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REVIEW

The lifetimes of organosulphur compounds in the troposphere

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Dimethyl sulphide and other reduced sulphur compounds, produced by marine biogenic activity and other processes, play a significant role in the global biogeochemical cycling of the element. The rates of their reactions with atmospheric oxidants are reviewed and their lifetimes in the troposphere due to the various reactions are computed. Sufficient data are available on the tropospheric abundance of the hydroxyl radical (OH) and on the rates of its reactions with the sulphur compounds for reasonable estimates to be made of the sulphur lifetimes with respect to OH. Summertime lifetimes of 14–87 h for $(CH_3)_2S$ are computed at different latitudes. In the case of the tropospheric concentrations of the nitrate radical (NO_3), few data are available. There is a similar paucity of data on its rates of reactions with the sulphur compounds, and so large uncertainties exist in the computed lifetimes. These are, in any case, much longer than those due to OH. The possibility exists that iodine photochemistry, producing iodoxyl (IO) radicals, may efficiently oxidize the reduced sulphur and other organic compounds in the marine troposphere leading to lifetimes of the order of hours. Few data exist on the rates or mechanisms of these reactions and these are identified as representing the greatest uncertainties in the estimates of organosulphur lifetimes in the troposphere.

Keywords: Tropospheric chemistry, lifetimes, dimethyl sulphide, reduced sulphur compounds, hydroxyl, nitrate, iodoxyl radicals

INTRODUCTION

A substantial body of data is now available describing the occurrence of dimethyl sulphide and other reduced sulphur species in the troposphere as a result of their production by marine biogenic activity and other processes.[1–4] In order to understand better the processes governing the distribution of these species, the role they play in the global biogeochemical sulphur budget and particularly their contribution to the deposition of acidity to the earth's surface, their atmospheric chemistry has been extensively modelled. One of the critical parameters required for such studies is the atmospheric lifetime of the sulphur species. This in turn is dependent upon their rates of reaction with oxidizing species and the tropospheric concentrations of the oxidants. There are considerable uncertainties in the magnitude of these terms at the present time and so only a range of values for the lifetimes can be computed. Despite these limitations several studies have used precise (although probably erroneous) values for the lifetimes and it is therefore appropriate to delineate the current state of knowledge in this field, and to identify those areas of greatest uncertainty.

Organic molecules react in the troposphere mainly by photolysis and with ozone (O_3), hydroxyl (OH) and nitrate (NO_3) radicals. The absorption cross-sections of all sulphides in the relevant actinic region ($\lambda > 290$ nm) are small and hence direct photolysis is negligible.[5] The reactions with O_3 are also too slow to be of any significance in the troposphere (for example, the rate constants for the reactions of $(CH_3)_2S$ and H_2S with ozone are 8×10^{-19} and $<2 \times 10^{-20}$ cm^3 s^{-1} respectively[6]). This leaves oxidation by OH and NO_3 as the possible reaction pathways to be considered.[7] However, it has recently come to light that the photochemistry of iodine in the maritime troposphere may play a significant role in the oxidation and removal of organic molecules and the currently available evidence for this will be assessed. Hydroperoxyl (HO_2) is also an important reactive species in the troposphere but a total lack of data on its reactions with the organosulphur compounds prevents its consideration at present.

The rates of reaction of the various sulphur species with OH, NO_3 and IO are first reviewed, followed by an assessment of the tropospheric concentrations of the oxidants. The atmospheric lifetimes of the sulphur species are then estimated.

RATES OF REACTION WITH THE HYDROXYL RADICAL (OH)

Although the reactions of the reduced sulphur species with OH have been studied in some detail few data are available at temperatures (T) relevant to tropospheric modelling (i.e T in the range 240–300 K). The rates of these reactions will be considered at two specific temperatures, at 265 K, taken to be the annual mean temperature of the troposphere, and 298 K, taken to be typical of daytime surface temperature maxima.

