

**Birkbeck ePrints: an open access repository of the
research output of Birkbeck College**

<http://eprints.bbk.ac.uk>

Thompson, Katherine C., Canosa-Mas, Carlos E.
and Wayne, Richard P. (2002) Kinetics and
mechanism of the reaction between atomic chlorine
and dimethyl selenide; comparison with the reaction
between atomic chlorine and dimethyl sulfide.
Physical Chemistry Chemical Physics **4** (17) 4133-
4139.

This is an author-produced version of a paper published in *Physical Chemistry Chemical Physics* (ISSN 1463-9076). This version has been peer-reviewed but does not include the final publisher proof corrections, published layout or pagination.

All articles available through Birkbeck ePrints are protected by intellectual property law, including copyright law. Any use made of the contents should comply with the relevant law.

Citation for this version:

Thompson, Katherine C., Canosa-Mas, Carlos E. and Wayne, Richard P. (2002) Kinetics and mechanism of the reaction between atomic chlorine and dimethyl selenide; comparison with the reaction between atomic chlorine and dimethyl sulfide. *London: Birkbeck ePrints*. Available at:
<http://eprints.bbk.ac.uk/archive/00000238>

Citation for the publisher's version:

Thompson, Katherine C., Canosa-Mas, Carlos E. and Wayne, Richard P. (2002) Kinetics and mechanism of the reaction between atomic chlorine and dimethyl selenide; comparison with the reaction between atomic chlorine and dimethyl sulfide. *Physical Chemistry Chemical Physics* **4** (17) 4133-4139.

Kinetics and mechanism of the reaction between atomic chlorine and dimethyl selenide; comparison with the reaction between atomic chlorine and dimethyl sulphide

Katherine C. Thompson*

Division of Physical and Inorganic Chemistry, School of Life Sciences, University of Dundee, Dundee DD1 4HN, UK.

Current address (2005): School of Biological and Chemical Sciences, Birkbeck College University of London, Gordon House, 29 Gordon Square, London, WC1H 0PP

Carlos E. Canosa-Mas and Richard P. Wayne.

Physical and Theoretical Chemistry Department, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK.

Abstract

Dimethyl selenide is the most abundant gaseous selenium species in marine environments. In this work, the value of the rate coefficient for the gas-phase reaction between dimethyl selenide and Cl atoms has been determined for the first time. The value of the second-order rate coefficient obtained was $(5.0 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The very fast nature of the reaction means that, when estimating the lifetime of dimethyl selenide in the atmosphere, loss due to reaction with Cl atoms should be considered along with loss due to reaction with O_3 and with OH and NO_3 radicals.

Analysis of the available kinetic data suggests that at 760 Torr the dominant reaction pathway for the reaction of Cl atoms with dimethyl selenide will be the addition of Cl to the Se atom forming an adduct of the type $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$. Theoretical calculations, at the B3LYP/6-311++G(2df,p)/B3LYP/6-311++G(d,p) level of theory, show that at 298 K the value of $\Delta_r H^\ominus$ for the formation of the adduct is $-111.4 \text{ kJ mol}^{-1}$. This value may be compared to $-97.0 \text{ kJ mol}^{-1}$, the value calculated for $\Delta_r H^\ominus$ for the formation of the analogous sulphur adduct, $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$, following the reaction between Cl atoms and dimethyl sulphide. Variational RRKM theory was used to predict the thermal decomposition rates of the two adducts back to starting materials. The estimated rate constant for the decomposition of the selenium adduct to the reactants is $5 \times 10^{-5} \text{ s}^{-1}$, compared to 0.02 s^{-1} in the case of the sulphur adduct. However, our calculations suggest that the $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$ adduct, which initially is formed highly excited, will not be stabilised under atmospheric conditions, but rather that it will decompose to yield CH_3SeCl and CH_3 , a process that is calculated to be exothermic with respect to the initial reactants by 5.8 kJ mol^{-1} . The formation of $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$ and CH_3 from the sulphur adduct, on the other hand, is endothermic by 20.8 kJ mol^{-1} with respect to the initial reactants, and is thus not expected to occur.

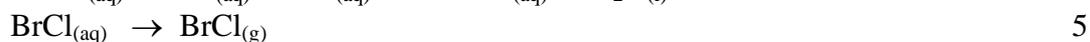
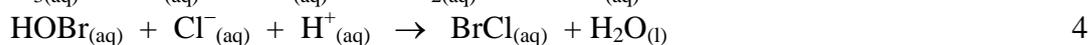
Introduction

Selenium is an essential element for both plant and animal life. In humans it is linked to the correct functioning of the thyroid and the immune system,¹ but only a trace amount is required, an excess of selenium being harmful. Selenium-containing compounds are present in the atmosphere in both gaseous and particulate forms. Anthropogenic sources of selenium in the atmosphere are reported to total $(3 - 10) \times 10^9 \text{ g yr}^{-1}$, whilst natural sources contribute $(6 - 32) \times 10^9 \text{ g yr}^{-1}$, almost all of which comes from the marine biosphere.² The most abundant gaseous selenium-containing compound to be identified in marine air is dimethyl selenide, CH_3SeCH_3 ,³⁻⁵ although other organo-selenide species have also been detected: they include methyl selenol, CH_3SeH , and dimethyl diselenide, $\text{CH}_3\text{Se}_2\text{CH}_3$.^{4,5} The source of these organic forms of selenium is biological, certain bacteria and algae being able to reduce inorganic forms of Se into methylated forms.⁵⁻⁸ Inorganic forms of selenium are more toxic than organic forms, and it has been suggested that biomethylation followed by volatilisation into the gas phase is one mechanism used by biological species to cope with elevated selenium levels.⁹

Once released into the gas phase, the lifetime of dimethyl selenide is small, a matter of hours or even minutes, since, although dimethyl selenide is not readily photolysed in the troposphere,¹⁰ the compound is highly reactive towards the atmospheric oxidants. The kinetics and products of the reactions between the oxidants OH, NO_3 and O_3 have been studied previously;^{10,11} however, no value has been reported to date for the rate constant, k_1 , for the reaction of dimethyl selenide with atomic chlorine, Cl



Several sources of gas-phase Cl atoms exist in the marine boundary layer. The reactions of the oxides of nitrogen and ozone with sea-salt aerosol (or sea-water ice) convert aqueous phase Cl^- ions into photolytically labile gas-phase forms of chlorine; for instance, gas-phase ClNO_2 or BrCl may be generated in the reactions^{12,13}



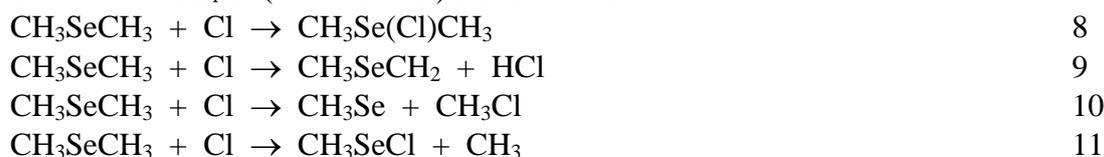
And these compounds will be photolysed during the day, liberating free Cl atoms



