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Proton transfer reaction rate coefficients between H_3O^+ and some sulphur compounds

Luca Cappellin[a], Michael Probst[b], Jumras Limtrakul[c], Franco Biasioli[a,*], Erna Schuhfried[b], Christos Soukoulis[a], Tilmann D. Märk[b], Flavia Gasperi[a]

[a] IASMA Research and Innovation Centre, Fondazione Edmund Mach, Food Quality and Nutrition Area, Via E. Mach, 1, 38010, S. Michele a/A, Italy
[b] Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria
[c] Department of Chemistry and National Nanotechnology Center of Excellence, Kasetsart University, Bangkok 10900, Thailand

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ABSTRACT

Volatile sulphur compounds (VSCs) are key compounds in many fields of basic and applied science and technology, such as environmental sciences, food science, geochemistry, petrochemistry, agriculture, biology and medicine. Proton transfer reaction mass spectrometry (PTR-MS) allows for on-line monitoring of volatile organic compounds (VOCs) and, in particular, of VSCs with ultra low detection limits and a fast response time. In principle, with PTR-MS, absolute quantification of VOC concentrations without calibration is possible, provided the branching ratios are known. However, for this, the reaction rate coefficients between VOCs and the hydronium ion have also to be known. Several well-established theories may be used to determine ion-neutral molecule reaction rate coefficients. In the case of H_3O^+–VOC reactions proceeding in a PTR-MS drift tube, a key factor to be considered is the centre-of-mass energy, which is generally much higher than the thermal energy, due to the additional translational (drift) energy of the ion. Nevertheless, it is common practice to employ collision theories that do not show an explicit dependence on the centre-of-mass energy.

First we review basic aspects of ion-neutral reactions in the PTR-MS drift tube and various methods to calculate reaction rate coefficients. Next, we calculate, on the basis of quantum chemical methods and different theoretical approaches for ion-molecule collisions, reaction rate coefficients between selected sulphur compounds and H_3O^+. Finally, we discuss proper methods for the calculations of ion-neutral molecule reaction rate coefficients in the context of PTR-MS and the corresponding experimental parameters involved.

1. Introduction

In recent years increasing attention has been paid to the further development of proton transfer reaction-mass spectrometry (PTR-MS), a technique which is already very successful in the on-line monitoring of volatile organic compounds (VOCs) thanks to its fast response time and low detection limits [1]. In fact, PTR-MS allows for the detection of VOCs at pptv levels [2] and, especially with the newly available TOF based set-ups, can measure entire spectra within a split second. PTR-MS is considered an essential tool for environmental chemists [3] and environmental sciences are probably the field wherein PTR-MS is mostly applied [1]. It has, however, also been applied successfully in food science and technology [4,5], agronomy [6], genetics [7] and medical science [8].

The PTR-MS technique is based on the chemical ionization of VOCs by hydronium ions H_3O^+, which takes place in a buffer gas, usually air, flowing in a drift tube. For trace organic compounds contained in the air buffer gas that have larger proton affinity than water, a proton transfers from the ionizing agent H_3O^+ to the VOC [1]

$$H_3O^+ + \mathrm{VOC} \rightarrow H_2O + \mathrm{VOC{\cdot}H^+}. \quad (1)$$

Fragmentations of the VOC·H$^+$ ions may then occur and must be investigated experimentally [1]. The ionic products are then detected at the end of the drift tube by a mass analyser. There exist different approaches for determining the concentration of the volatile neutral reactants starting from the measured product ion counts. A possible way is to calibrate the instrument using test gas mixtures containing known concentrations of the selected volatile compounds. Depending on the properties of the organic species, many procedures have been proposed to generate these reference samples. Dynamic dilution of volatile compounds from standard gas cylinders [3] is prevailing but this method is unsuitable for certain classes of compounds. For example, this method has been replaced by diffusion methods [9] or permeation methods [10] to deal with carboxylic acids. However, also these

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[*] Corresponding author. Tel.: +39 0461 615187; fax: +39 0461 650956.
E-mail address: franco.biasioli@iasma.it (F. Biasioli).