Dimethyl sulphide [$(CH_3)_2S$]

The kinetics of the reaction of $(CH_3)_2S$ with OH have been studied using direct measurements in the absence of oxygen (O_2) and the rate constant values reported fall into two distinct groups. The work of Atkinson *et al.*[8] Macleod *et al.*[9] and Kurylo[10] gives values of (8–10) × 10^{-12} cm^3 s^{-1} at room temperature. Relative rate constant values within this range at room temperature and one atmosphere of air have also been found.[11,12]

The second group of values fall in the range (3.2–4.3) × 10^{-12} cm^3 s^{-1}.[13–16] Investigations by Wallington[14] and Wine[17] into the effect of O_2 led to the observation that the rate constant increased from 4.8 × 10^{-12} to 5.18 × 10^{-12} cm^3 s^{-1} as the total air pressure changed from 343 ro 593 torr.

Hynes *et al.*[16] studied the reaction using two techniques. The first used flash photolysis–resonance fluorescence and gave 4.45 × 10^{-12} cm^3 s^{-1} at 298 K in an argon buffer. A pulse laser photolysis–pulsed laser induced fluorescence technique was also employed to investigate the reaction in air and O_2 and a value of 6.3 × 10^{-12} cm^3 s^{-1} was obtained at 298 K and 730 torr. A large variation with temperature was found over the range 250–310 K, a value of 13.6 × 10^{-12} cm^3 s^{-1} being observed at 265 K.

Such a strong temperature dependence has not been observed by other workers, although Hsu *et al.*[18] verified the small positive activation energy previously observed[16] and obtained a rate constant of 5.5 × 10^{-12} cm^3 s^{-1} at 298 K. It has been postulated that the reaction is a branching reaction, with abstraction favoured over addition at higher temperatures, the reaction in air at 298 K proceeding 70% by abstraction.[16]

It has been suggested that the observed rate constant may vary with the technique used for OH radical production.[14] Irradiation of methyl nitrite–nitric oxide (CH_3ONO–NO) gave a rate constant of 9.3 × 10^{-12} as opposed to 8.5 × 10^{-12} cm^3 s^{-1} when hydrazine–ozone (N_2H_4–O_3) was used. Extrapolation of both these results to zero oxygen (O_2) gave values of 8.3 × 10^{-12} and 5.3 × 10^{-12} cm^3 s^{-1} respectively. These values are below the higher values obtained in the absence of O_2, so giving support to the lower group of values for the rate constant.

Atkinson,[19] in his comprehensive review of reaction rate constants, recommends a value of 6.3 × 10^{-12} cm^3 s^{-1} for this reaction and this will be used here as the best available value for the computation of atmospheric lifetimes. The strong temperature dependence observed by Hynes *et al.*[16] has not been found by other workers and will not be considered here.

Hydrogen sulphide (H_2S)

Direct measurements of the rate constant for the reaction of H_2S with OH have been made using flash photolysis techniques,[13, 20–22] and discharge flow[23–25] with values found in the range (3.1–5.5) × 10^{-12} cm^3 s^{-1} at 298 K. An indirect determination also yielded a value within this range[11] while values of 4.4 × 10^{-12} and 5.2 × 10^{-12} cm^3 s^{-1} have also been obtained.[26,27] In their review of kinetic data, Baulch *et al.*[28] gave a preferred value of 4.8 × 10^{-12} cm^3 s^{-1} at 298 K. The temperature dependence of the rate constant has been found to be insignificant over the range of interest and may be ignored.

Dimethyl disulphide [$(CH_3)_2S_2$]

A direct measurement for the rate of reaction of $(CH_3)_2S_2$ with OH has been reported[13] giving values of (2.1 ± 1.2) × 10^{-10} and (2.5 ± 1.4) × 10^{-10} cm^3 s^{-1} at 298 K respectively. These are in close accord with the values of (2.23 ± 0.8) × 10^{-10} cm^3 s^{-1} [11] and (2.1 ± 0.2) × 10^{-10} cm^3 s^{-1},[29] both found at 298 K. The mean of these values will be adopted here.

Methyl sulphide (CH_3SH)

The rates obtained for the reaction of CH_3SH with OH are generally in good agreement, values in the range (2.1–3.6) × 10^{-11} cm^3 s^{-1} being obtained.[8, 9, 13, 27,30–32] One anomalously high value of 9.0 × 10^{-11} cm^3 s^{-1} has been found indirectly by Cox and Sheppard[11] but a mean value of 3.4 × 10^{-11} cm^3 s^{-1} will be used here.

