AIP | The Journal of
Chemical Physics

The formation of SO5− by gas phase ion–molecule reactions

O. Möhler, T. Reiner, and F. Arnold

Citation: J. Chem. Phys. **97**, 8233 (1992); doi: 10.1063/1.463394

The formation of SO_5^- by gas phase ion–molecule reactions

O. Möhler, T. Reiner, and F. Arnold
Max-Planck-Institut für Kernphysik, P.O. Box 10 39 80, D-6900 Heidelberg, Germany

(Received 27 May 1992; accepted 26 August 1992)

A flow tube apparatus was used to investigate the formation of SO_5^- ions by gas phase ion–molecule reactions. The reactions studied in an N_2 buffer gas at 2.5 hPa pressure and room temperature (298 K) included SO_2 and O_2 reactions with O_2^-, O_3^-, CO_3^-, SO_2^-, and SO_3^- as well as their hydrates. Reaction rate constants were measured and the major product channels were identified for most reactions. The free energy changes for the hydration reactions of SO_3^-, SO_4^-, and SO_5^- were derived from equilibrium constant measurements. The present investigations clearly show that SO_5^- ions are formed in the gas phase by the association of O_2 to SO_3^- and by the switching reaction of $SO_3^-H_2O$ with O_2. An effective binary rate constant of 2.0×10^{-12} $cm^3\,s^{-1}$ was measured for the association reaction at 2.5 hPa N_2 and the rate constant of the switching reaction was 5.0×10^{-11} $cm^3\,s^{-1}$. Also the reaction of $O_3^-H_2O$ with SO_2 probably yields SO_5^- by a switching process having a rate constant of 1.8×10^{-9} $cm^3\,s^{-1}$. The heat of formation of SO_5^- was estimated to be less than -715 kJ/mol. The present results have implications to the negative ion chemistry of the atmosphere and are important for measurements of atmospheric SO_2 concentrations by chemical ionization mass spectrometry.

INTRODUCTION

Negatively charged sulphur oxides play an important role both in the aqueous phase and in gas phase atmospheric processes. Within cloud droplets, the dissolved oxysulphur anions HSO_3^-, SO_3^-, SO_4^-, and SO_5^- are known to be important intermediates in the oxidation mechanisms of sulphur(IV) species.[1-3] The sulphate anion SO_4^{2-}, that is the main contributor to the acidity of rain drops, is the terminal species of these oxidation processes. The aqueous phase oxidation of atmospheric sulphur(IV) is not yet fully understood. For example, the SO_5^- ion was observed in solutions but little is known about its role in the oxidation processes. It is thought to be produced by the reaction of SO_3^- with O_2.[4] Gas phase ion–molecule reactions involving oxysulphur anions may influence the atmospheric ion chemistry. In the troposphere, Möhler and Arnold[5] observed, for example, negative ion species with masses 64, 80, 96, and 113±1 amu that may be identified as SO_2^-, SO_3^-, SO_4^-, and SO_5^-.

Very recently, it was found at our laboratory that the formation of SO_5^- ions by gas phase ion–molecule reactions may be used to measure the concentration of atmospheric sulphur dioxide.[6,7] Sulphur dioxide is an important species in the atmospheric sulphur cycle. It has both natural and anthropogenic sources.[8-11] In the stratosphere, it is photooxidized to H_2SO_4, and therefore contributes mainly to the formation of the stratospheric aerosol layer.[12,13] In the present work we have investigated the formation of SO_5^- ions by gas phase ion–molecule reactions. The results are important for our novel atmospheric SO_2 measurements. In this paper, we focus on the measurements of reaction rate constants and product ion distributions. The implications to SO_2 detection will be discussed elsewhere.[7]

Little is known about the gas-phase ion chemistry of SO_5^-. Vacher *et al.*[14] have investigated the stability of $SO_5^-(SO_2)_n$ clusters formed in SO_2–O_2 mixtures. The kinetics of some ion–molecule reactions involving SO_2^-, SO_3^-, and SO_4^- have also been investigated previously.[15,16] The SO_2^- ion is, e.g., produced by the reaction

$$O_2^- + SO_2 \rightarrow SO_2^- + O_2, \qquad (1)$$

whereas the reaction

$$O_2^-(H_2O)_n + SO_2 \rightarrow \text{products} \qquad (2)$$

yields SO_4^- ions at least for $n=1$.[15] Albritton *et al.*[16] investigated the O^- transfer reactions

$$O_3^- + SO_2 \rightarrow SO_3^- + O_2, \qquad (3)$$

$$CO_3^- + SO_2 \rightarrow SO_3^- + CO_2 \qquad (4)$$

at different energies and in different buffer gases. The measured rate constants decreased with increasing kinetic energy of the ions but did not depend on the kind of the buffer gas (He and Ar) at pressures in the range between 0.17 and 0.6 hPa.