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Table 1
Calculated polarisability (α), dipole moment (μ_D) and thermal proton transfer reaction rate coefficient at $T = 300$ K for selected volatile sulphur compounds. Results using both ADO theory and parameterised trajectory calculations are reported.

VOC	Formula	α (Å^3)	μ_D (D)	k_{ado} ($\times 10^{-9}$ cm^3/s)	k_{cap} ($\times 10^{-9}$ cm^3/s)
Dimethyl sulphide	CH3–S–CH3	7.46	1.60	2.50	2.67
Ethylmethyl sulphide	CH3–S–CH2–CH3	9.38	1.63	2.63	2.76
Diethyl sulphide	CH3–CH2–S–CH2–CH3	11.34	1.66	2.76	2.87
Allylmethyl sulphide	CH2═CH–CH2–S–CH3	11.39	1.61	2.74	2.84
Dimethyl disulphide	CH3–S–S–CH3	10.79	2.02	2.94	3.17
Diethyl disulphide	CH3–CH2–S–S–CH2–CH3	14.83	2.19	3.40	3.48
Dipropyl disulphide	CH3–CH2–CH2–S–S–CH2–CH2–CH3	18.79	2.21	3.47	3.63

latter procedures are not ideal as they need very stable experimental conditions (coefficient temperature, pressure, flow rate) and show large memory effects [11]. Moreover, in principle, the PTR-MS apparatus should be calibrated for each single VOC. This implies the general difficulty of obtaining an authentic standard for every VOC. Thus if several compounds are involved, the calibration procedure becomes lengthy and costly. Moreover, whenever the instruments are operated under different experimental conditions a new calibration procedure needs to be carried out. Therefore, it is common to use a quite different approach, which does not involve a calibration procedure but is based on response factor determinations.

As reported in [12], simple kinetic calculations for the chemical ionization reactions occurring in the PTR-MS drift tube under standard PTR-MS conditions lead to approximate VOC concentrations in terms of the measured ion count signals via

$$[\mathrm{VOC}] = \frac{1}{kt}\frac{[\mathrm{VOCH}^+]}{[\mathrm{H_3O}^+]}, \tag{2}$$

where [VOCH$^+$] and [H_3O^+] are the ion counts of the mass spectrometer, k is the rate coefficient of the proton transfer reaction described by Eq. (1), and t is the residence time of the ion in the drift tube, typically about 100 μs, which is determined as described in [11]. Ion count rates are however affected by mass discrimination in the spectrometer and must be corrected by discrimination factors that can be determined using, for example, the procedure proposed in [11]. Eq. (2) is an important tool for calculating VOC concentrations, provided reaction rate coefficients are known. Experimental determinations of reaction rate coefficients between H_3O^+ and VOCs are difficult and associated with large errors [13,14], nevertheless they are often used as a benchmark for theoretical calculations [15].

Particularly with regard to PTR-MS applications in environmental sciences, Zhao and Zhang [15] published a list of reaction rate coefficients of interest for atmospheric studies. They employed average-dipole-orientation (ADO) theory to compute collision rate coefficients along with quantum chemical calculations for the determination of the polarisabilities and dipole moments of neutral molecules. In general, however, literature data are inconsistent and scarce, especially for particular classes of compounds, one of them being molecules containing sulphur. Such sulphur compounds are important in environmental sciences (pollution [16], emission from waste and waste treatment plants [17]; cloud formation [18]), geochemistry, petro chemistry, agriculture, biology (e.g., disulphide bonds in proteins), and medicine. Further, in food sciences, they are key aroma compounds that have highly undesired off-flavours [19], but which can have also a positive impact as, e.g., in truffle [20], cheese [21] or coffee [22]. Aiming at facilitating the use of PTR-MS, in the present study we address the determination of reaction rate coefficients between H_3O^+ and selected sulphur compounds (listed in Table 1) and discuss important points for a better estimation of the collision parameters for the protonation reaction in PTR-MS.

