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Atmospheric DMSO Degradation in the Gas Phase: Cl−DMSO Reaction. Temperature Dependence and Products

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The reactions of Cl atoms and ClO radicals with CH_3SOCH_3 (DMSO) have been studied using the discharge flow method with direct detection of DMSO, ClO, and products by mass spectrometry. The absolute rate constant at room temperature measured for reaction 1, $(CH_3)_2SO + Cl \rightarrow$ products, was $k(1) = (1.7 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. For reaction 2, $(CH_3)_2SO + ClO \rightarrow$ products, only an upper limit could be established, $k(2) \leq 6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Reaction 1 has been found to proceed through adduct formation and further decomposition involving the cleavage of the C−S bound. The pressure effect on the Cl−DMSO reaction from 0.5 to 3 Torr was negligible, and the temperature dependence in the range 273−335 K was also very slight. The results obtained are related to previous studies of sulfur compounds, and the atmospheric implications are also discussed in relation to the homogeneous sinks of DMSO. Tropospheric lifetimes of DMSO based on average Cl and ClO concentrations and the measured rate constants have been calculated showing that the contribution of reaction 1 must be of minor relevance in the marine boundary layer. Reaction 2 is so slow that it does not play any role within the atmospheric sulfur chemistry.

Introduction

DMS has been recognized as the main natural source of sulfur in the atmosphere. It is produced in oceanic waters by both benthic and planktonic marine organisms (*1*) suggesting that it may be found in the surface's ocean. It is thought to originate from the decomposition of dimethyl-sulfoniopropionate produced by marine organisms in particular phytoplankton (*2*). In the remote marine boundary layer, where contributions from anthropogenic SO_2 are small, the gas-phase oxidation of DMS is thought to be the most important source of oxidized sulfur compounds such as SO_2, methanesulfonic acid (MSA), dimethyl sulfoxide, dimethyl sulfone, and H_2SO_4. Although sulfur compounds are minor constituents of the Earth's Atmosphere, they play a significant role in various global scale phenomena, including the climate (*3*) and the generation of acid rains. In this sense, excellent reviews on laboratory and field research are now available (*4*), and periodical evaluations of sulfur compounds levels in the atmosphere are published (*5*).

Dimethyl sulfoxide has been observed in the marine boundary layer (*6*) and in rainwater samples and aerosols (*7*). Furthermore DMSO has been identified as a product of the OH initiated oxidation of DMS in laboratory chamber studies (*8*−*10*). The addition of OH to DMS to form the $CH_3S(OH)CH_3$ adduct and further reaction with O_2 is considered as the main production source of DMSO in chamber studies and in the atmosphere. Recently (*11*), it has been reported that the reactions of DMS with halogen oxides, mainly BrO, may be an additional source of DMSO in the remote marine boundary layer. DMSO is also found in the seawater as a result of bacterial transformation of DMS, but this is not expected to represent a direct source since it is highly soluble in the liquid phase.

The fate of DMSO in the atmosphere is poorly understood. Its removal from the gas phase may be due to a combination of heterogeneous processes and homogeneous reactions with OH, NO_3, O_3, and Cl atoms. In relation to the heterogeneous fate of DMSO it is recognized as an important precursor of MSA (*12*), although recent observations disagree on the uptake of DMSO onto the particles. Putaud et al. (*13*) estimate low losses of DMSO from the gas phase due to its small Henry's constant, while for Sciare et al. (*7*) the DMSO could account for 40% of the MSA observed in rainwater.