The present paper reports flow tube investigations of the kinetics of reactions (1) to (4) at thermal energy and at a buffer gas pressure of 2.5 hPa N_2. These reactions were studied to check the consistency of our results with the previous measurements mainly made in He and Ar buffer gases at pressures less than 1 hPa. Some new information on reaction channels and product ions were obtained. Additionally, we studied the following reactions:

$$CO_3^-H_2O + SO_2 \rightarrow \text{products}, \qquad (5)$$

$$O_3^-H_2O + SO_2 \rightarrow \text{products}, \qquad (6)$$

$$O_3^-(H_2O)_2 + SO_2 \rightarrow \text{products}, \qquad (7)$$

$$SO_3^- + O_2 + N_2 \rightarrow SO_5^- + N_2, \qquad (8)$$

$$SO_3^-H_2O + O_2 \rightarrow SO_5^- + H_2O, \qquad (9)$$

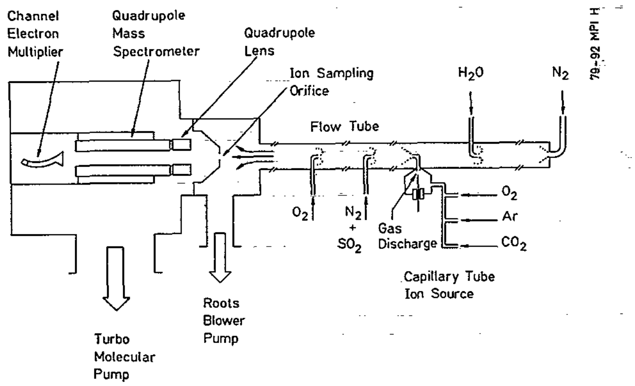

FIG. 1. Flow tube apparatus with ion source, reactant gas inlets, and mass filter device.

$$SO_2^- + O_2 + N_2 \rightarrow SO_4^- + N_2 . \tag{10}$$

These reactions are particularly important for atmospheric SO_2 detection by SO_5^- formation.

EXPERIMENT

The experimental technique used for the present measurements rests on the flowing afterglow technique developed by Ferguson *et al.*[17] The apparatus was already used for previous kinetic studies and was described in detail by Möhler and Arnold.[18] It is briefly reviewed here, emphasizing the modifications made for the present studies. The experimental setup (Fig. 1) mainly consists of the flow tube, the ion source, the quadrupole mass spectrometer, and the pumping system. All ion–molecule reactions were studied in an N_2 buffer gas passed through the flow tube at a pressure of 2.5 hPa with a mean velocity of 63 m/s. A roots blower pump maintained the gas flow. Ions and reactant gases were added through several inlet ports directed with or against the buffer gas flow. Reactant and product ions enter the quadrupole mass spectrometer through a small sampling orifice (diameter 0.2 mm) located in the center of a conically shaped entrance electrode. The ions are focused into the mass spectrometer at low axial energies by an additional quadrupole lens. They are detected by a channel electron multiplier operated in the pulse counting mode. A gas pressure of less than 5×10^{-5} hPa in the mass spectrometer was maintained by a large turbo molecular pump.

The reactant ions O_2^-, O_3^-, and CO_3^- were produced selectively with the capillary tube ion source (CIS) developed in our laboratory and described by Möhler and Arnold.[18] To produce O_2^- and O_3^-, the CIS was operated with a gas composed of gas flows of 1.5 slm (liter per minute at standard temperature and pressure) Ar and 0.1 slm O_2. When an additional flux of only 3 sccm (cm^3 per minute at standard temperature and pressure) CO_2 was added, the ion chemistry within the capillary tube of the CIS altered, resulting in a selective production of CO_3^- ions. Thus accurate comparison between O_2^-, O_3^-, and CO_3^- reactions was achieved simply by switching on and off the CO_2 flux without changing any other experimental parameter. The source gas flow was about 13% of the N_2 buffer gas flow. Therefore, the total buffer gas in the reaction zone of the flow tube was composed of 86.6% N_2, 12.6% Ar, and 0.8% O_2. If CO_2 was added to produce CO_3^- ions, its contribution to the gas flow was less than 0.1%.

Hydration of the reactant ions was achieved by adding water vapour through an inlet port located upstream from the ion source. The water concentration in the flow tube was about 1.5×10^{15} cm^{-3}. Within the first few cm downstream from the ion inlet, a hydration equilibrium of O_2^-, O_3^-, and CO_3^- was achieved. For the $O_2^-(H_2O)_n$ ions, the measured relative abundances of about 2% for $n=0$ and $n=1$, 70% for $n=2$, 25% for $n=3$, and less than 1% for $n=4$ agreed well with the results of equilibrium calculations based on thermochemical data.[19] The hydrate ion abundance of $O_3^-(H_2O)_n$ was 3% for $n=0$, 52% for $n=1$, 44% for $n=2$ and less than 1% for $n=3$. For the $CO_3^-(H_2O)_n$ ions, the measured abundances were 23% for $n=0$, 70% for $n=1$, and 7% for $n=2$, also in good agreement with theoretical data.[19]

By switching the water flux on and off, the reactions of the core ions and the hydrate ions could easily be compared to each other. The O_3^- ions are partly hydrated within the CIS before entering the flow tube. The H_2O impurity of the CIS gases was about 1 ppm. Without any additional water in the flow tube, the CIS produced about 35% O_3^- and 65% $O_3^-H_2O$. The hydration of O_3^- in the CIS is due to the high pressure of about 50 hPa. No thermochemical data on the formation of $O_3^-H_2O$ was found in the literature. Once entered the flow tube, no further hydration of O_3^- was observed. Thus the reactivity of O_3^- and $O_3^-H_2O$ could be studied independent of each other. For the O_2^- and CO_3^- ions, the hydration in the CIS was observed to be less than 10% and 1%, respectively.