Carbon disulphide (CS_2)

A wide range of values for the rate constant of the reaction of CS_2 with OH at 298 K has been found, from 3 × 10^{-15} cm^3 s^{-1} [33,34] to 1.5 × 10^{-12} cm^3 s^{-1} [35] and 1.7 × 10^{-12} cm^3 s^{-1}.[36] Initially the high values were attributed to reactions of OH with the photolysis products of CS_2, rather than CS_2 itself and Baulch *et al.*[37] and the NASA Panel for Data Evaluation[38] gave a preferred value based on the lower estimates. More recent work has indicated that the discrepancy may be due to a dependence on the O_2 partial pressure in the system.[39] An increase in the reaction rate when sufficient O_2 was present has also been observed.[36] The value of (2.7 × 0.6) × 10^{-12} cm^3 s^{-1} obtained by Barnes *et al.*[39] at 298 K in 760 torr synthetic air using Fourier transform infrared spectroscopy has been adopted by DeMore *et al.*[40] and will be used here.

Carbonyl sulphide (COS)

An upper limit value for the rate constant for the reaction of COS with OH of 9 × 10^{-15} cm^3 s^{-1} has been measured[41] and a value of 6 × 10^{-16} cm^3 s^{-1} has been adopted by Baulch *et al.*[28] However, more recently values of (1.92 ± 0.25) × 10^{-15} and 2 × 10^{-15} cm^3 s^{-1} have been measured at room temperature[42,43] and will be used here.

RATES OF REACTION WITH THE NITRATE RADICAL (NO_3)

Much less study has been made of the reaction of the sulphur compounds with the nitrate radical (NO_3) than with OH. Atkinson *et al.*[44] indirectly determined a rate constant for the reaction of $(CH_3)_2S$ with NO_3 at 298 K of (9.6 ± 1.1) × 10^{-13} cm^3 s^{-1}. Wallington *et al.*[45] used flash photolysis to obtain a value of (7.5 ± 0.5) × 10^{-13} cm^3 s^{-1} and later[46] obtained an Arrhenius expression giving a value of (8.1 ± 1.3) × 10^{-13} cm^3 s^{-1} at 298 K. A value of (10 ± 2) × 10^{-13} cm^3 s^{-1} independent of temperature between 278 and 318 K has also been found.[47] All these values fall in the range (7.5–10) × 10^{-13} cm^3 s^{-1}.

Macleod *et al.*[48] studied the reaction of NO_3 with CH_3SH, $(CH_3)_2S_2$, CS_2 and COS and obtained rate constants of (10 ± 3) × 10^{-13}, (0.42 ± 0.09) × 10^{-13}, < 0.008 × 10^{-13} and < 0.0004 × 10^{-13} cm^3 s^{-1} respectively in a mixture of 80% N_2 and 20% O_2 at 760 torr and 297 K. The temperature dependence of these values is not known. Rate constants for the reaction of NO_3 with CH_3SH and $(CH_3)_2S_2$ have also been determined by flash photolysis,[46] giving values of (8.1 ± 0.6) × 10^{-13} and 5.0 × 10^{-13} cm^3 s^{-1} respectively, but with large error limits on the latter. An upper limit of 0.3 × 10^{-13} cm^3 s^{-1} was estimated for the NO_3 radical reaction with H_2S[46] and a value of 0.2 × 10^{-13} cm^3 s^{-1} has also been obtained.[49]

RATES OF REACTION WITH IODINE—CONTAINING RADICALS

At present very few data are available on the rates or mechanisms of the reaction of reduced sulphur compounds with iodine-containing radicals. Indeed, very few data on the kinetics of the reactions of iodoxyl (IO) or other iodine radicals with any species are available. The reaction rates of IO with a few compounds of atmospheric importance [e.g. nitric oxide (NO), nitrogen dioxide (NO_2) and carbon monoxide (CO)] have been inferred by extrapolating from the rates of analogous reactions involving radicals containing bromine (Br) or chlorine (Cl)[50] but experimental validations of these estimates have not been made.

