cl}]}{\Delta t}$$

$$k_{3a} \leq 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The reaction between BrO and DMSO was carried out in excess of DMSO injected through inlet 4. BrO radicals were formed in reaction (8) between O atoms (inlet 1) and excess Br_2 (5×10^{13} molecule cm^{-3} , inlet 2) and were introduced into

the reactor through the central tube of the movable injector. The average flow velocity was near 600 cm s^{-1} . First, the rate of BrO decay was measured in the absence of DMSO in the reactor and was found to be in the range $(2.2\text{--}4.0)$ s $^{-1}$. Addition of DMSO did not lead to significant changes in the kinetics of BrO. For the maximum concentration of DMSO used, 4.5×10^{13} molecule cm^{-3} , the rate of DMSO consumption was found to be less than 4.0 s $^{-1}$. These data allowed to derive an upper limit for the rate constant of reaction (4):

$$k_4 \leq 4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Discussion

Kinetic and mechanistic data from the present work for reaction $\text{Cl} + \text{DMSO}$ (1) can be compared with those reported in three previous studies^{14–16} (Table 1). Our value of k_1 is in good agreement with that of Martínez *et al.*,¹⁶ which was determined under similar experimental conditions and with the same experimental technique. In contrast, the values of k_1 measured in photoreactors^{14,15} at atmospheric pressure using the relative rate method are much higher. One possible explanation for this discrepancy can be the pressure dependence of the rate constant due to the stabilization of the intermediate adduct $[(\text{CH}_3)_2\text{S}(\text{O})\text{Cl}]^*$ at high pressure:



Indirect evidence for the adduct formation channel (1c) at atmospheric pressure^{14,15} is the detection of DMSO_2 among the final products, the formation of DMSO_2 being associated with secondary chemistry initiated by the addition pathway of reaction (1).¹⁴ Another sulfur containing product observed in these two studies was SO_2 . The mechanism leading to SO_2 formation proposed in ref. 14 includes the H atom abstraction channel (1a) as the initial step. In the present study channel (1a) was shown to be dominant (near 90%) at 1 Torr total pressure. Another pathway of reaction (1) observed in the present study is the methyl radical forming channel (1b) for which a branching ratio of around 10% was determined. This last channel proceeds most probably through the excited intermediate adduct formation followed by its decomposition with elimination of CH_3 . We have not observed any signal at $m/z = 113/115$, corresponding to the possibly stabilized adduct $(\text{CH}_3)_2\text{S}(\text{O})\text{Cl}$. This fact combined with the mechanistic data discussed above shows that the addition pathway of reaction (1) was negligible under the experimental conditions of this study. The mechanistic data from the present study are in contradiction with the observations of Martínez *et al.*¹⁶ These authors have not detected any HCl formation (the major reaction product in the present study) and they reported the qualitative detection of the $(\text{CH}_3)_2\text{S}(\text{O})\text{Cl}$ adduct formation. The

Table 1 Summary of the rate constant data for the reaction $\text{Cl} + \text{DMSO} \rightarrow \text{products}$ (1)

P/Torr	k_1^a	Technique ^b	Method ^c	Reference
760	7.4 ± 1.8	Phr/FTIR/GC	R	Barnes <i>et al.</i> ¹⁴
740	7.4 ± 1.0	Phr/FTIR	R	Falbe-Hansen <i>et al.</i> ¹⁵
0.5–3.0	1.7 ± 0.3	DF/MS	A	Martínez <i>et al.</i> ¹⁶
1.0	2.05 ± 0.35	DF/MS	A	This work

^a units of 10^{-11} cm^3 molecule $^{-1}$ s $^{-1}$; uncertainty as quoted by authors; ^b Phr = Photoreactor, FTIR = Fourier Transform IR Spectroscopy, GC = gas chromatography, DF = discharge flow, MS = mass spectrometry; ^c R = relative measurements, A = absolute measurements.

formation of other products at $m/z = 98/100$ (attributed to $\text{CH}_3\text{S}(\text{O})\text{Cl}$) and at $m/z = 50/52$ (CH_3Cl , secondary product formed in reaction of CH_3 with Cl_2) was also observed. Considering these data Martínez *et al.* concluded that reaction (1) proceeds through an addition mechanism. The formation of CH_3 and $\text{CH}_3\text{S}(\text{O})\text{Cl}$ observed in their study was attributed to the partial decomposition of the stabilized adduct on the time-scale of the experiments. This conclusion disagrees with the present study where HCl was identified as the major primary product of reaction (1) at low pressure, whereas we did not find any evidence for the occurrence of the addition channel. Martínez *et al.*¹⁶ have not observed any pressure dependence of the rate constant of the $\text{Cl} + \text{DMSO}$ reaction in the pressure range 0.5–3.0 Torr. Thus, if the addition channel is supposed to be the major route under these experimental conditions, it means that the measured value of k_1 is near the high pressure limit. In this case it is difficult to explain the large difference between the values of k_1 measured at low pressure in ref. 16 and in the present study and those determined at atmospheric pressure.^{14,15} One can note that even a higher value for k_1 at 1 atmosphere pressure of $\text{N}_2 + \text{O}_2$ was very recently reported by Arsene *et al.*:²⁸ $k_1 = (3.4 \pm 0.7) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. It should be noted that the difference in the values of k_1 obtained at low and high pressure may be due not only to the different reaction mechanisms but also to other reasons, *e.g.* experimental artifacts. However, considering the above discussion and the mechanistic data from the present study, the adduct formation pathway of reaction (1) does not seem to be of importance at pressures around 1 Torr.