The reactant gas SO_2 was added 12.5 cm downstream from the ion inlet port using a gas mixture of 100 ppmV SO_2 in N_2. The N_2/SO_2 addition was controlled by a mass flow controller. The SO_2 concentration in the reaction zone of the flow tube was calculated from the known reactant and buffer gas flows and the pressure. The reaction rate constants were derived from the exponential decrease of the reactant ion count rates (A^-) with increasing SO_2 concentration (SO_2)

$$\ln \frac{(A^-)}{(A^-)_0} = -k_A t_r (SO_2), \tag{11}$$

where $(A^-)_0$ is the measured ion signal at zero SO_2 flux, k_A is the rate constant for the reaction of A^- with SO_2, and t_r is the residence time of ions in the reaction zone, measured by electrically pulsing the ion swarm in the flow tube. The residence time was 9.7 ms for the SO_2 reactions. For the O_2 reactions, t_r was only 5.9 ms due to the smaller distance between the O_2 port and the mass spectrometer. The ratio v_i/v_g of the ion velocity v_i and the mean gas velocity v_g in the flow tube was 2.1 in our experiments. For other flow tubes used in flowing afterglow and SIFT apparatuses, v_i/v_g ranges between 1.6 and 2.2.[20]

Two sets of experiments were carried out to investigate reactions (4) and (5). In the first one (exp. 1), the CO_3^- ions were produced as described above. In the second (exp. 2), an oxygen reduced environment was chosen in the CIS. The CO_3^- ions were produced selectively in a source gas composed of 1.3 slm Ar and 3 sccm CO_2. The O_2 impurity in the source and buffer gases was less than 0.5 ppm. Ion hydration was achieved as described above. The oxygen reduced CIS gas composition was also chosen to investigate reactions (8), (9), and (10). The CO_3^- ions produced by the CIS were converted into SO_3^- via reactions (4) and (5). The SO_2 concentration in the flow tube was about 5×10^{11} cm^{-3}. In addition to CO_3^-, the CIS produced O_2^- ions with a relative abundance of 3%. These ions were converted into SO_2^- by reaction (1). The O_2 reactant gas was added 72 cm downstream the SO_2 inlet port. At this position, more than 99% of the original CO_3^- and O_2^- ions had already been converted into SO_3^- and SO_2^-, respectively. A similar procedure as for the SO_2 concentration was applied to determine the O_2 concentration in the flow tube.

The estimated uncertainty of our k values is about ±30% for the SO_2 reactions of CO_3^-, O_2^-, and O_3^-, mainly resulting from the uncertainties of the reactant gas concentrations in the flow tube and the mean residence time of the ions in the reaction zone. The rate constants for the SO_2 reactions of hydrated ions are uncertain by about ±40%. For the rate constants of O_2 reactions, an error of ±50% was estimated.

RESULTS AND DISCUSSION

SO_2 reactions

In a first set of experiments (exp. 1), reactions (1) to (7) were investigated. The reactant ions were prepared as described above with the ion source gas mainly composed of Ar (94%) and O_2 (6%). The measured decrease in the count rate of the reactant ions with increasing SO_2 concentration, (SO_2), is shown in Figs. 2 to 4. The count rates follow the expected decline [cf. Eq. (11)] except for values less than about 100 s^{-1}. The enhancement at the lowest count rates is probably due to fragmentation of product ions during ion sampling in the mass spectrometer. The product ions and their possible fragmentation channels are discussed in a later section.

Using Eq. (11), the reaction rate constants were derived from the slopes of the least square fits to the experimental data. The results of the fits are also shown in the Figs. 2 to 4. The measured rate constants are summarized in Table I. Our data agree well with previously measured rate constants also given in Table I. It should be mentioned, that the previous measurements[15,16] were made in He and Ar buffer gases at pressures between 0.17 and 0.6 hPa using the NOAA flowing afterglow (FA) and flow drift tube (FDT) systems whereas our measurements were made in an N_2 buffer gas at a slightly higher pressure of 2.5 hPa. Nevertheless, at least reactions (1) to (3) should be comparable in these systems. They occur on almost every collision and should, therefore, have no strong dependence on the buffer gas composition and pressure at thermal energies. Collision rate constants, calculated from the theory of Su and Chesnavich[21] based on trajectory calculations, are also shown in Table I. According to Ridge,[22] this theory most closely reflects the experimental data on unit efficiency ion–molecule reactions.