Recent investigations about DMSO−OH reactions have been reported (*9, 10, 14*−*16*) with proposed rate constants ranging from 0.6 to 1 × 10^{-10} cm^3 molecules^{-1} s^{-1}. Nevertheless a complete agreement in relation to the products of the reaction is not found. From Hynes and Wine (*14*) and Urbanski et al. (*15*) a yield of unity is expected in CH_3 and $CH_3S(O)OH$, (methanesulfinic acid, MSIA) after OH addition to DMSO, while Sorensen et al. (*9*) have observed $DMSO_2$ as a main product. The NO_3−DMSO reaction shows a room-temperature rate constant of $(5.0 \pm 3.8) \times 10^{-13}$ cm^3 molecules^{-1} s^{-1} (*16*), and the kinetics of DMSO with O_3 seems to be very slow $k < 1 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}. Up to now, only a previous relative measurement of the reaction Cl−DMSO has been reported with a room-temperature kinetic rate constant of $k = (7.4 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (*16*). In that work, yields of 28 ± 12% on SO_2 and 8 ± 2% in $DMSO_2$ were found, the latter argued as a result of DMSO secondary reactions with oxidizing intermediates such as peroxy radicals or ClO.

Recently (*17*) it has been found that heterogeneous reactions of nitrogen oxides on sea salt particles can lead to significant concentrations of photolytic precursors of Cl atoms in the marine boundary layer. It seems that the main atmospheric source of atomic chlorine is the $ClNO_2$ generated by heterogeneous reaction of N_2O_5 vapor with moist NaCl (*18*). Since global average estimates of Cl atoms concentrations range from 10^3 to 10^4 atom cm^{-3} (*19, 20*) in marine areas, the effect on the removal of DMSO should be evaluated and compared to that of the OH−DMSO reaction, presumably the most relevant sink. The relative rate of these two reactions may define the global distribution of products from the atmospheric oxidation of DMS under local conditions.

These precedents together with the unknowns on the kinetic behavior of the system DMSO−Cl, like the not fulfilled mass balance or the temperature dependence or the influence of pressure, make further investigations necessary. In this work we report the first absolute kinetic study of the Cl−DMSO reaction, its temperature dependence in the range 273 to 335 K for pressures from 0.5 to 3.0 Torr, the observations of the products of reaction, and the possible mechanism.

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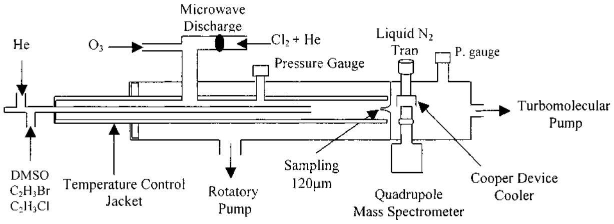

FIGURE 1. Schematic diagram of the experimental system.

Some results concerning the reaction between ClO and DMSO, which had not been studied previously, are also reported for room-temperature and low-pressure conditions.

Experimental Section

The kinetic experiments were carried out using the discharge-flow technique and a detection system based on mass spectrometry. The apparatus is shown schematically in Figure 1. The reactor consists on a 2.7 cm internal diameter and 100 cm length Pyrex flow tube with a jacket for the thermostating liquid circulation (SilOil). A movable injector (120 cm length, 1 cm i.d.) was used for the introduction of the reactants. The inner surfaces of the reactor and the movable injector were coated with halocarbon wax to reduce heterogeneous losses of atoms and radicals. The reactor was pumped by means of a rotary pump (70 m^3 h^{-1}), and the pressure was measured by means of a 10 Torr full-scale capacitance gauge. The quadrupole mass spectrometer (VG Smart IQ$^+$) was equipped with electron impact ion source and a Channeltron electron multiplier. The energy of the ionising electrons was typically $E_e = 40$ eV. The high vacuum chamber was pumped by means of a turbo-molecular pump (Varian V 550 L·s^{-1}), and a copper device cooler with liquid nitrogen surrounding the electron impact source was used to reduce the background spectrum. The detection limits for DMSO and ClO were 2×10^9 and 7×10^9 molecule cm^{-3}, respectively.