2. Theoretical considerations and methods

2.1. Determination of polarisability and dipole moment

The dipole moments and polarisabilities of the seven selected sulphur compounds (4 sulphides including allylmethyl sulphide, and 3 disulphides) were calculated, three of them for the first time, by quantum chemical methods. The main contributions to the dipole polarisability are nearly additive with respect to atoms and bonds given the charge state does not change and therefore, to a first approximation, do not depend much on the molecular geometry. Molecular dipole moments on the other hand crucially depend on molecular geometry. The dipole polarisability is a linear response property of the wave function whereas the dipole moment is a first-order coordinate operator acting on the wave function. This means that the calculation of polarisability requires higher-level quantum chemical methods than are necessary for electrostatic moments like the dipole moment in order to achieve the same level of accuracy. Nevertheless, both quantities can nowadays routinely be calculated by quantum chemical program packages and the task is reduced to select an accurate, yet computationally still affordable, method. Hybrid density functional like B3LYP generally give good results [23], while Hartree–Fock and standard Kohn–Sham calculations in the local density approximation are not suitable. Since we could not find literature data for high-level quantum chemical calculations of polarisabilities or dipole moments specifically for organic sulphides to compare with our B3LYP results, we performed a few higher-level calculations using MP2 theory. They showed the expected degree of similarity with the B3LYP results. For example, the MP2 polarisability of CH3-S-CH3 with the aug-cc-pvDZ basis set is 7.24 Å^3 while the B3LYP value is 7.38 Å^3. The corresponding dipole moments are 1.84 and 1.67 D, respectively. With the larger basis sets used in our actual calculations described below – for which MP2 calculations are already lengthy – the differences between MP2 values (1.80 D and 7.32 Å^3, respectively) and the B3LYP results are even smaller. Of course, calculations are greatly simplified if only gas-phase properties are desired and no environmental (e.g., solution) effects are present which can alter dipole moments considerably. This is the case for the presently intended calculations and application to PTR-MS drift tubes. In our calculations the aug-cc-pVTZ basis set [24] was used. It is known that this rather large basis set gives almost converged results for many properties and test calculations with the even larger aug-cc-pVQZ basis set for the present compounds did not show any significant changes in the polarisabilities and dipole moments. The Gaussian 03 program [25] was used for the calculations.

2.2. Determination of reaction rate coefficients

Proton transfer reactions between H_3O^+ and VOCs that have a proton affinity larger than water are exothermic. They are typically barrierless and occur at collision rate, provided the exothermicity is large enough [26], usually above 20 kJ/mol. For instance, in the case of dimethyl sulphide the exothermicity is 140 kJ/mol. Therefore, it is legitimate to employ ion-neutral molecule collision theories. A first approximation of the collision rate coefficient between an ion and a polarisable molecule is given by the so called Langevin collision rate k_L which reads [27]

$$k_L = q\sqrt{\frac{\pi\alpha}{\mu\varepsilon_0}}, \tag{3}$$

where q is the ion charge, μ is the reduced mass of the system, α is the polarisability of the neutral reactant, and ε_0 is the permittivity of the free space. k_L provides a good approximation of the reaction rate k for non-polar molecules and in the high temperature limit. A better approximation, which can account for the effect of a permanent dipole moment of the neutral molecule, is the average-dipole-orientation (ADO) theory, developed by Su and Bowers [28,29]. The ADO collision rate coefficient is given by

$$k_{\mathrm{ADO}} = q\sqrt{\frac{\pi\alpha}{\mu\varepsilon_0}} + C\frac{q\mu_D}{\varepsilon_0}\sqrt{\frac{1}{2\pi\mu KT}}, \tag{4}$$