Recently Martin *et al.*[51] and Barnes *et al.*[52] have published values of (1.5 ± 0.5) × 10^{-11} and (3 ± 1.5) × 10^{-11} cm^3 s^{-1} for the IO reaction with $(CH_3)_2S$, with dimethyl sulphoxide [$(CH_3)_2SO$] forming as a major product. A 1:1 stoichiometry between $(CH_3)_2S$ reactant and $(CH_3)_2SO$ product was found. Values for other reduced sulphur species are still not available.

TROPOSPHERIC CONCENTRATIONS OF HYDROXYL RADICAL (OH)

Hydroxyl concentrations in the troposphere vary with the ultraviolet (UV) actinic flux, and with the ambient concentrations of water, ozone, carbon monoxide, methane and nitrogen dioxide. Despite extensive study, considerable uncertainties still exist in the estimation of the concentrations of OH in the troposphere, values in the range (0.5–5) × 10^6 OH cm^{-3} daytime mean and (0.3–3) × 10^6 OH cm^{-3} 24-h mean being suggested by a review of measurements and model studies.[53] Whilst such long-term global mean concentrations may be used to calculate the atmospheric lifetimes of relatively long-lived compounds which will be well mixed throughout the global troposphere, they are not appropriate for use with more reactive species such as the organosulphur compounds. In this case it is necessary to use OH concentrations over shorter averaging periods and over smaller spatial scales. Such data are not currently available from direct measurements and so the results of a modelling study must be used.

The seasonal latitudinal- and altitude-dependent set of OH concentrations calculated by Crutzen and Fishman[54] has previously been used for the calculation of the lifetimes of organic molecules.[55] However, it appears that they underestimated the contribution made to tropospheric carbon monoxide concentrations from biological sources, and hence may have underestimated the OH concentrations. Logan *et al.*[56] modelled global tropospheric photochemistry constrained by observed concentrations of water, ozone, carbon monoxide, methane, nitric oxide, nitrogen dioxide and nitric acid and despite the paucity of data on nitric oxide and nitrogen dioxide concentrations being a potential weakness in this model, their data, summarized in Table 1, will be used in this analysis. The noontime groundlevel [OH] values generated by this model are ~50% higher than those previously calculated.[54]

TROPOSPHERIC CONCENTRATIONS OF NITRATE—RADICAL (NO_3)

Nitrate radicals form in the atmosphere as a result of the reaction of nitrogen dioxide with ozone. Once formed, NO_3 may react with NO_2 and a third body to form N_2O_5 to give a temperature-dependent equilibrium. Because of its rapid photolysis by light of $\lambda < 670$ nm, NO_3 can only build up to significant concentrations at night. Furthermore, because of its rapid reaction with liquid water on particle surfaces and present as aerosol,[57] and because of the reaction of N_2O_5 with water to form nitric acid,[58] the concentration of NO_3 is expected to fall as relative humidity increases. This is borne out by the very few measurements of NO_3 made to date by long-path

Table 1 Hydroxyl concentrations (from Ref. 56)

		[OH] × 10^6 cm^{-3}			
		Ground level		4 km	
Latitude	Season	Noon max.	Daytime mean	Noon max.	Daytime mean
60°N	Summer	2	1	2	1
	Winter	1	—	1	—
45°N	Summer	3	1.5	5	2.5
	Winter	1	—	1.5	1
15°N	Summer	5	2.5	7	3.5
	Winter	3	1.5	4.5	2.5
0°	Summer	6	3	7	3.5
	Winter	6	3	7	3.5
15°S	Summer	6	3	7	3.5
	Winter	4	2	4.5	2.5
45°S	Summer	4.5	2.5	4.5	2.5
	Winter	2	—	2	1
60°S	Summer	2	1	2	1
	Winter	2	—	2	—

spectroscopy. In moderately polluted continental air in California 350 ppt NO_3 (and on one occasion 431 ppt NO_3) has been found[59,60] while relatively clean air at semiarid and desert sites had 10–100 ppt NO_3.[61] However, at a coastal site in Ireland values <10 ppt NO_3 were found[62] and in oceanic air at Mauna Loa, mid-Pacific, at an altitude of 3 km NO_3 concentrations of 0.3 ppt (± 50%) have been measured.[63]