Cl atoms, precursors of ClO radicals in our experiments, were generated by passing a Cl_2/He mixture through a microwave discharge (2450 MHz) in a Pyrex sidearm coated with phosphoric acid in order to increase the Cl_2 dissociation yield, which could be checked by mass spectrometry at $m/e = 70, 72$. The decrease of the Cl_2 signal gave a measure of the efficiency of the process, from 15 to 50% depending on the experimental conditions, pressures, and fluxes. Cl atoms concentrations were measured from the titration reaction

$$\mathrm{Cl + BrCH = CH_2 \rightarrow Br + ClCH = CH_2}\ (3)$$
$$k = 1.4 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (21)$$

following the consumption of BrCH═CH_2 ($m/e = 107$) or the rising signal at $m/e = 62$ (ClCH═CH_2). Reference signals of bromoethene and chloroethene were obtained from known flows from their respective volume-calibrated storage balloons. Generally a good agreement was found between these two measurements and the direct calculation from the decrease of Cl_2.

ClO radicals were produced in an excess of O_3 to ensure a complete consumption of the Cl atoms

$$\mathrm{Cl + O_3 \rightarrow ClO + O_2}\ (4)$$
$$k = 1.2 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (22)$$

and were detected at $m/e = 51$. ClO signal was calibrated in complementary experiments by the titration reaction

$$\mathrm{ClO + NO \rightarrow NO_2 + Cl}\ (5)$$
$$k = 1.7 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (22)$$

with an excess of NO introduced through the injector and measuring the NO_2 formed at $m/e = 46$ using a reference NO_2 signal from an absolute calibration. In these calibration experiments, to generate ClO, Cl atoms were used in excess over O_3 to avoid the reaction

$$\mathrm{NO + O_3 \rightarrow NO_2 + O_2}(6)$$
$$k = 1.8 \times 10^{-14}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (22)$$

which would contribute to the NO_2 signal disturbing the ClO titration. O_3 was produced externally by passing pure O_2 through an ozone generator (Ozogas, 5 g/h) and purified and stored in a liquid N_2 trap before use. DMSO (diluted in He) was introduced through the movable injector.

The concentrations of reactants in the reactor were calculated from their pressure decrease rates in calibrated volume bulbs and the flows of the carrier gas, helium, were regulated and measured by mass flow controllers. For reaction 2, DMSO was stored in a glass trap in the liquid phase with a known volume and ended in a calibrated capillary. Different concentrations could be obtained by bubbling different flows of He through the trap and measuring the decrease in the capillary and the time of bubbling.

The chemicals used had the following purities: helium (Praxair, 99.999%), passed through a N_2 trap before entering the reactor; O_2 (Praxair, 99.999%), Cl_2 (Praxair, >99.8%), CH_3-$SOCH_3$ (Aldrich, 99.9%), C_2H_3Br (Aldrich, 98%), C_2H_3Cl (Fluka, ≥99.5%), NO (Praxair, ≥99%), NO_2 (Praxair, ≥99.5%). The reactants were purified from trap-to-trap distillation before use.

Results

Reaction DMSO + Cl. For reaction 1 the kinetic experiments were conducted under pseudo-first-order conditions with Cl atoms in great excess over DMSO with a ratio [Cl]/[DMSO] from 10 to 150. In most of the experiments the concentration of DMSO was close to 2×10^{11} molecule cm^{-3} and Cl atoms ranged from 1×10^{12} to 1×10^{13} atom cm^{-3}. Although an exact measurement of the DMSO was not required it could be estimated from the rate of its pressure decay in the storage balloon. Cl atoms were introduced in the reactor through a fixed port, while DMSO and bromoethene or chloroethene for Cl calibration entered the flow tube through the sliding injector (Figure 1). The flow velocities were fixed around 2500 cm/s giving times of reaction up to 30 ms.