where μ_D is the permanent dipole moment of the neutral reactant and T the temperature. C is a parameter which depends on the temperature T and on the ratio $\mu_D/\alpha^{1/2}$ and assumes values between 0 and 1. In the particular limits $C = 0$ and $C = 1$, k_{ADO} reduces to the Langevin value and to the locked-dipole expression, respectively. Su and Bowers published tabulated values of C for different values of T in the range of 50–650 K [30]. However, in the appendix of a later study, Su et al. [31] suggested that those tabulated values were not correct and presented new results for $T = 300$ K. Although the ADO theory has theoretical inconsistencies [32], it is generally found to match experimental ion-neutral molecule reaction rate coefficients within a typical error in the range of 10–20% [33,29]. It is worth noticing that the expression for k_{ADO} introduces a temperature dependence not present in the one for k_L. Generalizing the use of ADO theory for ion-neutral molecule collisions taking place in a drift tube, as it is the case for the PTR-MS instrument, has led as noticed by Blake et al. [34] to the rather common, yet questionable practice of employing room-temperature in the k_{ADO} expression in Eq. (2). In fact, the translational energy of the colliding ion leads to a centre-of-mass energy largely exceeding that of thermal collisions.

The quantitative description of such phenomena in drift tubes dates back to the work of Wannier [35], followed by McFarland [36]. They showed that the total kinetic energy of an ion may be written as

$$KE_{ion} = \frac{1}{2}mv^2 + \frac{1}{2}Mv^2 + \frac{3}{2}k_bT, \tag{5}$$

where m is the mass of the ion, M is the mass of the buffer gas, v is the drift velocity of the ion and T is the drift tube temperature. In the above expression, two terms are added to the thermal energy of the ion. The first term represents the drift energy and the second is the random field energy, accounting for random velocity components due to ion-neutral molecule collisions [35]. Under typical PTR-MS working conditions, the 0.03 eV thermal energy represents a small fraction of the 0.25 eV total kinetic energy of the ion. The centre-of-mass kinetic energy for an ion-neutral molecule collision is [36]:

$$KE_{cm} = \frac{3}{2}k_bT + \left(\frac{m_N}{m_N + m}\right)\left(KE_{ion} - \frac{3}{2}k_bT\right), \tag{6}$$

where m_N is the mass of the neutral molecule. The last equation can be used to estimate an effective temperature for ion-neutral molecule collisions in a (PTR-MS) drift tube:

$$T_{eff} = T + \left(\frac{v^2}{3k_b}\right)\left[\frac{m_N(m + M)}{m + m_N}\right]. \tag{7}$$

The above expression differs slightly from Eq. (2) given by Blake et al. [34], since the latter represents the effective ion translational temperature. Common values for ion drift velocity and drift tube temperature in a PTR-MS apparatus are $v = 930$ m/s and $T = 380$ K. If H_3O^+ is the primary ion and, for example, dimethyl sulphide is the neutral reactant, we calculate a $T_{eff} = 1656$ K. Therefore, it is clear that the second term on the right hand side of Eq. (7) is larger than the drift tube temperature under the usual PTR-MS conditions.

Extensive trajectory calculations have been carried out by Su and Chesnavich [37] to predict the rate coefficients k_{cap} of ion-polar molecule capture collisions. Results have then been parameterised as $k_{cap} = K_{cap}k_L$ [38,39], where K_{cap} is expressed as a function of the reduced parameter $x = (\mu_D/2\alpha k_bT)^{1/2}$. Hence, K_{cap} is easily calculated from α and μ_D. Su [40] made a remarkable effort to parameterise the kinetic energy dependence of K_{cap} within a 5% error for a wide range of temperatures (50–1000 K) and centre-of-mass kinetic energies (from thermal to several eV):