This latter value is supported by model calculations which also give a mean nighttime NO_3 concentration at ground level at 45°N of ~0.3 ppt.[64] Because the model calculations depend upon the sequence in Eqns [1] and [2],

$$NO + NO_2 \rightleftharpoons N_2O_5 \quad [1]$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad [2]$$

where the rate of the second reaction is not reliably known,[65,66] some (unknown) uncertainty must be inherent in the derived NO_2 concentrations. However, although an NO_3 concentration of 10 ppt has been used in connection with organosulphur decomposition rates,[67] the value of 0.3 ppt (7.5×10^{-6} cm^{-3}) seems to be more appropriate as it is in the maritime atmosphere that interest in biogenic sulphur is mainly centred. The value of 10 ppt is however also used in the following calculations to represent nighttime conditions in clean continental air.

TROPOSPHERIC CONCENTRATIONS OF IODOXYL RADICAL (IO)

To date, no measurements of the tropospheric abundance of IO or other iodine-containing radicals have been reported. However, their probable precursor, methyl iodide (CH_3I), has been observed in the marine troposphere in the ppt range,[68] and the biogenic source postulated for this compound has been subsequently confirmed by field and laboratory experiments.[69,70] The possible role of iodine in tropospheric photochemistry has been studied in detail[50] and it is suggested that iodine atoms resulting from the photolysis of CH_3I will rapidly react with ozone forming IO radicals (Eqns [3] and [4]).

$$CH_3I + h\nu \rightarrow CH_3 + I \quad [3]$$

$$I + O_3 \rightarrow IO + O_2 \quad [4]$$

The rate of this latter reaction has been estimated to be $(9.5 \pm 1.5) \times 10^{-13}$ cm^3 s^{-1}.[71] Chameides and Davis[50] suggest that, once formed, IO is removed from the troposphere principally by photolysis and by reaction with nitric oxide.

The *marine tropospheric photochemistry of iodine* at a latitude of 30° has been modelled using a 23-step reaction scheme, CH_3I concentrations in the range 1–50 ppt and a range of values for the various reaction rate constants.[50] Since gas kinetic data are not available for many of the reactions involving iodine, values were obtained by extrapolating from the rates of the analogous Cl and Br reactions (for which the rate constants are known). Daytime IO concentrations in the range $\sim(1-70) \times 10^7$ cm^{-3} were calculated, [IO] increasing non-linearly with [CH_3I]. The sensitivity of the model to variations in the assumed ambient conditions was investigated and IO concentrations found to be relatively insensitive to the latitude and time of year or to carbon monoxide and ozone concentrations. Changes in [NO_x] did significantly alter the computed [IO] values. However, it seems likely that IO may also be removed from the atmosphere by self-combination of IO + IO,[51] leading to lower concentrations than those predicted by this model.

Unfortunately, at the present time large uncertainties exist in the estimates of the source strength of the organic iodine species and in the details of the iodine photochemical system, allowing crude estimates only to be made of the abundance of IO in the troposphere. However it should be noted that the modelled values of $(1-70) \times 10^7$ cm^{-3} are probably up to two orders of magnitude greater than the daytime abundance of OH in the marine troposphere. These values take no account of the observed spatial and temporal variations of CH_3I concentrations in seawater.