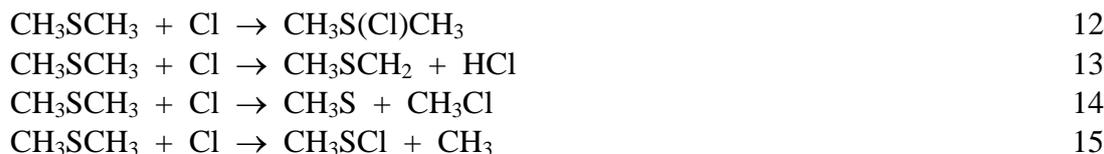
No direct measurement of Cl atom concentrations in the troposphere has been made (because of severe experimental difficulties), but Cl_2 and BrCl have both been observed at parts per trillion (ppt) levels in marine air.^{14,15} Attempts to estimate the concentration of Cl atoms in marine air have been reported in a number of studies. Behnke *et al.*¹³ estimated a 12 hour average concentration of $1.8 \times 10^5 \text{ molecule cm}^{-3}$ at 60°N from a modelling study, whilst Spicer *et al.*¹⁴ predicted a peak value of $1.3 \times 10^5 \text{ molecule cm}^{-3}$ in the marine boundary layer based on a measured concentration of

Cl₂. Wingenter *et al.*¹⁶ suggested a 5-hour average concentration of Cl atoms in the marine troposphere after dawn of 3.3×10^4 molecule cm⁻³, from analysis of measurements of the relative decay of selected organic compounds in parcels of air. Thus, as both Cl atoms and dimethyl selenide are species present in the marine boundary layer, it is important to ascertain the extent to which reaction (1) is an important route for loss of dimethyl selenide in the atmosphere.

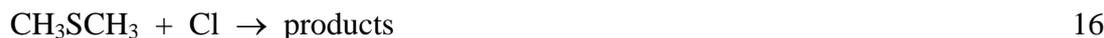
In this paper, we describe experimental investigations of the kinetics of Cl-atom loss in the presence of CH₃SeCH₃. Although the products of reaction (1) were not determined experimentally in our study, some theoretical calculations were undertaken so that the thermodynamically feasible pathways could be established. The values of $\Delta_r H^\ominus$ (at $T = 298$ K) for the reactions



were calculated using the Gaussian-98 suite of programs.¹⁷ These particular pathways were chosen since they are the analogues of those for the reaction of atomic chlorine with dimethyl sulphide

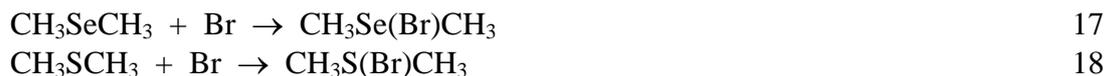


that have previously been considered to be the most likely to occur and have been studied in some detail.¹⁸⁻²² However, although a number of studies have been undertaken on the nature of the general reaction



significant disagreements exist in the literature with respect to the thermochemistry of the possible reaction pathways^{12-15,18,21-24} For this reason, it was thought prudent to calculate the values of $\Delta_r H^\ominus$ for reactions (12) – (15), as well as for reactions (8) – (11), in the present work.

For comparison, the values of $\Delta_r H^\ominus$ for the formation of an adduct between a Br atom and dimethyl selenide and dimethyl sulphide:



were also determined.

Experimental

The reaction between atomic chlorine and dimethyl selenide was studied using the discharge-flow technique. The flow tube and other apparatus used have been described previously.²⁵ All experiments were performed at $P = 1.5$ Torr and at room temperature (298 ± 2 K). Helium was used as the main flow gas in all experiments, and linear flow velocities of between 37.0 and 50.7 m s^{-1} were employed.

The reactions were studied under pseudo-first order conditions and the data were treated using the integrated form of the rate equation, $\ln[\text{Cl}]_t = k't + \text{constant}$. The concentration of dimethyl selenide was varied in the range $(2.0 - 10.1) \times 10^{11} \text{ molecule cm}^{-3}$, and was always at least a factor of 5 (and up to a factor of 36) greater than the concentration of Cl atoms. Chlorine atoms were detected by resonance fluorescence at $\lambda \sim 138 \text{ nm}$, resulting from the $(3p)^2P_{3/2} \leftarrow (4s)^4P_{3/2}$ transition. The incident light for the resonance fluorescence was supplied by passing a dilute ($< 4\%$) mixture of molecular chlorine in helium through a microwave discharge. A BaF_2 window separated the lamp from the fluorescence cell and a CaF_2 lens was placed between the cell and the photomultiplier (Hamamatsu, R6835). The best detection limit achieved was $6 \times 10^8 \text{ molecule cm}^{-3}$, for a signal to noise ratio 1:1 and an integration time of 10 s. The source of Cl atoms in the flow tube was the reaction of atomic fluorine with a large excess of HCl



The fluorine atoms were produced by passing a dilute ($\sim 0.5\%$ F_2 in He) mixture of F_2 through a microwave-discharge.

Materials

The helium used for the main flow gas and resonance-fluorescence lamp was supplied by BOC with a stated purity of 99.9% and 99.999%, respectively. In both cases, the helium was passed through a mixture of molecular sieves (BDH, 4A, 5A and 13X, held at liquid N_2 temperature) before use. HCl (Aldrich, 99.5+%), chlorine (BDH, 99.9%) and dimethyl selenide (Strem, 99.9%) were subjected to freeze-pump-thaw cycles before use. The fluorine (Messer 1% in 99.999% He) was used as supplied.

Computations

All calculations were performed using the Gaussian-98 suite of programs¹⁷ running on a Silicon Graphics Origin 200 computer. Optimisation was carried out on the geometries of the species CH_3SeCH_3 , CH_3SCH_3 , $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$, $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$, $\text{CH}_3\text{Se}(\text{Br})\text{CH}_3$, $\text{CH}_3\text{S}(\text{Br})\text{CH}_3$, CH_3SeCH_2 , CH_3SCH_2 , HCl, CH_3Se , CH_3S , CH_3Cl , CH_3SeCl , CH_3SCl and CH_3 , at the B3LYP/6-311++G(d,p) level of theory.^{26,27} The use of the B3LYP functional allows some corrections for electron-correlation effects to be made (not considered at the Hartree-Fock level) but is generally less computationally demanding than conventional *ab initio* correlation methods, such as the second-order Møller-Plesset method (MP2).

Frequency calculations were performed on the optimised geometries, again at the B3LYP/6-311++G(d,p) level of theory. No suggested value for a scaling factor for frequencies predicted at this level of theory was found in the literature; however, Mebel *et al.*²⁸ recommend a scaling factor of 1.00 when working at the B3LYP/6-311G(d,p) level, and Bauschlicher and Partridge²⁹ recommend a scaling factor of

0.989 when working at the B3LYP/6-311+G(3df,2p) level. It was therefore decided not to use a scaling factor.