$$k_{cap}(T, KE_{cm}) = K_{cap}(\tau, \varepsilon)k_L, \tag{8}$$

where $K_{cap}(\tau,\varepsilon)$ is the parameterised locking coefficient that depends on the reduced parameters $\tau = \mu_D/(\alpha T)^{1/2}$ and $\varepsilon = \mu_D/(\alpha KE_{cm})^{1/2}$. The major purpose was to provide a useful benchmark in response to the increasing amount of experiments aiming at measuring dependencies of ion-polar molecule collision rate coefficients as a function of kinetic energy. For example, studies on ligand exchange cross sections using guided ion beam mass spectrometry found that trajectory parameterisation correctly reproduced the kinetic energy dependence of the cross sections for exothermic reactions at centre-of-mass energies below 0.3 eV [41]. The correct magnitude was also reproduced for reactions having free-energy differences larger than 5 kJ/mol, while in the case of ligand exchange reactions with lower free-energy differences, reaction cross sections tended to be overestimated by about 20%. In general, trajectory parameterisation is the theory most widely used to estimate rate coefficient collision limits in theoretical and experimental studies of reaction kinetic energy dependencies.

3. Results and discussion

3.1. Polarisability and dipole moment at equilibrium molecular geometries

As mentioned above, only the dipole moment, not the polarisability, depends strongly on the molecular geometry. In sulphides, the C–S–C unit is responsible for their dipole moments. It is quite rigid and therefore the difference between the dipole moment at the nuclear equilibrium position and the vibrationally averaged one can safely be assumed to be very small. We calculated the properties from the geometries optimized by the same method (B3LYP) and basis set (aug-cc-pVTZ). For some compounds the aug-cc-pVQZ basis set was also employed, leading to comparable results. In the equilibrium structures of all sulphides the C–S–C angles are close to 100° and the C–S distances are close to 1.831 Å with deviations of less than 1° and 0.005 Å, respectively. Table 2 reports the calculated polarisabilities and dipole moments of the selected sulphur compounds, along with benchmark literature data. All results of quantum chemical calculations are affected by a typical uncertainty of 2–3%. As far as dimethyl sulphide, ethylmethyl sulphide, diethyl sulphide and dimethyl disulphide are concerned, theoretical estimates of polarisabilities and dipole moments with quantum chemical methods have recently become available on NIST [42]. For comparison, in Table 2 we report the data from NIST estimated with the same method we employed, namely B3LYP. A good agreement with our results is found. In the case of allylmethyl sulphide, diethyl disulphide, dipropyl disulphide, our estimates of the polarisability

Table 2
Comparison of calculated polarisabilities and dipole moments with available literature data.

VOC	α (Å^3)				μ_D (D)		
	Present work		Literature		Present work	Literature	
	Basis set		Exp	Theor		Exp	Theor
Dimethyl sulphide	aug-cc-pvTZ	7.46	7.55[a]	7.46[a]	1.60	1.554[b]	1.60[a]
Ethylmethyl sulphide	aug-cc-pvTZ	9.38		9.38[a]	1.63		1.63[a]
	aug-cc-pvQZ	9.37			1.62		
Diethyl sulphide	aug-cc-pvTZ	11.34		11.41[a]	1.68	1.556[c]	1.59[a]
	aug-cc-pvQZ	11.34			1.63		
Allylmethyl sulphide	aug-cc-pvTZ	11.39		11.22[d]	1.61		
Dimethyl disulphide	aug-cc-pvTZ	10.79		10.79[a]	2.02		2.02[a]
Diethyl disulphide	aug-cc-pvTZ	14.84		14.49[d]	2.20		
	aug-cc-pvQZ	14.82			2.19		
Dipropyl disulphide	aug-cc-pvTZ	18.81		18.17[d]	2.22		
	aug-cc-pvQZ	18.78			2.20		

[a] Literature data from NIST [42]. Theoretical data from NIST data are calculated with the same method we employed (B3LYP). The basis set is aug-cc-pvTZ for dimethyl sulphide, ethylmethyl sulphide and dimethyl disulphide, aug-cc-pvDZ for diethyl sulphide (polarisability) and cc-pvTZ for diethyl sulphide (dipole moment).

[b] CRC Handbook of Chemistry and Physics, 2009–2010, 90th edition.

[c] Ref. [45].