For a bimolecular reaction between Cl and DMSO, the integrated rate constant that applies to our experimental conditions with Cl atoms in excess is

$$\mathrm{Ln}([\mathrm{DMSO}]_o/[\mathrm{DMSO}]) = k't \quad \text{with } k' = k\,[\mathrm{Cl}]\ (1)$$

The temporal profiles of DMSO were followed versus time, as it may be seen in Figure 2, where some typical kinetic runs using different [Cl] are shown. The experimental data follow the model, and the pseudo-first-order kinetic rate constants may be calculated from linear regression. Before and after each kinetic run, additional experiments were conducted in which the losses of reactants were evaluated separately. DMSO was expected to be lost on the walls of the reactor due to its low vapor pressure (0.37 Torr at 293 K). For the experiments concerning reaction 1, with low [DMSO], no heterogeneous losses were observed in the presence or absence of other coreactants, like Cl_2, see Figure 1; an upper limit of $k_W < 1\ s^{-1}$ was estimated. In the case of Cl atoms, they entered the injector through a fixed position but they were exposed to different lengths of injector. The Cl atoms were titrated versus time (injector position) with bromoethene and chloroethene coming from the sliding injector as described in the Experimental Section. From these calculations Cl losses in the injector walls of $k = 2-3\ s^{-1}$ were measured, which do not disturb the pseudo-first-order model

TABLE 1. Measured Second-Order Rate Constants *k*(1) for the Reaction Cl + DMSO → Products at Different Temperatures and Pressures[a]

P	0.5 Torr	1.0 Torr	1.0 Torr	1.0 Torr	3.0 Torr
T	298 K	273 K	298 K	335 K	298 K
k/(cm^3 molecule^{-1} s^{-1})	$(1.6 \pm 0.2) \times 10^{-11}$	$(1.6 \pm 0.2) \times 10^{-11}$	$(1.7 \pm 0.3) \times 10^{-11}$	$(1.4 \pm 0.3) \times 10^{-11}$	$(2.0 \pm 0.3) \times 10^{-11}$

[a] Errors are σ.

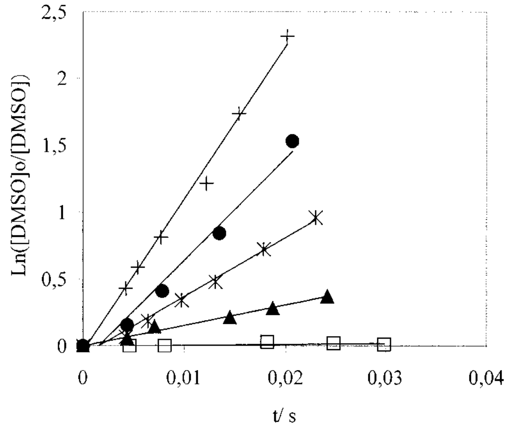

FIGURE 2. Pseudo-first-order plots at different chlorine concentrations obtained for reaction 1. [Cl] in units of atom cm^{-3}: [Cl] = 7.0 × 10^{12} (+), 4.6 × 10^{12} (●), 3.0 × 10^{12} (*), 1.0 × 10^{12} (▲), and 0 (□). The solid lines are the linear least-squares fits.

since Cl concentrations remained essentially constant during the experiment. Anyway, they were taken into account for the calculations.

To derive the rate constant of reaction 1, a correction on the eq 1 was applied to take into account the axial diffusion of DMSO. The experimental pseudo-first-order kinetic rate constants, k'_{exp}, obtained as described before, were corrected by (*23*)

$$k' = k'_{\mathrm{exp}}\,(1 + k'_{\mathrm{1exp}} \times D_{\mathrm{DMSO/He}}/v^2) \quad (2)$$

where v is the linear velocity of the gas mixture in the reactor (cm s^{-1}) and $D_{\mathrm{DMSO/He}}$ is the effective diffusion coefficient (cm^2 s^{-1}) calculated from the volumes of atomic diffusion (*24*). As $D_{\mathrm{DMSO/He}}$ is pressure and temperature dependent it was calculated for each experimental conditions. At room temperature and 1 Torr pressure $D_{\mathrm{DMSO/He}} = 270$ cm^2 s^{-1}. In most of the experiments the corrections on k' due to the axial diffusion was around 2%. The second-order rate constants, k, were then calculated by plotting the pseudo-first-order constant versus the corresponding Cl concentration (eq 1) and applying weighted least-squares fittings. A linear dependence on [Cl] with zero intercept was always found. Typical results obtained for different temperatures and pressures are shown in Figure 3, and the results are summarized in Table 1.