The absolute energies (SCF energies) of all the compounds in their optimised geometries were calculated at the B3LYP/6-311++G(2df,p) level of theory; the absolute energies of Cl and Br atoms were also computed at this level. The values obtained were used along with the thermal corrections obtained from the frequency calculations, to calculate the value of $\Delta_r H^\ominus$ at 298 K for reactions (8) – (15) and reactions (17) and (18).

Results

Kinetic studies

$\ln[\text{Cl}]$ was plotted as a function of reaction time for a number of different concentrations of dimethyl selenide; an example of such a ‘first-order plot’ is shown in figure 1. The slopes of the first-order plots are the *pseudo*-first-order rate constants, k' , which themselves should be a linear function of the concentration of dimethyl selenide with gradient equal to the second-order rate constant, k_1 , as shown in figure 2. The intercept of the line of best fit is zero at the 95 % confidence limits. The value of the rate coefficient obtained from the slope of the second-order plot is $(5.0 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; the error represents the 95 % confidence limits of the linear regression. The relatively large value of the error reflects the rather scattered nature of the second-order plot. The cause of the scatter is not known: such scatter may be due to a heterogeneous process, although this suggestion is purely speculative.

Energy and Geometry Calculations

Figures 3 and 4 show the optimised geometries of the adducts $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$ and $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$ obtained at the B3LYP/++G(d,p) level of theory. Table 1 gives the frequencies predicted for these optimised structures, alongside the frequencies predicted for dimethyl selenide and dimethyl sulphide. Table 2 gives the calculated absolute energies of all species considered. Table 3 summarises the values of $\Delta_r H^\ominus$ calculated in this work, along with published values for comparison. To the best of the authors’ knowledge, the values of $\Delta_r H^\ominus$ for reactions (8) – (11) have not been reported previously.

Discussion

Heats of reaction

The heats of reaction ascribed in table 3 to DeMore *et al.*³⁰ are values obtained from the heats of formation recommended by these authors for the various species. The values of Stickel *et al.*¹⁸ and of Nakano *et al.*³¹ are based on experimental observations, whilst those of McKee,²³ Wilson and Hirst,²⁴ and Resende and De Almeida²¹ are based on *ab initio* calculations.

As can be seen from table 3, the value of $\Delta_r H^\ominus$ calculated in this work for the formation of the adduct $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$ (reaction (12)) agrees fairly well with the value of Wilson and Hirst but not with the values calculated by McKee or Resende and De Almeida. Wilson and Hirst performed a MP4(Full)/6-311+G(2df,p)//MP2(Full)/6-311G(p,d) calculation, and Resende and Almeida performed a QCISD(T)/DZP//MP2(Full)/DZP level calculation. The earlier study by McKee

involved the use of a rather small basis set, the level of theory being PMP2/6-31G(d)//HF/3-21G(d).

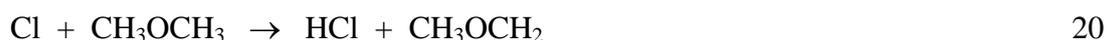
Experimental evidence suggests that the binding energy of the $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$ adduct is greater than that determined by McKee or by Resende and De Almeida. The experimentally determined value of $\Delta_r H^\circ$ for reaction (18), the reaction of Br atoms with dimethyl sulphide to form the adduct $\text{CH}_3\text{S}(\text{Br})\text{CH}_3$, obtained by Stickel *et al.*¹⁸ is in reasonable agreement with the value predicted in this work, which is a little higher than the value determined experimentally by Nakano *et al.*³¹ and the value calculated of McKee. Stickel *et al.* observed that the bromine adduct was considerably less stable with respect to the reactants than the chlorine analogue, $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$. In the case of the Br adduct, decomposition back to reactants occurs on the microsecond timescale, whilst the $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$ adduct is stable with respect to decomposition back to reactants on the millisecond timescale.²² It therefore appears that the bromine adduct is less stable than the chlorine adduct and that the values of $\Delta_r H^\circ$ predicted by McKee and Resende and De Almeida for reaction (12) are rather too low.

The values of $\Delta_r H^\circ$ obtained in this work are in excellent agreement for reaction (13) and in fair agreement for reaction (14) with the values obtained from the recommended heats of formation of DeMore *et al.*, but are in poor agreement with those calculated by Resende and De Almeida. The value of $\Delta_r H^\circ$ predicted in this work for reaction (15) does not agree that presented by Resende and De Almeida, but does agree within error with the value estimated by Stickel *et al.* based on an estimated heat of formation for CH_3SCl . In summary, the values of $\Delta_r H^\circ$ calculated by us for the possible pathways of the reaction between Cl and CH_3SCH_3 are generally in good agreement with those based on estimated or experimentally determined values of heats of formation, however, the agreement is poorer with the only other computational investigation that examined all four of these channels.

Mechanism of reaction

In view of what is already known¹⁸ about the mechanism of reaction 16, the reaction of atomic chlorine with dimethyl sulphide, it seems that the reaction between Cl atoms and dimethyl selenide is likely to occur either *via* the initial addition of the Cl atom to the Se atom, reaction (8), or *via* the abstraction by Cl of an H atom from dimethyl selenide, reaction (9). The likely relative importance of these two channels will now be discussed.

The rate coefficient for reaction (13), the S-analogue of abstraction-reaction (9), appears to be $\sim 1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁸ This value is very similar to the rate coefficient of $1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction between Cl atoms and dimethyl ether³²



a reaction that occurs solely by an abstraction mechanism.

It might therefore seem that the rate coefficient for abstraction of a hydrogen from dimethyl selenide, reaction (9), would also be $\sim 1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The much larger overall rate coefficient, k_1 , for the reaction of Cl atoms with dimethyl

selenide obtained in this work ($(5.0 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1.5 Torr) suggests that an addition process must operate alongside the abstraction, and that roughly one-third of reaction (1) proceeds *via* the abstraction process at this pressure, and the remainder *via* an addition channel, presumably:



If this interpretation is correct, the addition occurs at a rate approaching the collision-controlled limit and, even at 1.5 Torr, redissociation of the excited adduct $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3^*$ does not compete with other processes in which the adduct may participate (stabilisation or loss *via* processes other than the reverse of reaction (21)).

The immediate fate of the adduct obviously requires detailed consideration. However, since more is known about the fate of the sulphur adduct $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3^*$, it is convenient to discuss first possible decomposition routes of this latter species, formed in reaction (22):

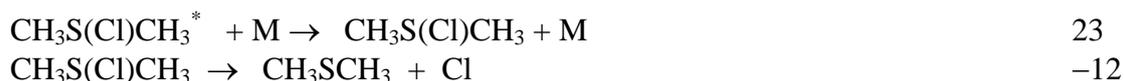


The decomposition routes considered are decomposition back to reactants (the reverse of reaction (22)), decomposition to yield CH_3S and CH_3Cl (overall reaction (14)), or decomposition to yield CH_3SCl and CH_3 (overall reaction (15)). Reaction (15) is, however, endothermic (table 3), and would not be expected to be of importance; this expectation is indeed borne out by experimental observations, Zhao *et al.*²⁰ finding that only 2 % of reaction (16) led to the formation of CH_3 .