Albritton *et al.*[16] studied the reactions (3) and (4) both in He and Ar buffers and at different pressures (see notes in Table I). They found no dependence of k_3 and k_4 neither on the kind of the buffer gas nor on the pressure. Our k_3 and k_4 are slightly larger, but agree well with the previous data within the measurement uncertainty. This result supports the finding that, at least at thermal energies, the rate constants of the O^- transfer reactions (3)

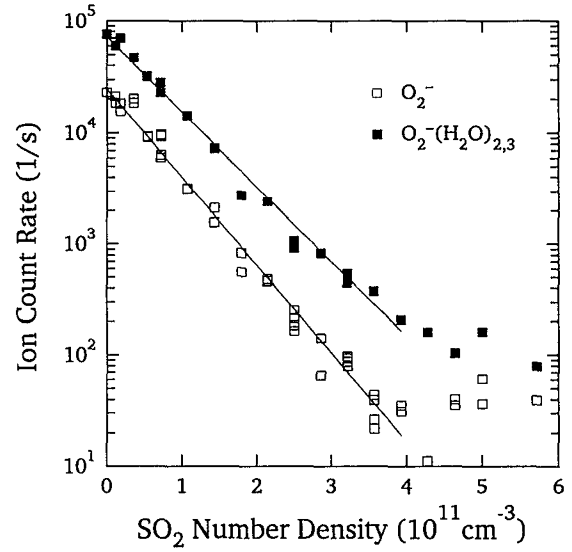

FIG. 2. Decrease of the measured ion signals vs the SO_2 concentrations in the flow tube for the reactions of O_2^- and $O_2^-(H_2O)_{2,3}$ with SO_2.

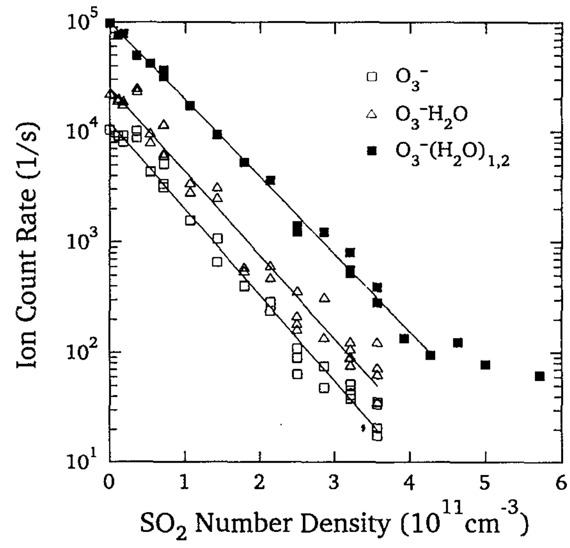

FIG. 3. Decrease of the measured ion signals vs the SO_2 concentrations in the flow tube for the reactions of O_3^-, $O_3^-H_2O$, and $O_3^-(H_2O)_{1,2}$ with SO_2.

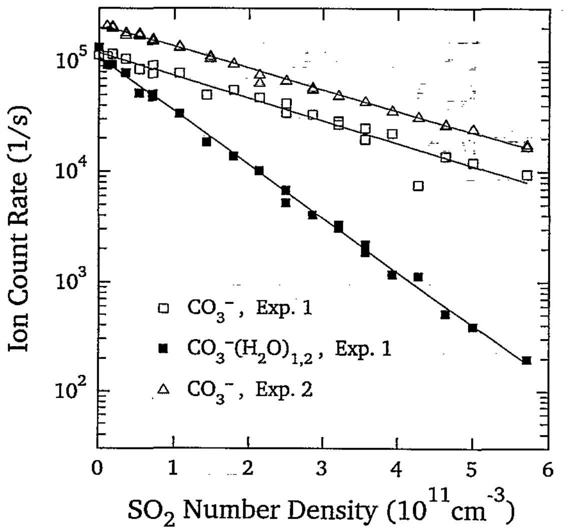

FIG. 4. Decrease of the measured ion signals vs the SO_2 concentrations in the flow tube for the reactions of CO_3^- and $CO_3^-(H_2O)_{1,2}$ with SO_2. For CO_3^-, the results of both experiment 1 and experiment 2 are shown. The slopes of both curves agree quite well with each other as should be expected.

and (4) do not depend on the pressure and the kind of the buffer gas as would be expected. Our measured k_6 and k_7 are also close to the collision rate constants. The rate constant k_7 was derived from the decrease of $O_3^-H_2O$ and $O_3^-(H_2O)_2$ being the major ions when water was introduced into the flow tube. The resulting effective rate constant $k_{\text{eff}}=1.73\times10^{-9}$ $cm^3\,s^{-1}$ is very close to k_6. Both hydrate ions were equally abundant and contributed to the measured decline to the same extent. It can therefore be concluded that the rate constant for $O_3^-(H_2O)_2$ should be around 1.7×10^{-9} $cm^3\,s^{-1}$. The measured $k_2=1.6\times10^{-9}$ $cm^3\,s^{-1}$ was derived from the count rate decrease of $O_2^-(H_2O)_2$ (74%) and $O_2^-(H_2O)_3$ (26%), and therefore gives the effective rate constant for the reactions of both ions. Fahey *et al.*[15] measured a rate constant of 1.7×10^{-9} $cm^3\,s^{-1}$ for the SO_2 reactions of both $O_2^-H_2O$ and $O_2^-(H_2O)_2$. Both, k_1 and k_2 agree well with the previous data and are close to the collision rates.