ATMOSPHERIC LIFETIMES OF REDUCED SULPHUR SPECIES

The atmospheric lifetime (τ) of the reduced sulphur species are calcluated from Eqn [5] and are shown in Table 2. For short lifetimes ($\tau < 12$ h) the values used for [OH] are mean values for the daylight hours during summer and winter at varying latitudes, while the [NO_3] values are taken, probably unrealistically, to represent seasonal and latitudinal nighttime means. For

Table 2 Atmospheric lifetime of reduced sulphur species[a]

	$(CH_3)_2S$	H_2S	$(CH_3)_2S_2$	CH_3SH	CS_2	COS
Rate constant						
K_{OH}($cm^3\ s^{-1}$) at 298 K, 760 torr	6.3×10^{-12}	4.8×10^{-12}	$(2.1 \pm 0.2) \times 10^{-10}$	$(3.4 \pm 0.1) \times 10^{-11}$	$(2.7 \pm 0.6) \times 10^{-12}$	2×10^{-15}
K_{NO_3}($cm^3\ s^{-1}$)	$(7.5-10) \times 10^{-13}$	$\leq 0.3 \times 10^{-13}$	$(4.2 \pm 0.9) \times 10^{-14}$	$(8.1-10) \times 10^{-13}$	$< 8 \times 10^{-16}$	$< 4 \times 10^{-17}$
K_{IO}($cm^3\ s^{-1}$)	$(1.5-3.0) \times 10^{-11}$	n.a.[e]	n.a.	n.a.	n.a.	n.a.
Lifetime due to reaction with OH						
60° Summer	87 h	5 days	1.2–1.4 h	8.0–9.0 h	7–11 days	31 y
Winter[b]	> 18 days	> 24 days	> 12–14 h	80–84 h	> 35–55 days	> 100 y
45° Summer	60 h	77 h	0.8–1.0 h	5.0–6.0 h	5–8 days	23 y
Winter[b]	> 18 days	> 24 days	> 12–14 h	> 80–84 h	> 23–37 days	> 100 y
15° Summer	17 h	46 h	0.5–0.6 h	3–3.4 h	3–4 days	14 y
Winter	57 h	77 h	0.8–1.0 h	5.3–5.6 h	5–7 days	23 y
0° Summer	14 h	39 h	0.4–0.5 h	2.6–2.8 h	2–3 days	9 y
Winter	14 h	39 h	0.4–0.5 h	2.6–2.8 h	2–3 days	9 y
Lifetime due to reaction with NO_3						
Oceanic[c]	3–4 days	96 days	60–90 days	3–3.5 days	> 10 y	> 200 y
Continental[c]	1–1.4 h	69 h	2–3 days	1–1.3 h	> 116 days	> 6 y
Lifetime due to reaction with IO[d]						
	1–2 h	n.a.	n.a.	n.a.	n.a.	n.a.

[a] This work. [b] Assuming [OH] = 1×10^5 cm^{-3}. [c] Assuming [NO_3] = 0.3 ppt and 10 ppt in clean oceanic and continental nighttime air respectively. [d] Assuming [IO] = 1×10^7 cm^{-3}. [e] Abbreviation: n.a., data not available.

longer lifetimes ($\tau > 12$ h) diurnally-averaged 24-h mean concentrations are used. Because of the uncertainties in some of the rate constants a range of values for the lifetimes is given.

$$\tau = 1/k[OH] \text{ or } 1/k[NO_3] \text{ or } 1/k[IO] \qquad [5]$$

The estimates of atmospheric lifetimes due to reaction with OH are probably reasonably reliable, particularly at lower latitudes where actual [OH] values are likely to be close to the modelled values. At higher latitudes in the Northern Hemisphere, where the degree of cloudiness and pollutant concentrations (especially of NO_x and carbon monoxide) are highly variable, modelled [OH] may depart significantly from the actual values. Uncertainties also arise in the winter where [OH] is calculated to be below the lower limit of the model, but is assumed to be $< 1 \times 10^5$ cm^{-3}.

The daytime lifetime of dimethyl sulphide is calculated to be a minimum of 14 h at the equator summer and winter, increasing to 87 h in the summer and > 18 days in the winter at 60°. The lifetime due to reaction with NO_3 over the oceans (τ = 3–4 days) may be significantly shorter than that due to reaction with OH in winter in high latitudes. In high-latitude summers and in all seasons at low latitudes, reaction with OH will dominate the $(CH_3)_2S$ lifetime. However, in continental air, nighttime removal by NO_3 will be much faster in all seasons and at all latitudes than removal by OH.