The formation of CH_3S and CH_3Cl is exothermic with respect to the initial reactants. However, if the adduct $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3^*$ were involved, decomposition to yield CH_3S and CH_3Cl would involve the migration of the Cl atom from the sulphur atom to a carbon atom, accompanied by the breaking of a S–C bond. A rearrangement of this type would probably be associated with a low-entropy transition state, and thus a low reaction probability. It must, of course, be recognised that the products CH_3S and CH_3Cl could be formed *via* a pathway that does not involve the adduct. The theoretical study of Resende and De Almeida²¹ predicted that an adduct of the type $\text{CH}_3\text{SC}(\text{Cl})\text{H}_3$ may be formed following the reaction of atomic chlorine with dimethyl sulphide, a reaction which they report to be exothermic by 2.4 kJ mol^{-1} . The authors state that a transition state lying 107 kJ mol^{-1} higher in energy than the initial reactants must be passed in order to generate $\text{CH}_3\text{S} + \text{CH}_3\text{Cl}$. A *preliminary* search for an adduct of the form $\text{CH}_3\text{SC}(\text{Cl})\text{H}_3$ was undertaken in this work but no stable adduct was located. Experimental studies by Langer *et al.*¹⁹ have shown that the branching ratio for the formation of CH_3Cl from the reaction of Cl with CH_3SCH_3 , was very low, $(1.34 \pm 0.07) \times 10^{-3}$, supporting the idea that the pathway leading to the formation of CH_3Cl and CH_3S is not a kinetically favourable one.

It appears from the preceding discussion that the most likely fate of the initially formed excited $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3^*$ adduct is either decomposition back to reactants or stabilisation to $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$ followed by thermal decomposition back to reactants:





Variational RRKM theory, as described by Gilbert and Smith,³³ and implemented *via* the program Multiwell,^{34,35} was employed to investigate the relative importance of reactions (-22) and (23), and the rate at which reaction -12 might proceed. The formation of the excited adduct appears to occur without a barrier.¹⁸ The position of the transition state for reaction (-12) (and (-22)) was therefore determined by calculating the value of $k_{uni}^\infty(-12)$ for various S-Cl bond lengths, r . The transition state for the reaction will correspond to geometry for which the value of $k_{uni}^\infty(-12)$ calculated is minimised.

The potential energy curve was assumed to take the form of a Morse function

$$V(r) = D_e \left[1 - e^{-\beta(r-r_e)} \right]^2 \quad \text{I}$$

where r_e is the equilibrium bond length for the S-Cl bond, 2.68 Å, and D_e is the dissociation energy from the bottom of the potential well, taken as the difference in the SCF energies of CH₃SCH₃ and Cl, and the adduct. The parameter β is given by the equation

$$\beta = \left(\frac{2\pi^2\mu}{D_e} \right)^{1/2} \nu \quad \text{II}$$

where μ is the reduced mass for CH₃SCH₃ and Cl, and ν is the harmonic stretching frequency for a S-Cl bond. Analysis (using the visualisation software MolDraw)³⁶⁻³⁹ of the normal modes of vibrations calculated for CH₃S(Cl)CH₃, and shown in table 1, reveals that the vibration at 237.2 cm⁻¹ corresponds to stretching of the S-Cl bond. This value was used to determine the value of β , calculated to be 1.50 Å⁻¹. The relatively small value of β reflects the long-range nature of the interaction between the sulphur and the chlorine atoms.

The moment of inertia for the inactive 2-D rotation of CH₃S(Cl)CH₃ was taken as the geometric mean of the two larger and similar moments of inertia for the external rotation of the adduct; the different, smaller, value was taken as the moment of inertia for the active 1-D rotation. The density of states for CH₃S(Cl)CH₃ was calculated using the vibration frequencies shown in table 1 and the moment of inertia for this 1-D active external rotation.

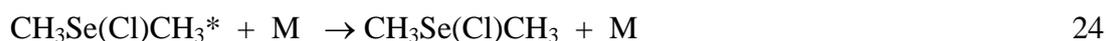
A simple Gorin-type model⁴⁰ was used to determine the density of states of the CH₃S(Cl)CH₃ species at various values of r . The vibrations of the species were taken to be those of CH₃SCH₃ itself (as given in table 1). The 2-D rocking motion of the CH₃SCH₃ group relative to the chlorine was taken to resemble a free 2-D rotation of the CH₃SCH₃ molecule. The position of the centrifugal barrier for this reaction was calculated to be when $r = 8.7$ Å, indicating that the transition state was likely to occur at a large value of r where any steric hindrance to rotation would be negligible. Nether the less, the long range nature of the bonding interaction between the S and Cl moieties would cause there to be a small hindrance to rotation, caused by the loss of

the weak S–Cl bonding interaction, present even at relatively large r . This was not taken into account in the calculations and would be expected to cause the value of k_{uni}^∞ (–12) obtained to be slightly higher than the true value.

The position of the transition state was determined as that which gave the lowest predicted value of k_{uni}^∞ (–12), and was found to be at $r = 7.9 \text{ \AA}$, significantly inside the position of the centrifugal barrier. The value of k_{uni}^∞ (–12) calculated was 0.02 s^{-1} .

Calculations performed to solve the Master Equation (and implemented *via* the program Multiwell) for the fate of $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3^*$ in a bath gas of N_2 at $P = 760 \text{ Torr}$ and $T = 298 \text{ K}$ showed that stabilisation of the adduct, reaction (23), dominated over decomposition to CH_3SCH_3 and Cl , reaction (–22).

We now turn to the selenium system, and consider possible fates of the $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3^*$ adduct. The routes considered are decomposition back to the starting materials, stabilisation to yield $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$ followed by thermal decomposition back to CH_3SeCH_3 and Cl , rearrangement and decomposition to form CH_3Se and CH_3Cl and the loss of a methyl group to form CH_3SeCl and CH_3 :



As for dimethyl sulphide in (the evidently unfavourable) reaction (14), splitting off CH_3Cl in reaction (25) would most likely occur *via* a low-entropy transition state. However, the formation of CH_3Se and CH_3Cl from $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3^*$ is 27.6 kJ mol^{-1} more exothermic than the formation of CH_3S and CH_3Cl from $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3^*$. It cannot therefore be assumed on thermochemical grounds alone that the decomposition of $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$ to yield CH_3Se and CH_3Cl will not occur. Incidentally, the alternative adduct, $\text{CH}_3\text{SeC}(\text{Cl})\text{H}_3$, was briefly searched for in the present work, but no stable adduct of this type was located.