The rate constant k_5 was derived from the measured $k_{\text{eff}}=1.14\times10^{-9}$ $cm^3\,s^{-1}$ for the $CO_3^-(H_2O)_n$ ions ($n=0,1,2$). The relative abundance of the reactant ions (23% for $n=0$, 70% for $n=1$, and 7% for $n=2$) did not significantly vary with the SO_2 concentration because a permanent hydration equilibrium of the reactant ions is established during their reaction with SO_2. This equilibrium is due to the large water concentration of 1.5×10^{15} cm^{-3} compared to a maximum SO_2 concentration of 6.0×10^{11} cm^{-3}. Thus the measured k_{eff} can be corrected for the relative contribution of the CO_3^- reaction to get the rate constant for $CO_3^-H_2O$. The resulting $k_5=1.4\times10^{-9}$ $cm^3\,s^{-1}$ clearly shows, that reaction (5) is a fast exothermic switching reaction occuring on almost every collision. This result is particularly important for atmospheric SO_2 measurements based on reaction (5).[6,7]

Reactions (1), (3), and (4) mainly yield the products specified in Table I.[15,16] During experiment 1, O_2 was present in the flow tube due to the O_2 contained in the CIS gas and, therefore, most of the expected primary products SO_2^- and SO_3^- were converted into SO_4^- and SO_5^- by O_2 association reactions. These O_2 reactions have been studied separately in experiment 2 and will be discussed below. In

TABLE I. Reaction rate constants. The reactant ions were produced selectively within the source gas mixtures Ar/O_2 and $Ar/O_2/CO_2$ (exp. 1) and Ar/CO_2 (exp. 2, no O_2 source gas, O_2 only added as reactant gas). The present measurements were made in a 2.5 hPa N_2 buffer gas at room temperature (298 K).

	Reaction		Rate constant k ($cm^3\,s^{-1}$) Present work exp. 1	exp. 2	Previous work	Collision rate k_c[a] ($cm^3\,s^{-1}$)
1	$O_2^-+SO_2$	$\rightarrow SO_2^-+O_2$	2.0(−9)[b]		1.9(−9)[c]	2.0(−9)
2	$O_2^-(H_2O)_{2,3}+SO_2$	→ products	1.6(−9)[d]		1.7(−9)[e]	1.6(−9)[f]
3	$O_3^-+SO_2$	$\rightarrow SO_3^-+O_2$	1.9(−9)		1.7(−9)[g]	1.7(−9)
6	$O_3^-H_2O+SO_2$	→ products	1.8(−9)			1.6(−9)
7	$O_3^-(H_2O)_2+SO_2$	→ products	1.7(−9)			1.5(−9)
4	$CO_3^-+SO_2$	$\rightarrow SO_3^-+O_2$	4.8(−10)	4.7(−10)	3.5(−10)[h] 4.0(−10)[i]	1.6(−9)
5	$CO_3^-H_2O+SO_2$	→ products	1.4(−9)	1.4(−9)		1.5(−9)
8	$SO_3^-+O_2+N_2$	$\rightarrow SO_5^-+N_2$		2.0(−12)[j]		6.2(−10)
9	$SO_3^-H_2O+O_2$	$\rightarrow SO_5^-+H_2O$		5.0(−11)		6.0(−10)
10	$SO_2^-+O_2+N_2$	$\rightarrow SO_4^-+N_2$		1.0(−12)[j]		6.4(−10)

[a] From trajectory calculations after Su and Chesnavich (Ref. 21).
[b] Notation: $1.9(-9)=1.9\times10^{-9}$.
[c] Fahey *et al.* (Ref. 15), flowing afterglow, 0.5 hPa He, 303 K.
[d] Effective rate constant for $n=2,3$.
[e] As[c], but at 207–304 K ($n=2$), 207–210 K ($n=3$).
[f] For $n=2$.
[g] Albritton *et al.* (Ref. 16), flowing afterglow (0.5 hPa He) and flow drift tube (0.32–0.6 hPa He, 0.17–0.27 hPa Ar), thermal energy.
[h] Albritton *et al.* (Ref. 16), flowing afterglow measurement.
[i] Albritton *et al.* (Ref. 16), flow drift tube measurement.
[j] Effective binary rate constant, 2.5 hPa N_2, 298 K.

that experiment the source gas was oxygen reduced and O_2 was added directly into the flow tube as a reaction gas.

When the reactions of hydrated ions were studied in experiment 1, the primary product ions also reacted further with O_2 and additionally became hydrated very rapidly. For reaction (2), $SO_4^-(H_2O)_n$ ($n=0,1,2$) were the terminal product ions. Concerning the reaction of $O_2^-H_2O$ with SO_2 both reaction channels

$$O_2^-H_2O+SO_2\rightarrow SO_4^-+H_2O(\Delta H_R^0=-328\ \text{kJ/mol}) \tag{2a}$$

$$\rightarrow SO_2^-H_2O+O_2[\Delta H_R^0 =15\ \text{kJ/mol}+\Delta H^0(SO_2^-\cdots H_2O)] \tag{2b}$$

are exothermic if the hydration enthalpy $\Delta H^0(SO_2^-\cdots H_2O)$ is less than -15 kJ/mol. The enthalpy change of the reactions, ΔH_R^0, are calculated from the heats of formation of the ions[23] and the neutrals.[24] Reaction (2b) may be followed by the switching reaction

$$SO_2^-H_2O+O_2\rightarrow SO_4^-+H_2O[\Delta H_R^0 =-341\ \text{kJ/mol}-\Delta H^0(SO_2^-\cdots H_2O)]. \tag{12}$$