[d] Literature data from http://www.thegoodscentscompany.com (last accessed on February 2010). All data are affected by a reported error of 0.5 Å^3. Even though it is not clearly stated in the reference, we assume that these are theoretical data.

are compatible with literature data. To the best of our knowledge, for these compounds no data on dipole moments have been published so far.

3.2. Thermally averaged disulphide dipole moments

For the disulphides, rotation around the S–S bond changes the dipole moments since the two C–S subunits of the C–S–S–C unit account for the largest contributions to the dipole moment of the molecules. The vectors of their partial dipole moments can add up or cancel out each other, depending on the C–S–S–C angle. Therefore, in addition to calculating the properties of the equilibrium structures, we estimated the rotationally averaged dipole moment for the disulphides. Although the S–S bond is a sigma bond, which, in principle, allows for free rotation, the preferred C–S–S–C angle in disulphides is not 180° which would minimize steric repulsion and dipole–dipole interaction, but rather 90°, which minimizes the orbital repulsion. This is analogous to the situation in hydrogen peroxide.

In order to derive the thermally averaged dipole moments for the disulphides, one needs three functions of the C–S–S–C angle θ: the relative energy function $E(\theta)$, the dipole moment function $\mu_D(\theta)$ and the probability of finding a specific angle $P(\theta)$ which amounts to a Boltzmann distribution at a given temperature. All three functions can be calculated without difficulties. We describe the details for CH_3–S–S–CH_3 which are entirely analogous for the other disulphides. Due to the periodicity of θ, $E(\theta)$ and $\mu_D(\theta)$ can be written in the form of sine or cosine functions of θ. In order to determine the amplitude and the phase in the two functions, it is sufficient to calculate $E(\theta)$ and $\mu(\theta)$ at $\theta = 0°$, 90° and 180°. Then one obtains the following approximate expressions:

$$E(\theta) = 0.45 \quad (1 - \sin(\theta)) \quad \text{and} \quad \mu_D(\theta) = \left| 2.92 \cos\left(\frac{\theta}{2}\right) \right|. \tag{9}$$

The situation is shown in Fig. 1 where the $E(\theta)$, $|\mu_D(\theta)|$ and the thermal distribution of θ at 300 K are plotted, together with the calculated values at 0°, 90° and 180°. After normalization one obtains the weighted average $\langle\mu_D\rangle^{300\,\mathrm{K}}$ as 2.05. One sees that $\langle\mu_D\rangle^{300\,\mathrm{K}}$ is only insignificantly different from the value of μ_D at 90° (2.00), in particular when considering that a 2–3% error arises already from the quantum chemical calculations. From Fig. 1 it can be seen that this result stems from the symmetric energy distribution together with a near-linear $\mu(\theta)$ around 90°. Therefore we can safely replace $\langle\mu_D\rangle^{300\,\mathrm{K}}$ by $\mu_D(90°)$.

3.3. Reaction rate coefficients

Table 1 reports results for the polarisabilities and dipole moments of selected sulphur compounds, along with their thermal reaction rate coefficients at 300 K, determined using both, ADO theory and parameterised trajectory calculations as discussed above.

Literature data on reaction rate coefficients for sulphur compounds reacting with H_3O^+ ions are scarce. To our knowledge, the published experimental data were all determined using the SIFT technique and usually have errors of 10–30%. In the case of dimethyl sulphide, four different experimental values are available. Williams et al. [14] determined a value of 1.7×10^{-9} cm^3/s, which differs from the 2.1×10^{-9} cm^3/s reported by Passarella [13] and by Lindinger et al. [12] and from the 2.5×10^{-9} cm^3/s reported by Arnold et al. [43]. Our theoretically calculated results are in good agreement with the latter. Williams et al. [14] also reported a rate coefficient of 2.4×10^{-9} cm^3/s for ethylmethyl sulphide (25% error), which is compatible with our calculation. For all other compounds experimental data are, to our knowledge, not available.