The occurrence of reaction (26), leading to the formation of CH_3SeCl and CH_3 , is exothermic by 5.8 kJ mol^{-1} , and if no additional activation barrier is associated with this process, then reaction (26) must be considered alongside reactions (–21) and (24) as one of the fates of the adduct first formed. Variational RRKM theory was therefore employed in the Se-system to determine whether stabilisation of the excited adduct dominated over decomposition to $\text{CH}_3\text{SeCH}_3 + \text{Cl}$, or $\text{CH}_3\text{SeCl} + \text{CH}_3$ at 760 Torr, 298 K.

In the case of both reaction (–8) (and (–21)) and (26), the position of the transition state was located variationally by varying the length of the bond to be broken, the Se–Cl bond in the case of reaction –8, and a Se–C bond in the case of reaction (26). Equation I was used to determine the shape of the potential well for stretching of the relevant bond. The values of D_e were again taken as the difference in the calculated

SCF energies of the appropriate species. The vibration frequency of the $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$ adduct at 199.2 cm^{-1} was found to correspond to the stretching frequency of the Se–Cl bond, and this value was therefore used to calculate the value of β according to equation II. The value obtained was $\beta = 1.28\text{ \AA}^{-1}$. The vibrational stretching frequency of the Se–C bond was taken as 589.4 cm^{-1} (the value calculated for the asymmetric stretching motion of this bond in $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$), giving $\beta = 2.61\text{ \AA}^{-1}$.

As before, a simple Gorin-type model was used to obtain the density of states of the adduct with various values of r . In the case of reaction (–8), the densities of states were calculated as described above for reaction (–12). In the case of reaction (26), the vibrations of the transition state were taken as those calculated in this work for a CH_3SeCl molecule: 3166.4, 3137.0, 3046.4, 1473.8, 1445.3, 1310.4, 923.3, 908.0, 571.3, 388.9, 185.0 and 159.6 cm^{-1} , and a CH_3 radical: 3281.7, 3281.5, 3101.6, 1402.6 (2-fold degenerate) and 537.5 cm^{-1} . The rocking motion of the CH_3SeCl and CH_3 units relative to each other was taken to be equivalent to the 2-D free rotations of CH_3SeCl and CH_3 . The torsional rotation of the CH_3SeCl and CH_3 units relative to each other was treated as a free rotation with a reduced moment of inertia of 3.213 amu \AA^2 .

The position of the transition state for reaction (–8) was found to be at 9.1 \AA , inside the position of the centrifugal barrier at 10.0 \AA . The value of k_{uni}^∞ (–8) calculated was $5 \times 10^{-5}\text{ s}^{-1}$. In the case of reaction (26), the centrifugal barrier was calculated to be at 4.8 \AA and the position of the transition state was found to be at 4.4 \AA . The value of the rate constant was k_{uni}^∞ (26) = 0.5 s^{-1} . The significantly larger rate constant relative to that for reaction (–8) reflects both the lower value of the critical energy required to give products and the looser nature of the transition state (stiff vibrational degrees of freedom are converted into loose 2-D rotations of two fragments, not one fragment as is the case in reaction (–8)).

Calculations performed to solve the Master Equation for the dissociation of $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3^*$ to either $\text{CH}_3\text{SeCH}_3 + \text{Cl}$, or to $\text{CH}_3\text{SeCl} + \text{CH}_3$ in a bath gas of N_2 at $P = 760\text{ Torr}$ and $T = 298\text{ K}$ showed that, although in the case of reaction (–21) stabilisation of the initially formed excited adduct, $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3^*$ dominates over decomposition to CH_3SeCH_3 and Cl , this is not the case for reaction (26). Of the initially formed excited adduct, $\sim 95\%$ will, in fact, decompose to $\text{CH}_3\text{SeCl} + \text{CH}_3$. Thus, if reaction (26) starting from $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3^*$ does indeed occur without a barrier, as has been assumed in this work, it appears that the reaction of CH_3SeCH_3 and Cl to form the adduct $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3^*$ will lead predominantly to the formation of $\text{CH}_3\text{SeCl} + \text{CH}_3$. This result appears to agree with the experimental evidence reported in this work, where a loss of Cl atoms was observed in the presence of CH_3SeCH_3 , at 1.5 Torr total pressure.

Atmospheric significance

A major objective of the present investigation was to establish whether or not reaction with atomic chlorine is an important loss route for dimethyl selenide in the atmosphere. For the reaction



27

the lifetime of dimethyl selenide with respect to loss through reaction (27) may be defined as $1/(k_{27}[\text{oxidant}])$, where [oxidant] is the concentration of the oxidant e.g. Cl, OH, O₃ etc. The work of Atkinson *et al.*¹⁰ has demonstrated that during the day dimethyl selenide has a natural lifetime, τ , with respect to chemical degradation by OH radicals and O₃ of only a few hours. Table 4 shows the lifetime of dimethyl selenide with respect to oxidation by chlorine atoms, OH radicals and ozone, the atomic chlorine concentrations in the first two cases are for scenarios that are thought to be realistic, but that nevertheless encompass concentrations that range rather widely (over a factor of five or more). The values indicate that the loss of dimethyl selenide due to reaction with atomic chlorine is significant over all the concentration range, and becomes of considerable importance at the higher end of the expected concentrations. The reaction should thus be included when estimating the lifetime of dimethyl selenide in the marine boundary layer.

The final products of the reaction of Cl atoms with dimethyl selenide formed in the atmosphere will now be discussed. The Se-containing product of reaction (9), the abstraction channel, is exactly the same as that formed when OH radicals abstract a hydrogen from dimethyl selenide



The fate of CH₃SeCH₂ in the atmosphere is suggested by Rael *et al.*¹¹ to be the formation of methaneseleninic acid, CH₃Se(O)OH. The vapour pressure of the acid is much lower than that of dimethyl selenide, and the compound would almost certainly be taken up rapidly onto atmospheric particles. However, as mentioned previously, the dominant reaction channel for reaction (1) at $P = 760$ Torr is not expected to be the abstraction of an H atom, but rather the addition of Cl to the Se atom of dimethyl selenide.

The addition of chlorine to dimethyl selenide, reaction (21), would lead to the formation of the adduct CH₃Se(Cl)CH₃^{*}. Our calculations suggest that this adduct, initially formed in an excited state, will not be stabilised but rather will decompose to give CH₃SeCl and CH₃ under atmospheric conditions. The CH₃ radical will react further in the atmosphere to yield formaldehyde.⁴³ The fate of CH₃SeCl is not known.

The atmospheric fate of the sulphur containing adduct, CH₃S(Cl)CH₃^{*}, also considered in this work, is another question that is currently unresolved. In this case, our investigations indicate that stabilisation of the adduct to CH₃S(Cl)CH₃ will occur before decomposition under atmospheric conditions. This results is in line with the observations of Urbanski and Wine²², who observed this sulphur adduct spectroscopically, and studied aspects of its chemistry. They found that the adduct reacts only very slowly with O₂, if at all, the rate constant being $< 4 \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹; however, a fast reaction between CH₃S(Cl)CH₃ and both NO and NO₂ was observed with $k_{\text{NO}} = (1.19 \pm 0.18) \times 10^{-11}$ and $k_{\text{NO}_2} = (2.70 \pm 0.41) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, and the authors concluded that reaction with NO or NO₂, thermal decomposition back to the starting materials or photo-decomposition to unknown products were the likely fate of the adduct in the atmosphere. The value of the rate constant for the thermal decomposition of the CH₃S(Cl)CH₃ adduct back to CH₃SCH₃ and Cl has been calculated in our work to be 0.02 s⁻¹ for conditions appropriate to the lower troposphere.