However, it seems likely that SO_4^- is directly formed by reaction (2a).[15] $O_2^-(H_2O)_2$ probably reacts via

$$O_2^-(H_2O)_2+SO_2\rightarrow SO_4^-H_2O+H_2O[\Delta H_R^0 =-256\ \text{kJ/mol}+\Delta H^0(SO_4^-\cdots H_2O)] \tag{2c}$$

$$\rightarrow SO_4^-+2H_2O(\Delta H_R^0=-256\ \text{kJ/mol}). \tag{2d}$$

Both reactions are exothermic.

The mechanisms of reactions (4) and (5) were studied in more detail in a second set of experiments in an oxygen reduced environment in the flow tube (exp. 2). Under these conditions, O_2 reactions of reactant and product ions could be neglected. The variation of the CO_3^- signal with the SO_2 concentration [reaction (4)] is shown in Fig. 4 together with the results of exp. 1. The rate constants k_4 and k_5 measured in exp. 2 both agree well with the results of exp. 1 (Table 1).

The CO_3^- and $CO_3^-H_2O$ ions may react via

$$CO_3^-+SO_2\rightarrow SO_3^-+CO_2(\Delta H_R^0=-196\ \text{kJ/mol}) \tag{4a}$$

$$\rightarrow SO_4^-+CO(\Delta H_R^0=-56\ \text{kJ/mol}), \tag{4b}$$

$$CO_3^-H_2O+SO_2\rightarrow SO_3^-H_2O+CO_2[\Delta H_R^0 =-137\ \text{kJ/mol}+\Delta H^0(SO_3^-\cdots H_2O)] \tag{5a}$$

$$\rightarrow SO_3^-+H_2O+CO_2(\Delta H_R^0 =-137\ \text{kJ/mol}) \tag{5b}$$

$$\rightarrow SO_4^-H_2O+CO[\Delta H_R^0 =3\ \text{kJ/mol}+\Delta H^0(SO_4^-\cdots H_2O)], \tag{5c}$$

but mainly SO_3^- and $SO_3^-(H_2O)_n$ were observed to be the product ions. Due to the fast product ion hydration, no relative abundances of reaction channels (5a) and (5b) could be measured. The reaction channels (4b) and (5c) contribute less than 1%. The enthalpy change of reaction (5c) is uncertain by the unknown hydration enthalpy of $SO_4^-H_2O$.

O_2 reactions

To investigate the O_2 reactions (8), (9), and (10), the reactant ions SO_2^- and SO_3^- were prepared as described in the experimental section. A controlled O_2 flow was added at a position, where already 99% of the original CO_3^- and O_2^- source ions have been converted into SO_2^- and SO_3^- by reactions with SO_2. The measured rate constants are compiled in Table I.

For the association reaction (8), an effective binary rate constant $k_8=2.0\times10^{-12}\ \text{cm}^3\ \text{s}^{-1}$ was measured at an N_2 buffer gas pressure of 2.5 hPa and a temperature of 298 K. A ternary association rate constant $k_8^{(3)}=3.0\times10^{-29}\ \text{cm}^6\ \text{s}^{-1}$ can be derived assuming that reaction (8) is not yet saturated at our experimental conditions. In the case of saturation the derived $k_8^{(3)}$ is a lower limit to the true association rate constant. The O_2 association to SO_2^- was observed to have an effective binary rate constant $k_{10}=1.0\times10^{-12}\ \text{cm}^3\ \text{s}^{-1}$ being close to k_8 (Table I). The corresponding ternary rate constant is $1.5\times10^{-29}\ \text{cm}^6\ \text{s}^{-1}$, provided that reaction (10) is not in the high pressure limit.

The exchange reaction (9) is significantly faster than the association reaction (8). Nevertheless, the measured rate constant is about a factor of 10 lower than the calculated collision rate (Table I). The major product ion of reactions (8) and (9) is SO_5^-. Other product ions were not observed and should not be expected. For example, the formation of SO_4^- by the reaction of SO_3^- with O_2 is endothermic by about 150 kJ/mol. The exothermicities of reactions (8) and (9) are uncertain by the unknown heat of formation $\Delta_f H^0(SO_5^-)$ and the hydration enthalpy $\Delta H^0(SO_3^-\cdots H_2O)$. Because reaction (9) should be exothermic or at most may be slightly endothermic, one obtains $\Delta_f H^0(SO_5^-)<[-601\ \text{kJ/mol}+\Delta H^0(SO_3^-\cdots H_2O)]$ from the known $\Delta_f H^0(SO_3^-)=-601$ kJ/mol (Lias *et al.*[23]). If reaction (9) is in fact slightly endothermic, this limit has to be increased by the amount of the endothermicity. For the hydration reaction $SO_3^-+H_2O+M\rightleftarrows SO_3^-H_2O+M$ only the free energy change $\Delta G^0=-24.7$ kJ/mol is known. Assuming an entropy change of

TABLE II. Measured abundance ratios $R_n=[X^-(H_2O)_n]/[X^-(H_2O)_{n-1}]$ and equilibrium constants $K_{eq,n}$ of hydrated ions and derived free energy changes $-\Delta G^0_{n-1,n}$ of the corresponding hydration reactions $X^-(H_2O)_{n-1}+H_2O+N_2\rightleftarrows X^-(H_2O)_n+N_2$ at a temperature of 298 K.