Spanel and Smith [44] employed the parameterised trajectory formulation from Su and Chesnavich [37] to calculate an

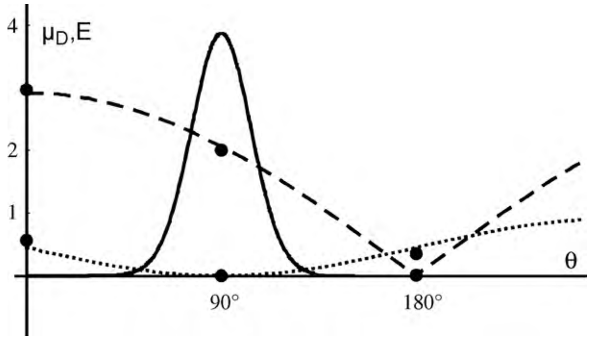

Fig. 1. $E(\theta)$ in eV, absolute value of $\mu_D(\theta)$ in Debye and the thermal Boltzmann distribution $P(\theta)$ at 300 K as a function of the C–S–S–C torsion angle θ. The same y-axis is used for $E(\theta)$ (dotted line) and $\mu_D(\theta)$ (dashed line) whereas an arbitrary scaling is used for the Boltzmann distribution. The dots denote quantum chemically calculated values.

Table 3
Proton transfer reaction rate coefficients $k_{cap}(T,KE_{cm})$ between hydronium ion (H_3O^+) and selected sulphur VOCs in the case of maximum (380 K) and minimum (300 K) drift tube temperatures in commercial PTR-MS apparatuses, for a drift velocity of 930 m/s. For comparison k_L, $k_{LD}(T_{eff})$, and $k_{cap}(T_{eff})$ are also reported (see text).

VOC	T (K)	k_L ($\times 10^{-9}$ cm^3/s)	$k_{LD}(T_{eff})$ ($\times 10^{-9}$ cm^3/s)	$k_{cap}(T_{eff})$ ($\times 10^{-9}$ cm^3/s)	$k_{cap}(T,KE_{cm})$ ($\times 10^{-9}$ cm^3/s)
Dimethyl sulphide	300	1.68	3.36	1.95	2.24
	380	1.68	3.32	1.94	2.19
Ethylmethyl sulphide	300	1.84	3.48	2.09	2.30
	380	1.84	3.44	2.08	2.26
Diethyl sulphide	300	1.99	3.61	2.23	2.39
	380	1.99	3.58	2.22	2.36
Allylmethyl sulphide	300	2.00	3.58	2.23	2.37
	380	2.00	3.54	2.22	2.34
Dimethyl disulphide	300	1.93	3.91	2.25	2.60
	380	1.93	3.86	2.24	2.54
Diethyl disulphide	300	2.23	4.29	2.54	2.83
	380	2.23	4.24	2.53	2.78
Dipropyl disulphide	300	2.47	4.50	2.77	2.98
	380	2.47	4.46	2.76	2.93

approximated value of 2.5×10^{-9} cm^3/s for dimethyl sulphide and 2.6×10^{-9} cm^3/s for dimethyl disulphide. In fact, they did not know the values of α and μ_D for those compounds and assumed $\alpha = 7$, $\mu_D = 1.5$ for dimethyl sulphide and $\alpha = 10$, $\mu_D = 1.5$ for dimethyl disulphide. While the former are close to our calculations, the latter are quite different. Zhao and Zhang [15] used ADO theory to determine collision rate coefficients for dimethyl sulphide. Since they do not explicitly state which T and KE_{cm} they were using, we assumed thermal conditions at 300 K and noted that the k_{ado} we estimated from these values is compatible with the 1.53×10^{-9} cm^3/s they report.