Acknowledgements

The authors would like to thank the NERC for support under grant GST/02/1516 and the Commission of the European Union (DGXII) for a grant in the HALOBUD project (PL970418) that supported closely related research. K. C. Thompson wishes to thank the NERC for a research studentship (GT4/96/236/MAS) that provided maintenance support and fees while the experimental aspects of this work were performed.

Table 1. Frequencies predicted at the B3LYP/6-311++G(p, d) level for dimethyl selenide, the adduct $\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$, dimethyl sulphide and the adduct $\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$.

CH_3SeCH_3 ν / cm^{-1}	$\text{CH}_3\text{Se}(\text{Cl})\text{CH}_3$ ν / cm^{-1}	CH_3SCH_3 ν / cm^{-1}	$\text{CH}_3\text{S}(\text{Cl})\text{CH}_3$ ν / cm^{-1}
3141.2	3167.7	3126.6	3154.3
3140.7	3166.9	3125.7	3153.9
3137.3	3156.7	3106.4	3139.3
3131.3	3155.5	3099.2	3136.6
3047.5	3057.7	3030.7	3048.2
3044.3	3056.1	3028.1	3046.7
1480.8	1470.7	1486.7	1472.1
1474.0	1462.2	1478.0	1465.4
1469.5	1459.5	1470.5	1460.2
1461.3	1451.5	1462.5	1452.9
1324.0	1324.0	1372.7	1370.7
1302.2	1304.0	1347.7	1348.3
978.8	994.1	1055.7	1065.5
925.1	918.9	990.9	980.0
895.4	900.1	951.5	950.0
860.8	879.0	916.2	930.8
589.5	589.4	729.5	725.3
574.3	573.9	678.3	674.2
208.5	218.6	259.4	273.3
151.1	199.2	177.3	237.2
144.7	138.3	175.9	167.1
	136.8		159.7
	124.1		136.0
	79.9		96.4

Table 2. Absolute energies calculated at the B3LYP/6-311++G(2df, p) for structures obtained at the B3LYP/6-311++G(d,p) level of theory.

Compound	Energy / Hartree	Energy at 298 K / Hartree
CH ₃ SeCH ₃	-2481.404614	-2481.325354
CH ₃ Se(Cl)CH ₃	-2941.616217	-2941.533772
CH ₃ SeCH ₂	-2480.742210	-2480.676911
CH ₃ Se	-2441.446243	-2441.407988
CH ₃ Cl	-500.157012	-500.116331
CH ₃ SeCl	-2901.713345	-2901.670604
CH ₃	-39.856560	-39.823883
HCl	-460.836627	-460.827599
Cl	-460.168344	-460.166928
CH ₃ SCH ₃	-478.075584	-477.995321
CH ₃ S(Cl)CH ₃	-938.281779	-938.198268
CH ₃ SCH ₂	-477.416925	-477.350554
CH ₃ S	-438.105973	-438.067418
CH ₃ SCl	-898.373867	-898.330435
CH ₃ Se(Br)CH ₃	-5055.541859	-5055.459777
CH ₃ S(Br)CH ₃	-3052.208184	-3052.124713
Br	-2574.102290	-2574.100874

Table 3. Values of $\Delta_r H^\ominus$ calculated in this work along with literature values for comparison.

Reaction	$\Delta_r H^\ominus$ at 298 K / kJ mol ⁻¹						
	This work	DeMore <i>et al.</i> ³⁰	Stickel <i>et al.</i> ¹⁸	McKee ^{*23}	Wilson and Hirst ²⁴	Resende and De Almeida ^{†21}	Nakano <i>et al.</i> ³¹
8	-111.4	—	—	—	—	—	—
9	-32.1	—	—	—	—	—	—
10	-84.1	—	—	—	—	—	—
11	-5.8	—	—	—	—	—	—
12	-97.0	—	—	-53.5	-81.0	-53.2	—
13	-41.8	-39.2	—	—	—	-10.5	—
14	-56.5	-41.0	—	—	—	-35.8	—
15	+20.8	—	+33 ± 17	—	—	+54.9	—
17	-90.6	—	—	—	—	—	—
18	-77.4	—	-59	-53.1	—	—	-51 ± -4

* Values for $\Delta_r H^\ominus$ at 0 K

† Value for $\Delta_r H^\ominus$ at 298.15 K

Table 4. Expected lifetimes for dimethyl selenide with respect to oxidation by Cl atoms, OH radicals and O₃.

Oxidant	Concentration / molecule cm ⁻³	Reference	Estimated tropospheric lifetime / hours
Cl atoms	1.8×10^5	13	3.1
Cl atoms	3.3×10^4	16	16.8
OH radicals	0.3×10^6	16	13.7
OH radicals	1.5×10^6	41	2.7
O ₃	7.0×10^{11}	42	5.8

Figure 1. Typical first-order plot for the reaction of Cl atoms with dimethyl selenide