				$-\Delta G^0_{n-1,n}$ (kJ/mol)	
Ion X^-		R_n	$K_{eq,n}$ (atm^{-1})	Present work	Previous work[a]
SO_3^-	$n=1$	0.67 ± 0.15	$1.3\pm0.5(4)$[b]	23.5 ± 1.0	24.7
	$n=2$	0.025 ± 0.01	$5.0\pm2.0(2)$	15.5 ± 1.0	
SO_4^-	$n=1$	1.0 ± 0.2	$2.0\pm0.5(4)$	24.7 ± 1.0	21.3
	$n=2$	<0.01	<200	<13.0	
SO_5^-	$n=1$	0.05 ± 0.01	$1.0\pm0.3(3)$	17.2 ± 1.0	

[a] Fehsenfeld and Ferguson (Ref. 25); measured in a flowing afterglow system at $T=296$ K.
[b] Notation: $1.3\pm0.5(4)=(1.3\pm0.5)\times10^4$.

about -100 kJ/mol being typical for the hydration of ions similar to SO_3^-, e.g., CO_3^- or NO_3^-,[19] the enthalpy change of the above reaction becomes about -55 kJ/mol.

No reliable data on the stability of SO_5^- ions can be derived from the present kinetic studies. However, fragmentation studies of mass selected SO_5^- ions made at our laboratory using a triple quadrupole mass spectrometer[7] showed that the collisional induced dissociation of SO_5^- is less effective than, e.g., that of the hydrated ions $CO_3^-H_2O$, $NO_3^-H_2O$, and $HCO_3^-H_2O$. The hydration enthalpies of these ions are around 60 kJ/mol. The SO_3^- ion was observed to be the major fragment ion of SO_5^- giving rise to the assumption, that the $SO_3^-\cdots O_2$ binding may be more stable than the water binding of the above ions. We may therefore conclude that the heat of formation of SO_5^- is probably less than -715 kJ/mol.

Hydration of SO_3^-, SO_4^-, and SO_5^- was also observed. The measured abundance ratios $R_n=[X^-(H_2O)_n]/[X^-(H_2O)_{n-1}]$ of the hydrated ions are shown in Table II. The ratios have been corrected for the known mass discrimination of the mass spectrometer. The correction factor was less than 1.2. The measured ratio may also be effected by fragmentation of the hydrated ions when they are focused into the rod system of the mass spectrometer. However, the field strength between the ion inlet orifice and the rod system was quite low due to the quadrupole lens and thus the effect of fragmentation on the measured R values is less than about 15%.

The abundance ratios shown in Table II reflect the equilibrium values of ion hydration in the flow tube within the given uncertainties. To establish that the hydration equilibrium was achieved, the hydration of O_2^-, CO_3^-, and NO_3^- was investigated under the same conditions. The known thermochemical data for the hydration of these ions was used to calculate the expected hydrate ion abundances. The results agreed well with the measured abundances (cf. Experimental section). The equilibrium constants $K_{eq,n}=R_n/(H_2O)$ [(H_2O) is the known water concentration in the flow tube] and the mean free energy change $-\Delta G^0_{n-1,n}$ of the corresponding hydration reactions are also given in Table II. Our ΔG^0 value for the hydration of SO_3^- is close to a previous result.[25] For the hydration of SO_4^- we got a somewhat higher value. The equilibrium constant for the association of the second water molecule is markedly reduced compared to the first for both SO_3^- and SO_4^-. For the hydration of SO_5^- we measured $-\Delta G^0=17.2\pm1.0$ kJ/mol. This value is significantly lower than the corresponding result for SO_3^- and SO_4^-.

SUMMARY AND CONCLUSIONS

The present investigations clearly showed, that SO_5^- is a stable ion in the gas phase. Various negative ion reactions yielding SO_5^- and SO_4^- were investigated. The measured rate constants for the SO_2 reactions of O_2^-, $O_2^-(H_2O)_{2,3}$, O_3^-, and CO_3^- agree fairly well with previous results. The measured rate constants of the SO_2 reactions of $O_2^-(H_2O)_{0,2,3}$, $O_3^-(H_2O)_{0,1,2}$, and $CO_3^-H_2O$ are very close to the collision rate k_c. The data also agree well with the $\mu_r^{-1/2}$ dependence of k_c, where μ_r is the reduced mass of the reactant ion and the SO_2 molecule. The precision of the measured SO_2 reaction rate constants is about ±10%.