In the range of temperatures studied (273−335 K), no significant changes were observed in the rate constants within the experimental error, as it may be concluded from Table 1. In all the cases those parameters possibly affected by temperature, such as wall losses or diffusion coefficients were taken into account. Concerning the pressure dependence of the reaction it was checked from 0.5 to 3 Torr at room temperature. The results show that reaction 1 is not sensitive to pressure changes within this limited range.

Further experiments were also conducted to identify the products and intermediates of reaction 1 increasing the concentrations of the reactants. In these experiments, [DMSO] ranged from 1×10^{12} to 3×10^{14} molecule cm^{-3} and [Cl] from 1×10^{12} to 9×10^{12} atom cm^{-3}. Due to the relatively high levels of the background signals coming from the reactants, only qualitative considerations are possible. The sensitivity for the different products was not high enough to afford a quantification of the yield of the possible channels of reaction. Among the main observations it should be noticed that no production of HCl as a function of time (with a detection limit of 2×10^{11} molecule cm^{-3}) was observed, what would suggest that the H-abstraction channel is negligible. Two weak peaks at $m/e = 113$ and 115, assigned to ($CH_3SOCH_3{}^{35}Cl$) and ($CH_3SOCH_3{}^{37}Cl$), with increasing intensities versus time could be seen. Peaks at $m/e = 98$, 100, 50, 52 which could be assigned to $CH_3SO\ {}^{35}Cl$, $CH_3SO\ {}^{37}Cl$, $CH_3\ {}^{35}Cl$, and $CH_3\ {}^{37}Cl$ also showed temporal dependent profiles.

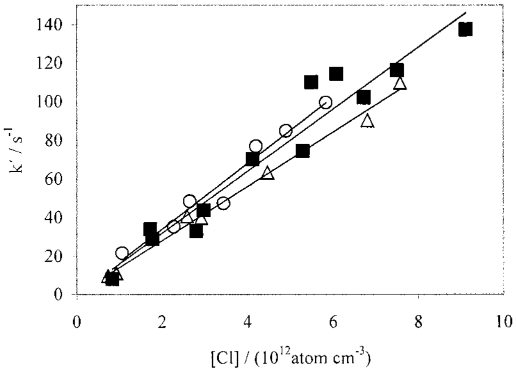

FIGURE 3. Pseudo-first-order rate coefficients, *k*′, versus [Cl] for the Cl + DMSO reaction at 1.0 Torr and different temperatures: *T* = 335 K (△), 298 K (○), and 273 K (■). The solid lines are the linear least-squares fits.

Reaction DMSO + ClO. No previous data were available in the literature concerning reaction 2. In this work it has been found to be very slow and so it required a significant increase of reactants to enable the study. However, the efficiency of the Cl_2 discharge decreased with increasing concentrations and so [ClO] could not be enhanced high enough to obtain a temporal decay of DMSO. The conditions were then inverted, with DMSO concentrations ($0.2 \times 10^{13}-4 \times 10^{14}$ molecule cm^{-3}) in excess over ClO which was monitored at $m/e = 51$, 53. Under these experimental conditions, the loss rate of DMSO in the wall of the reactor was typically 2−3 s^{-1}, very close to those obtained for the ClO losses on the injector wall. The kinetic data were analyzed like in the case of reaction 1. However the results were not so trustworthy due to the high uncertainties in the measurements of DMSO concentrations, see Figure 4. Although the pseudo-first-order rate constants clearly depend on the ClO concentration, significant contributions from secondary chemistry could be masked within these high error bars and so our measured rate constant for reaction 2, $k(2) \leq 6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at room temperature and 1.0 Torr, should be considered only as an upper limit value. $k(2)$ measured in this work is of the same order of magnitude than the corresponding rate constant obtained for the reaction of ClO with DMS ($k = 9.5 \pm 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}) (*22*). Up to now, no more data concerning ClO reactions toward sulfur compounds are available in the literature, and so quantitative trends cannot be stated.