The lifetimes over the oceans of methyl sulphide (CH_3SH) due to reaction with OH will be much shorter than those due to NO_3 at all latitudes during the summer, and at low latitudes during the winter. Only in high-latitude winters and in continental air will nighttime removal by NO_3 dominate. Oxidation of dimethyl disulphide, [$(CH_3)_2S_2$], carbon disulphide (CS_2) and carbonyl sulphide (COS) by OH is also much faster than that by NO_3 at all latitudes and in all seasons. Only in continental air with NO_3 concentrations of 10 ppt do the nighttime removal rates approach those due to OH, and then only in high latitudes.

It will be seen from Table 1 that the daytime mean OH concentrations derived by the model are similar at 4 km to those at ground level. No significant differences in atmospheric lifetimes at 0 and 4 km are therefore calculated. Also the temperature dependence of the rate constants for the reactions between the organosulphur compounds and OH in the range 298–265 K is negligible.

At the present time $(CH_3)_2S$ is the only reduced sulphur species for which a rate constant for the reaction with IO has been estimated. There is, however, great uncertainty in the concentration of IO present in the atmosphere and this leads to similar uncertainty in the estimation of sulphur species lifetimes. However if an IO concentration of 1×10^7 cm^{-3} is assumed, a $(CH_3)_2S$ lifetime of 1–2 h is obtained. It appears, therefore, that IO may be an important sink for dimethyl sulphide in the maritime troposphere, especially as IO concentrations are probably less sensitive to latitude and season than are those of OH. At times, oxidation by IO may be the dominant removal mechanism for the sulphur species.

DISCUSSION

The tropospheric lifetimes of the organosulphur compounds vary considerably from species to species, from season to season and with latitude. $(CH_3)_2S_2$ is rapidly oxidized by OH under all conditions (τ = 0.4–14 h), $(CH_3)_2S$, CH_3SH and H_2S less rapidly (τ = 3–87 h except in high-latitude winters). CS_2 is oxidized by OH rather more slowly (τ = 2– >55d) whilst COS reacts with OH only very slowly with a resultant lifetime in the atmosphere of years.

Dimethyl sulphide is the most important of these compounds as its excretion by marine phytoplankton and subsequent exchange over the air/sea interface represents a sulphur emission comparable in magnitude with that from fossil-fuel burning.[72] Its lifetime due to reaction with OH is probably a minimum of 14 h at the equator compared with 72–96 h due to reaction with 0.3 ppt NO_3. It seems likely therefore that nighttime oxidation by NO_3 is insignificant compared with the daytime process. As has been previously noted, however, $(CH_3)_2S$ may represent a major sink for NO_3 in the marine troposphere,[72] although the relative importance of this will vary with the large temporal and spatial changes in $(CH_3)_2S$ concentrations.

The role of IO in the oxidation and removal of reduced sulphur compounds in the troposphere is at present poorly known. However, the possibility that oxidants other than OH and NO_3 may play a part in the atmospheric chemistry of $(CH_3)_2S$ in particular has been proposed[1] and if IO is as reactive towards the reduced sulphur compounds as is OH then the fact that it is probably much more abundant in the marine troposphere than OH would mean that it would dominate the photo-oxidation and lifetimes of the reduced sulphur compounds. However, it should be noted that IO is produced in the troposphere from a precursor emitted at the earth's surface, whereas OH is produced throughout the troposphere and hence is more evenly distributed with altitude. This has important consequences for the fate of any products of a rapid reaction of $(CH_3)_2S$ with IO.[73]

Given the variability in computed lifetimes at different latitudes and different seasons and the uncertainties due to iodine photochemistry, care should be exercised in selecting appropriate values of the various parameters used in modelling studies of organosulphur chemistry in the troposphere. In particular, the seasonal and latitude-dependent nature of OH concentrations must be noted, together with the uncertainties in NO_3 concentrations over the oceans. Of overriding importance, however, is the lack of understanding of the role of iodine-containing radicals, their abundance in the marine troposphere, and their reactivity towards the reduced sulphur and other species. Further experimental data on the various reactions considered above, not only of reaction rate constants but also of product analyses and yields, would greatly enhance the present understanding of tropospheric sulphur chemistry.

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