This paper reports the first direct determination of the rate constant and of the primary products of reaction $\text{Br} + \text{DMSO}$ (2). Considering the partial rate constants for HBr and CH_3 forming channels ($k_{2a} = (1.1 \pm 0.3) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{2b} = (1.2 \pm 0.3) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively) and the upper limit for the overall rate constant ($k_2 \leq 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) determined in the present study, the following value can be recommended for the total rate constant of reaction (2) at $T = 298 \text{ K}$:

$$k_2 = (1.2 \pm 0.3) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

In the unique previous study¹⁷ the rate constant of reaction (2) was measured in a photoreactor at 740 Torr of synthetic air and $T = 296 \text{ K}$, using a relative rate method. The value of the rate constant measured with three different references (ethene, toluene, *p*-xylene) varied between 1.4 and $4.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the mean value of $k_2 = (2.4 \pm 1.6) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was finally recommended. This latter value is a factor two higher than that measured in the present study, although the two measurements agree if the rather high uncertainty reported in¹⁷ is considered. Among the final sulfur containing products of the Br initiated oxidation of DMSO Ballesteros *et al.*¹⁷ identified $\text{CH}_3\text{SO}_2\text{Br}$ as the main product and DMSO_2 with a yield of 4%. In the present study HBr and CH_3 were identified as the primary products of reaction (2), HBr being the major reaction product ($k_{2a}/k_2 \approx 0.9$).



Most probably reaction (2b) proceeds through an excited intermediate adduct formation, $[(\text{CH}_3)_2\text{S}(\text{O})\text{Br}]^*$, following by its decomposition with elimination of a methyl radical. Two mechanisms are possible for channel (2a): direct H atom abstraction and Br addition-HBr elimination mechanism.

The reactions of ClO and BrO with DMSO were found to be very slow. Neither the consumption of these radicals nor the formation of the possible products was observed when DMSO was added into the reactor and only the upper limits for the corresponding rate constants could be given in the present

Table 2 Estimated tropospheric chemical lifetime of DMSO under typical remote conditions

Species	Concentration/ molecule cm^{-3}	Rate constant at 298 K/ cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$	DMSO lifetime
OH	10^6 ^a	8×10^{-11} ^e	3.5 h
NO_3	$> 2.5 \times 10^7$ ^b	3.4×10^{-13} ^f	> 1.4 days
O_3	5×10^{11} ^c	$< 1 \times 10^{-19}$ ^g	> 230 days
Cl	5×10^3 ^d	7.4×10^{-11} ^f	31 days
ClO	1×10^8 ^d	$< 1.6 \times 10^{-14}$ ^h	> 174 days
Br	5×10^7 ^d	1.2×10^{-14} ^h	16.5 days
BrO	3.7×10^7 ^d	$< 4 \times 10^{-14}$ ^h	> 7.8 days

^a From ref. 29, ^b From ref. 30, ^c From ref. 31, ^d See text, ^e Average value from ref. 14, 15, 32, 33, ^f From ref. 14, 15, ^g From ref. 15, ^h This work.

study: $k_3 \leq 1.6 \times 10^{-14}$, $k_4 \leq 4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These results are in agreement with previous determinations: $k_3 \leq 6 \times 10^{-14}$,¹⁶ $k_4 = (1.0 \pm 0.3) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁷

The present results allow for the estimation of the DMSO tropospheric lifetime with respect to X and XO radicals (X = Br, Cl), whose typical concentrations and reaction rate constants with DMSO are summarized in Table 2 along with the similar data for OH, O_3 and NO_3 . Cl concentrations are in the range $(1\text{--}15) \times 10^3 \text{ atom cm}^{-3}$ in the remote troposphere,^{9,34} but can be as high as $10^5 \text{ atom cm}^{-3}$ ⁹ depending on local conditions. In that case, the DMSO lifetime toward the reaction with Cl atoms can be comparable with that toward NO_3 . The lifetime reported in Table 2 is calculated with an average Cl concentration of $5 \times 10^3 \text{ atom cm}^{-3}$. Estimated ClO concentrations lie between 2 and $20 \times 10^7 \text{ molecule cm}^{-3}$ ^{9,10} and an average value of $1 \times 10^8 \text{ molecule cm}^{-3}$ was used in the calculations. The lifetime obtained indicates that the reaction $\text{ClO} + \text{DMSO}$ is negligible in the DMSO oxidation process. Br-atom concentrations in the range $(1\text{--}10) \times 10^7 \text{ atom cm}^{-3}$ have been estimated for the springtime arctic troposphere.^{10,12} Measurements of BrO radical concentrations are available for the mean latitude free troposphere ($(2.5\text{--}5) \times 10^7 \text{ molecule cm}^{-3}$ ¹¹) and the spring polar troposphere (around 30 ppt¹³). The corresponding DMSO lifetimes are presented in Table 2. Considering the atmospheric concentrations of the halogenated species X and XO and the kinetic data from this study, the calculated lifetime of DMSO toward these species is much higher than that toward OH radicals. Thus the role of active halogen in DMSO oxidation can be considered as negligible.

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