TABLE 2. Tropospheric Chemical Lifetimes, τ, Estimated from Average Remote Concentrations and Gas-Phase Reactions

	concn/molecule cm^{-3}	k_{DMS}/cm^3 $molecule^{-1}$ s^{-1}	τ(DMS)	k_{DMSO}/cm^3 $molecule^{-1}$ s^{-1}	τ(DMSO)
OH	9.7×10^5 [a]	6.1×10^{-12} [f]	2 days	8.7×10^{-11} [h]	3.3 h
NO_3	7.4×10^6 [b]	1.0×10^{-12} [f]	2 days	5.0×10^{-13} [i]	3 days
O_3	7.4×10^{11} [c]	$<1 \times 10^{-18}$ [f]	>15 days	$<1 \times 10^{-19}$ [i]	>156 days
Cl	5.0×10^3 [d]	3.3×10^{-10} [g]	14 days	1.7×10^{-11} [j]	136 days
ClO	1.0×10^6 [e]	9.5×10^{-5} [f]	3.3 years	$\leq 6 \times 10^{-14}$ [j]	≥6 months

[a] From ref *29.* [b] From ref *30.* [c] From ref *31.* [d] From refs *19* and *20.* [e] From ref *32.* [f] From ref *22.* [g] From ref *26.* [h] From ref *15.* [i] From ref *16.* [j] Measured in this work.

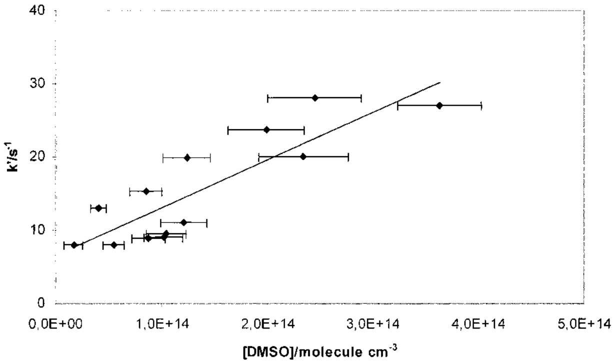

FIGURE 4. Pseudo-first-order rate coefficients, *k'*, versus [DMSO] for the ClO + DMSO reaction at 1.0 Torr and room temperature. The horizontal bars represent the errors (σ) in the measurements of [DMSO].

Discussion

In this article we report the first absolute study of the kinetics and mechanism of reaction 1 under low-pressure conditions. Previously to this work only a reference (*16*) reporting the results obtained in chamber experiments at atmospheric pressure and room temperature in the presence of O_2 was available. In that study the kinetic rate constant, $k_{298K} = (7.4 \pm 1.0) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, was obtained, and the formation of SO_2 and $DMSO_2$ with yields of (28 ± 12)% and (8 ± 2)%, respectively was found. $DMSO_2$ was argued to proceed not from a direct reaction of DMSO + Cl atoms but from DMSO reactions with long-lived intermediates or secondary chemistry. Only a minor part of the products was identified, and the large time scale of their experiments made it possible that secondary chemistry was responsible for additional losses of DMSO that would increase the apparent rate constant. This could explain the disagreement with the results obtained in this work, $k(1) = (1.7 \pm 0.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, where the fast discharge flow technique was allowed to obtain direct information from the elementary process.

From the data obtained in this study, reaction 1 may be considered as not affected by a change of temperature, with a near zero energy activation, which is consistent with the data available for other reactions of Cl atoms with sulfur compounds

$$Cl + H_2S \rightarrow HCl + SH$$
$$k = 3.7 \times 10^{-11} \exp[(210 \pm 100)/T]\ cm^3\ molecule^{-1}\ s^{-1}\ (25)$$

$$Cl + CH_3SH \rightarrow CH_3S + HCl$$
$$k = 1.2 \times 10^{-10} \exp[(150 \pm 50)/T]\ cm^3\ molecule^{-1}\ s^{-1}\ (25)$$

For Cl addition processes, like the system Cl−DMS at high pressures, a very slight temperature dependence was also found by Stickel (*26*) in the range 240−421 K.