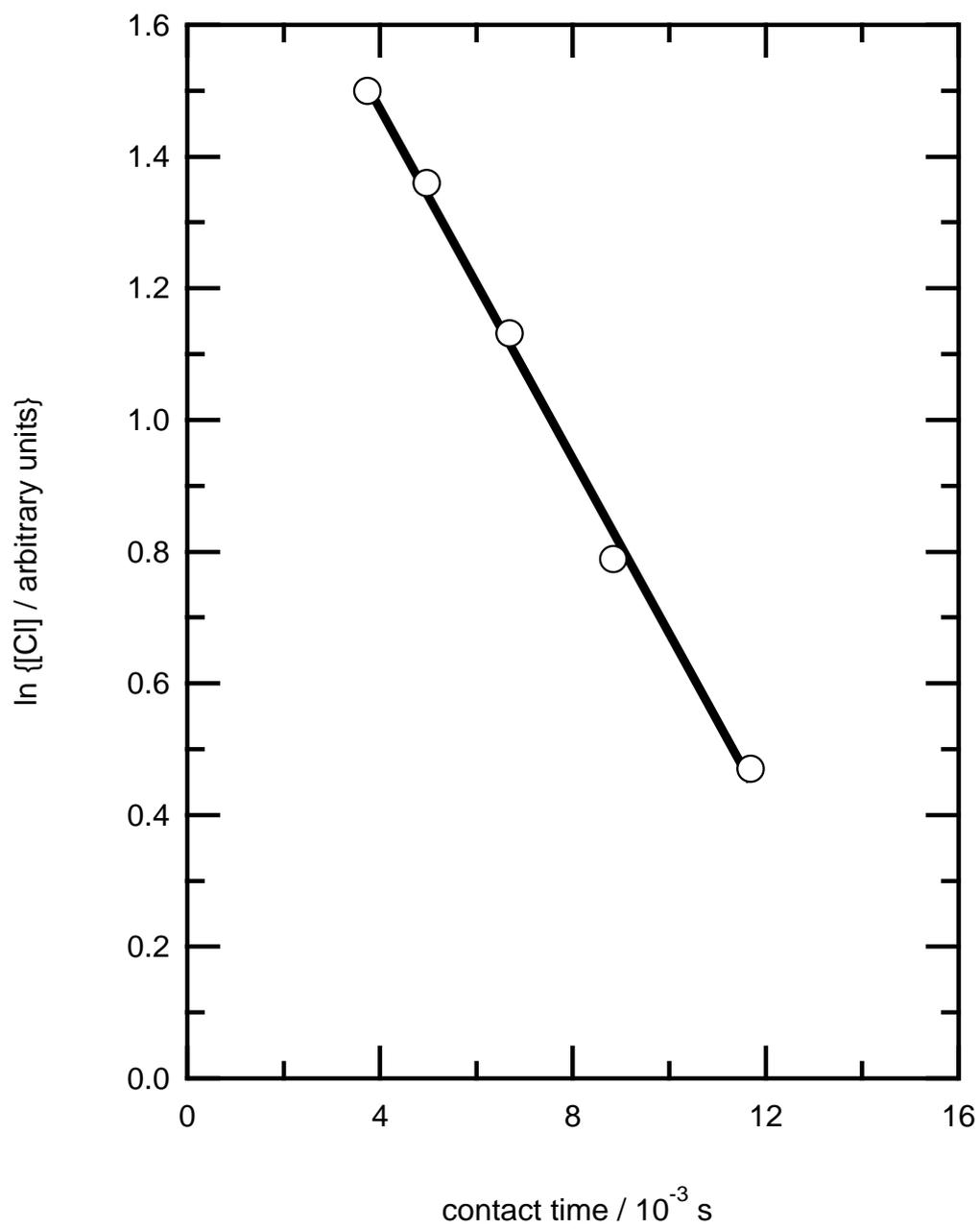


Figure 2. Second-order plot obtained for the reaction of Cl atoms with dimethyl selenide

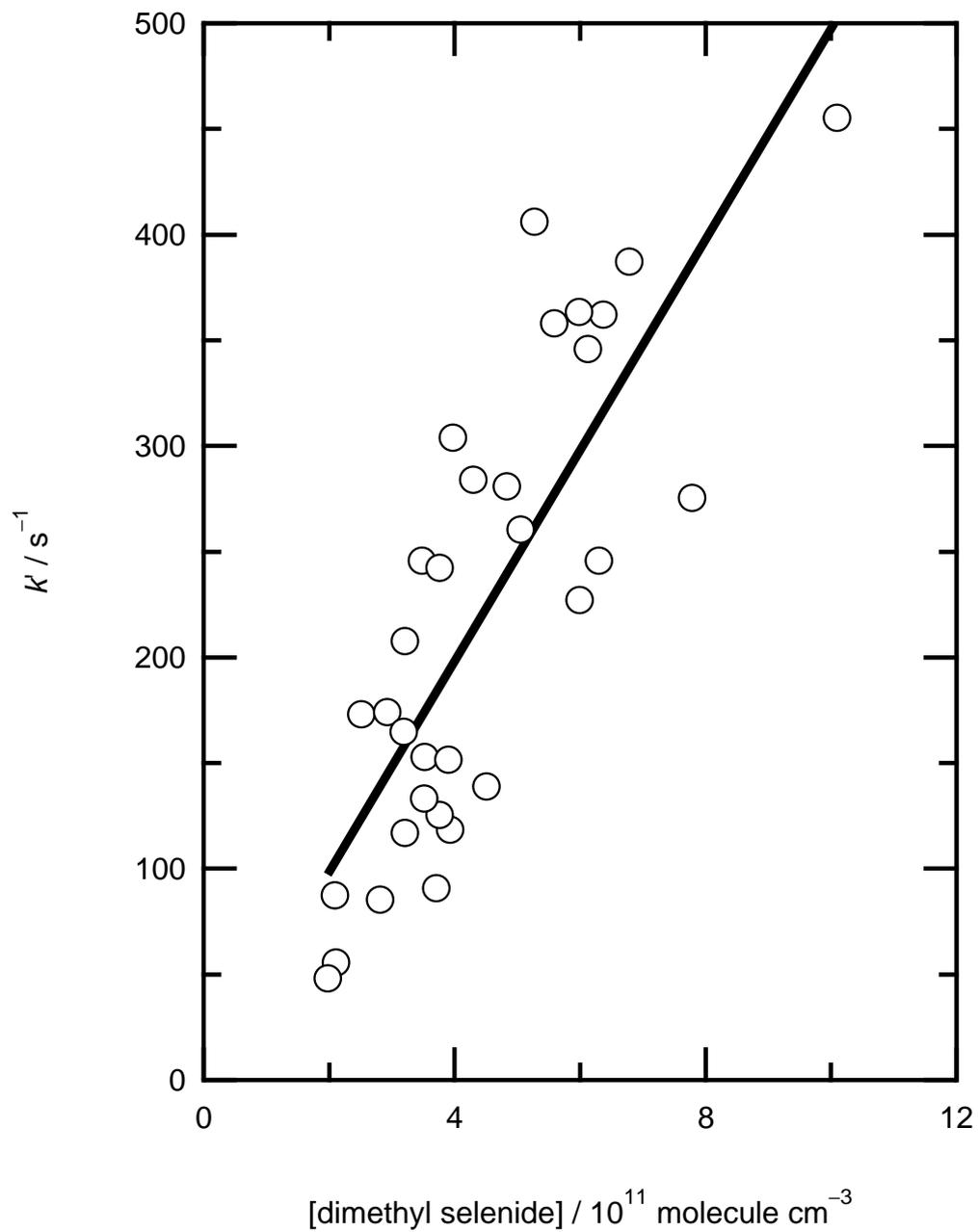
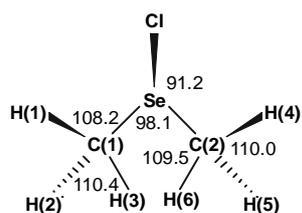


Figure 3 Optimised geometry of the dimethyl selenide – chlorine adduct

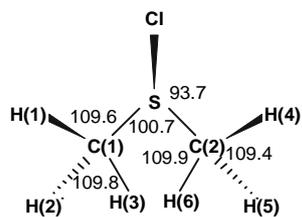


Geometrical parameters for both methyl groups are identical. All parameters given are bond angles (in degrees). The dihedral angles (in degrees) are:

- C(2)–Se–C(1)–H(1) = 58.6
- C(2)–Se–C(1)–H(2) = 176.9
- C(2)–Se–C(1)–H(3) = –63.6
- Cl–Se–C(1)–H(1) = –32.7

Both C–Se bond lengths are 1.96 Å. All C–H bond lengths are 1.09 Å. The Se–Cl bond length is 2.73 Å.