The SO_2 reactions of CO_3^- and $CO_3^-H_2O$ are particularly important for atmospheric SO_2 measurements by a method recently developed at our laboratory and described in detail elsewhere.[6,7] The method relies on the conversion of CO_3^- ions into SO_5^- ions. This conversion was found to be a two-step mechanism. The major product ions of the first reaction step are SO_3^- and $SO_3^-H_2O$. These ions further react with O_2 forming SO_5^-. An effective binary rate constant of 2.0×10^{-12} $cm^3\,s^{-1}$ was measured for the O_2 association to SO_3^- at an N_2 buffer gas pressure of 2.5 hPa. For the switching reaction of $SO_3^-H_2O$ with O_2 the measured rate constant is 5.0×10^{-11} $cm^3\,s^{-1}$. Probably, the SO_5^- ion is also formed by the reaction of $O_3^-H_2O$ with SO_2. The rate constant for this reaction is 1.8×10^{-9} $cm^3\,s^{-1}$. Because O_2 was present in the flow tube when this reaction was investigated, the SO_5^- ions being the major terminal product ions may have been produced also by primary SO_3^- formation and subsequent O_2 association. The formation of both, SO_3^- and SO_5^-, by reaction (6) are exothermic processes.

The present results also have implications for the ion chemistry of ambient negative ions in the lower atmosphere. The hydrates of O_2^-, O_3^-, and CO_3^- are known to play a major role in the first steps of the ion-chemical evolution in the lower atmosphere.[26] O_2^- and O_3^- ions are converted rapidly into $CO_3^-(H_2O)_n$ by reactions with CO_2, O_3, and H_2O. The CO_3^- hydrates further react, e.g., with NO, NO_2, and HNO_3. Because SO_2 normally is less abundant than CO_2, O_3, and H_2O, it should not compete with the fast reactions of these gases with O_2^- and O_3^-. However, in the upper troposphere the abundance of SO_2 is similar to the abundance of the the nitrogen compounds and should therefore be considered as a possible reaction partner for the further conversion of CO_3^- hydrates. Possible reactions of the SO_5^- hydrates with other trace gases, e.g., those having large gas-phase acidities like HNO_3, H_2SO_4, or HCN should be examined in the laboratory.

ACKNOWLEDGMENTS

We thank Andreas Krieger for his assistance in the laboratory and the technical staff of the Max-Planck-Institut für Kernphysik, Heidelberg for the support. This research was funded in part by the Bundesminister für Forschung und Technologie (BMFT) and the European Community (EC).

[1] T. E. Graedel and C. J. Weschler, Rev. Geophys. Space Sci. **19**, 505 (1981).
[2] J. H. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution* (Wiley, New York, 1986).
[3] J. A. Lind, A. L. Lazrus, and G. L. Koh, J. Geophys. Res. **92**, D4, 4171 (1987).
[4] E. Hayon, A. Treinin, and J. Wilf, J. Am. Chem. Soc. **94**, 47 (1972).
[5] O. Möhler and F. Arnold (unpublished material).
[6] O. Möhler and F. Arnold, Geophys. Res. Lett. **19**, 1763 (1992).
[7] O. Möhler, T. Reiner, and F. Arnold (paper in preparation).
[8] P. J. Crutzen, Geophys. Res. Lett. **3**, 73 (1976).
[9] J. F. Vedder, E. P. Condon, E. C. Y. Inn, K. D. Tabor, and M. A. Kritz, Geophys. Res. Lett. **10**, 1045 (1983).
[10] S. A. McKeen, S. C. Liu, and C. S. Kiang, J. Geophys. Res. **89**, D3, 4873 (1984).
[11] D. J. Hofmann, Nature (London) **349**, 659 (1991).
[12] R. P. Turco, R. C. Whitten, and O. B. Toon, Rev. Geophys. Space Phys. **20**, 233 (1982).
[13] F. Arnold and T. Bührke, Nature (London) **301**, 293 (1983).
[14] J. R. Vacher, M. Jorda, E. Le Duc, and M. Fitaire, Int. J. Mass Spectrom. Ion Proc. **114**, 149 (1992).
[15] D. W. Fahey, H. Böhringer, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. **76**, 1799 (1982).
[16] D. L. Albritton, I. Dotan, G. E. Streit, D. W. Fahey, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. **78**, 6614 (1983).
[17] E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, Adv. At. Mol. Phys. **5**, edited by D. R. Bates and I. Estermann (Academic, New York, 1969).
[18] O. Möhler and F. Arnold, J. Atm. Chem. **13**, 33 (1991).
[19] R. G. Keesee and A. W. Castleman, J. Phys. Chem. Ref. Data **15**, 1011 (1986).
[20] D. Smith and N. G. Adams, Adv. At. Mol. Phys. **24**, 1 (1988).
[21] T. Su and W. J. Chesnavich, J. Chem. Phys. **76**, 5183 (1982).
[22] D. P. Ridge, in *Structure/Reactivity and Thermochemistry of Ions*, edited by P. Ausloos and S. G. Lias (Reidel, Dordrecht, 1987), p. 15.
[23] S. G. Lias, J. E. Bartmess, J. F. Liebmann, J. L. Holmes, R. D. Levin, and W. G. Mallard, J. Phys. Chem. Ref. Data **17**, Suppl. No. 1 (1988).
[24] G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere* (Reidel, Dordrecht, 1984).
[25] F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys. **61**, 3181 (1974).
[26] F. Arnold, in *Proceedings of the Dahlem Konferezen*, edited by E. D. Goldberg (Springer, Berlin, 1982), p. 273.