From the mass spectroscopic peaks described in the results section, an addition mechanism involving an adduct formation is proposed. The adduct, supposed to be relatively stable since it maybe followed under the time reaction scale, may decompose into CH_3SOCl and CH_3. This is confirmed by the fact that CH_3SO could not be identified, which suggests that the formation of CH_3Cl occurs after the adduct decomposition by subsequent reaction of CH_3 with the Cl_2 in excess (not completely dissociated in the microwave discharge).

The high lifetime of the Cl−DMSO adduct is not surprising if we take into account the calculations of McKee (*27*), who predicted that a relatively stable adduct of the type $CH_3S(Cl)OCH_3$ and a binding energy of −7.4 kcal mol^{-1} at 0 K, could be formed as an intermediate in reaction 1. In a related case, like the Cl−DMS reaction (*26*), a long-lived Cl−DMS adduct was also found which did not decompose within the time scale of the experiments (several milliseconds). Our observations are also consistent with other previous results concerning DMSO−OH reactions. While DMS shows both abstraction and reversible adduct formation, the reactions of DMSO follow predominantly an addition mechanism (*9, 10, 15*). Furthermore, the fragments found in this work by mass spectrometry confirm the results of Urbanski et al. (*15*) who showed a yield of 100% in CH_3 and MSIA from the cleavage of a C−S bond in the DMSO−OH adduct. Our results are also supported by bond dissociation energy (BDE) calculations. The source of the difference in Cl reaction mechanism between DMS and DMSO probably lies in the sulfur-carbon BDE. As C−S BDE is estimated to be (308.4 ± 5.0 kJ mol^{-1}) in DMS and (236.0 ± 16.7 kJ mol^{-1}) in DMSO, the bond is more labile in the second case and the adduct may undergo direct dissociation. Nevertheless, a small branching ratio (<0.1) in the abstraction channel should not be ruled out since the background at m/e = 36, 38 was relatively high and so, if the production of HCl is small it would not contribute significantly enough at its parent peaks as to be detected.

An estimation of the gas-phase lifetime of DMSO may be obtained from the reaction rates at room temperature with the tropospheric agents such as OH, NO_3, O_3, Cl, ClO, taking into account their average concentrations in remote areas and the measured room temperature rate constants, Table 2. Considering that DMSO is produced from the OH-DMS reaction mainly in marine areas, where DMS is emitted by the phytoplankton, and that heterogeneous reactions of nitrogen oxides on sea salt particles can lead to photolytic precursors of Cl atoms, the local Cl concentrations may be as high as 10^4−10^5 atom cm^{-3} (*19, 28*). So, in these marine areas, the calculated DMSO lifetime from the reaction with Cl atoms may be as low as 6.8 days, comparable to that from NO_3 (3 days). Nevertheless, even under these local conditions OH constitutes the main DMSO sink. Using an average Cl concentration of 5.0×10^3, Table 2, the DMSO lifetime lies in the order of 136 days. From our results (Table 1) the Troposphere's temperature profile would not affect this sink of sulfur species. So, although Cl atoms scavenge DMS efficiently, Table 2, giving lifetimes of few days, comparable to those of OH, NO_3, and ozone, the gas-phase chemistry of

DMSO is dominated by the OH initiated processes and, in a less extent, by reaction with NO_3 radical. The effect of reaction 1 in the removal of DMSO should be considered in mechanistic models of sulfur atmospheric chemistry only under high Cl concentrations and as a minor homogeneous sink. Lifetimes of DMS and DMSO in the order of several months are calculated due to ClO reactions, Table 2, showing that reaction 2 has a negligible effect on the removal of DMSO.

Finally, for a complete evaluation of DMSO processes, the heterogeneous losses must be considered and compared to homogeneous reactions. Up to now this is not possible due to the disagreement concerning the uptake rate of DMSO onto particles (*12, 13*). So, further investigations in this sense are required to quantify the relative importance of homogeneous and heterogeneous processes.

Acknowledgments

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