We already pointed out that under PTR-MS standard conditions, ion-neutral molecule reactions proceed with energies larger than thermal energy. This leads to a non-negligible decrease in the reaction rate coefficient as compared to thermal conditions. Let us consider for example dimethyl sulphide. The thermal k_{cap} at $T = 300$ K is 2.60×10^{-9} cm^3/s. If we now increase the primary ion drift velocity to 930 m/s and keep $T = 300$ K, using the parameterised trajectory calculations in Eq. (8), we get a significant drop in the rate coefficient to 2.18×10^{-9} cm^3/s. In Table 3 we report a full list of reaction rate coefficients at standard PTR-MS conditions, namely $T = 380$ K, $v = 930$ m/s. Values at $T = 300$ K, $v = 930$ m/s are also reported. The table compares the results obtained using the different theories. Su's parameterised kinetic energy dependence of ion-neutral molecule reaction rate coefficients $k_{cap}(T,KE_{cm})$ [40] probably provides the most accurate results, since the kinetic energy and temperature dependence have been explicitly considered. To the best of our knowledge, no literature data are available in this case. As already mentioned, $k_{cap}(T,KE_{cm})$ has been parameterised by Su within a reported error of 5%. Moreover, a 3% uncertainty in the quantum chemical results for both the polarisability and the dipole moment increases the error on $k_{cap}(T,KE_{cm})$ by about another 1–2%. For comparison, we report reaction rate coefficients calculated with the parameterised trajectory formulation of Su and Chesnavich [37], using an effective temperature T_{eff}, as defined in Eq. (7), to account for the increased translational energy of the incident ion with respect to thermal collisions. Values from Langevin and locked dipole theory are also listed as approximate lower and upper limits, respectively. Results from ADO theory are not presented in the list since no parameterizations are available in the literature for the (effective) used temperature.

Future studies on sulphur compounds employing PTR-MS techniques may be facilitated by the now readily available $k_{cap}(T,KE_{cm})$ reported in Table 3. Depending on the experimental set-ups, the drift tube temperature and the primary ion velocity may differ from the standard values we considered. It is apparent from Table 3 that at a drift tube temperature of 380 K variations by about 10 K do not significantly affect the reaction rate coefficients. It can be shown that a 5% increase or decrease from 930 m/s of the ion drift velocity leads to approximately a 1% change in the rate coefficient. In any case, since the theoretical values of polarisability and dipole moment are now known, the proper reaction rate coefficients may be calculated by means of the parameterised trajectory calculations from Su [40]. Absolute concentration determination employing the calculated reaction rate coefficients implies that the product ions do not undergo fragmentation or that the branching ratios are known. For instance, literature indicates that fragmentation is not present in the case of dimethyl sulphide in both SIFT [44] and PTR-MS conditions [20]. For dimethyl disulphide, SIFT data indicate no fragmentation while Aprea et al. [20] measured in PTR-MS conditions a fragment at $m/z = 79$ (14% of the base peak). This further points out the differences between SIFT and PTR-MS applications.

4. Conclusions

Computational chemistry methods are used to predict polarisabilities and dipole moments of selected sulphur VOCs. Our results are compatible with literature data, where available. Based on these results we determined thermal rate coefficients of proton transfer reactions at 300 K between H_3O^+ ions and sulphur compounds using both ADO theory and parameterised trajectory calculations. Good agreement is found upon comparison with both experimental and theoretical literature data. In the case of diethyl sulphide and diethyl disulphide, no available data were found in the literature. A detailed description of the effective temperature used in PTR-MS is given and proton transfer rate coefficients under the conditions of modern PTR-MS instrument were determined. We estimated the reaction rate coefficients between H_3O^+ and these sulphur compounds at standard PTR-MS working conditions and find values about 20% smaller than the thermal reaction rate coefficients, due to the significant role played by the non-negligible drift velocity of the primary ion H_3O^+. On the other hand, variations of instrumental parameters in standard applications of PTR-MS do not strongly affect reaction rate coefficients and lead only to changes up to a few percents.

The determination of absolute VOC concentrations in PTR-MS laboratory studies involving sulphur VOCs will be facilitated by the newly available theoretical reaction rate coefficients. Moreover, the theoretical results of the present work could become a benchmark for future experimental studies on this important class of compounds.

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