Figure 4 Optimised geometry of the dimethyl sulphide – chlorine adduct



Geometrical parameters for both methyl groups are identical. All parameters given are bond angles (in degrees). The dihedral angles (in degrees) are:

$$\begin{aligned} \text{C(2)-S-C(1)-H(1)} &= 57.1 \\ \text{C(2)-S-C(1)-H(2)} &= 175.5 \\ \text{C(2)-S-C(1)-H(3)} &= -65.4 \\ \text{Cl-S-C(1)-H(1)} &= -37.3 \end{aligned}$$

Both C-S bond lengths are 1.82 Å. All C-H bond lengths are 1.09 Å. The S-Cl bond length is 2.68 Å.

References

- 1 M. P. Rayman, *Lancet*, 2000, **356**, 233.
- 2 R. A. Duce, in 'Atmospheric Biogeochemical Cycles of Selenium, Arsenic and Boron', ed. C. F. Boutron, Les Editions de Physique, Les Ulis, 1996.
- 3 D. Tanzer and K. G. Heumann, *Atmos. Environ.*, 1990, **24**, 3099.
- 4 D. Amouroux and O. F. X. Donard, *Geophys. Res. Lett.*, 1996, **23**, 1777.
- 5 D. Amouroux and O. F. X. Donard, *Mar. Chem.*, 1997, **58**, 173.
- 6 Y. K. Chau, P. T. S. Wong, B. A. Silverberg, P. L. Luxon, and G. A. Bengert, *Science*, 1976, **192**, 1130.
- 7 G. A. Cutter and K. W. Bruland, *Limnol. and Oceanogr.*, 1984, **29**, 1179.
- 8 T. D. Cooke and B. K. W., *Environ. Sci. Technol.*, 1987, **21**, 1214.
- 9 J. H. Ansele, P. J. Pellechia, and D. C. Yoch, *Environ. Sci Technol.*, 1999, **33**, 2064.
- 10 R. Atkinson, S. M. Aschmann, D. Hasegawa, E. T. Thompson-Eagle, and W. T. J. Frankenberger, *Environ. Sci. Technol.*, 1990, **24**, 1326.
- 11 R. M. Rael, E. C. Tuazon, and W. T. Frankenberger, *Atmos. Environ*, 1996, **30**, 1221.
- 12 B. J. Finlayson-Pitts, M. J. Ezell, and J. N. J. Pitts, *Nature*, 1989, **337**, 241.
- 13 W. Behnke, C. George, V. Scheer, and C. Zetzsch, *J. Geophys. Res.*, 1997, **102**, 3795.
- 14 C. W. Spicer, E. G. Chapman, B. J. Finlayson-Pitts, R. A. Plastridge, J. M. Hubbe, J. D. Fast, and C. M. Berkowitz, *Nature*, 1998, **394**, 353.
- 15 K. L. Foster, R. A. Plastridge, J. W. Bottenheim, P. B. Shepson, B. J. Finalyson-Pitts, and C. W. Spicer, *Science*, 2001, **291**, 471.
- 16 O. W. Wingenter, M. K. Kubo, N. J. Blake, S. T. W. Jr., D. R. Blake, and F. S. Rowland, *J. Geophys. Res.*, 1996, **101**, 4331.
- 17 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, in 'Gaussian 98', Pittsburgh, PA, 1998.
- 18 R. E. Stickel, J. M. Nicovich, S. Wang, Z. Zhao, and P. H. Wine, *J. Phys. Chem.*, 1992, **96**, 9875.
- 19 S. Langer, B. T. McGovney, and B. J. Finlayson-Pitts, *Geophys. Res. Lett.*, 1996, **23**, 1661.
- 20 Z. Zhao, R. E. Stickel, and P. H. Wine, *Chem. Phys. Lett.*, 1996, **251**, 59.
- 21 S. M. Resende and W. B. D. Almeida, *J. Phys. Chem. A*, 1997, **101**, 9738.
- 22 S. P. Urbanski and P. H. Wine, *J. Phys. Chem. A*, 1999, **103**, 10935.
- 23 M. L. McKee, *J. Phys. Chem.*, 1993, **97**, 10971.
- 24 C. Wilson and D. M. Hirst, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2831.
- 25 E. S. N. Cotter, N. J. Booth, C. E. Canosa-Mas, D. J. Gray, D. E. Shallcross, and R. P. Wayne, *Phys. Chem. Chem. Phys.*, 2001, **3**, 402.
- 26 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

- 27 C. T. Lee, W. T. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
- 28 A. M. Mebel, K. Morokuma, and M. C. Lin, *J. Chem. Phys.*, 1995, **103**, 7414.
- 29 C. W. Bauschlicher, Jr. and H. Partridge, *J. Chem. Phys.*, 1995, **103**, 1788.
- 30 W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, 'Chemical kinetics and photochemical data for use in stratospheric modeling, report 97-4', Jet propulsion laboratory, Pasadena, CA, 1997.
- 31 Y. Nakano, M. Goto, S. Hashimoto, M. Kawasaki, and T. J. Wallington, *J. Phys. Chem. A*, 2001, **105**, 11045.
- 32 M. E. Jenkin, G. D. Hayman, T. J. Wallington, M. D. Hurley, J. C. Ball, O. J. Nielsen, and T. Ellermann, *J. Phys. Chem.*, 1993, **97**, 11712.
- 33 R. G. Gilbert and S. C. Smith, 'Theory of Unimolecular and Recombination Reactions', Blackwell Scientific Publications, Oxford, 1990.
- 34 J. R. Barker, in 'Multiwell software', Ann Arbor, 2001.
- 35 J. R. Barker, *Int. J. Chem. Kinet.*, 2001, **33**, 232.
- 36 P. Ugliengo, D. Viterbo, G. Borzani, and G. Chiari, in 'Moldraw', Torino, 1993.
- 37 P. Ugliengo, D. Viterbo and G. Borzani, *J. Appl. Cryst.*, 1988, **21**, 75.
- 38 P. Ugliengo, G. Borzani and D. Viterbo, *Z. Kristallogr.* 1988, **185**, 712.
- 39 P. Ugliengo, D. Viterbo and G. Chiari, *Z. Kristallogr.* 1993, **207**, 9.
- 40 E. Gorin, *Acta Physiochim. USSR*, 1938, **9**, 691.
- 41 R. Prinn, R. F. Weiss, B. R. Miller, J. Huang, F. N. Alyea, D. M. Cunnold, P. J. Faser, D. E. Hartley, and P. G. Simmons, *Science*, 1995, **269**, 187.
- 42 J. A. Logan, *J. Geophys. Res.*, 1985, **90**, 463.
- 43 Wayne R. P., "Chemistry of Atmospheres", Oxford University Press, Oxford, 2000.