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Theoretical chemical ionization rate constants of the concurrent reactions of hydronium ions (H_3O^+) and oxygen ions (O_2^+) with selected organic iodides

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Abstract

Short chain volatile iodinated organic compounds (VIOCs) are of great importance in many fields that include atmospheric chemistry, agriculture and environmental chemistry related to nuclear power plant safety. Proton-transfer-reaction mass spectrometry (PTR-MS) allows for fast, sensitive and on-line quantification of VIOCs if the chemical ionization (CI) reaction rate coefficients are known. In this work, the theoretical CI rate coefficients for the reactions of hydronium ions (H_3O^+) and oxygen ions (O_2^+) with selected atmospherically important short chain VIOCs are determined. The neutral CH_3I, CH_2I_2, C_2H_5I, iso-C_3H_7I, n-C_3H_7I, n-C_4H_9I, 2-C_4H_9I, n-$C_5H_{11}I$, 2-$C_5H_{11}I$, 3-$C_5H_{11}I$ have been chosen because these compounds are of atmospheric and environmental importance in the field of safety of nuclear plant reactors. Theoretical ion-molecule collision rate coefficients were determined using the Su and Chesnavich theory based on parametrized trajectory calculations. The proton affinity, ionization energy, dipole moment and polarizability values of the neutral molecules were determined from density functional theory and coupled-cluster calculations. The newly calculated rate constants facilitate the use of the CI mass spectrometry in the atmospheric quantification of selected VIOCs.

1 Introduction

In conjunction with their atmospheric chemistry importance that includes oxidizing capacity of the troposphere [4], atmospheric new particle formation and the tropospheric [10, 26] and stratospheric [33] ozone depletion potentials, volatile iodinated organic compounds (VIOCs) are now understood to play a significant role in the environmental

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chemistry safety field of nuclear power plant reactors. That is, following the three infamous major nuclear power plant accidents that include Three Mile Island (U.S.A.) [9], Chernobyl (Ukraine) [28] or Fukushima (Japan) [18], the scientific community has come to understand that many different VIOCs are formed within the reactor containment building during such an accident [15, 3]. These VIOCs may then be released into the outside environment if the reactor building containment wall is breached. Consequently, detailed characterization of these VIOCs' physical and chemical properties are needed to better understand chemical and physical processes responsible for the atmospheric formation of different fission products to better apply and execute appropriate mitigation strategies to protect the public.

Two prevalent analytical techniques used to detect and quantify atmospheric VIOCs include gas phase chromatography (GC) coupled with a mass spectrometer (MS) or an electron capture detector (ECD). Two more recent atmospheric field measurement techniques of atomic iodine, iodine oxides, short chain alkyl iodides and total photolabile VIOCs include long-path differential optical absorption spectroscopy (DOAS) [31] and a vacuum UV resonant fluorescence (RF) spectroscopy [2]. While GC-ECD and GC-MS are two very sensitive quantitative techniques used to detect gas phase alkyl iodides in laboratory settings and field environments, they may not offer the necessary time resolution and response time that is needed to measure fast changing atmospheric concentration profiles of VIOCs. The two optical DOAS and RF techniques are fast and sensitive, but are not selective enough and do not allow for quantification of specific VIOCs within a complex atmospheric matrix. On the other hand, the chemical ionization mass spectrometric (CIMS) technique has the potential for fast, selective, sensitive and on-line measurements of given VIOCs when continuous qualitative or quantitative information of rapid changes in the gas phase concentration of these VIOCs are needed.

The proton-transfer-reaction mass spectrometer (PTR-MS) is a form of CIMS that uses chemical ionization (CI) [13] within a flow-drift-tube [25] connected in series to a mass analyzer. Here, two common CI reagents include hydronium (H_3O^+) and molecular oxygen (O_2^+) ions. However, the proton transfer from the H_3O^+ ion to the reactant molecule within the drift-tube of the PTR-MS can only be applied to gas-phase compounds with proton affinities (PA) higher than that of water, $PA(H_2O) = 691.0 \pm 3$ kJ.mol^{-1} [17, 21]. Further, the given proton transfer reaction is observed to be efficient if the difference in PA is larger than ~ 35 kJ mol^{-1}.[5] While H_3O^+ ions are good proton sources, O_2^+ ions are often used as an alternative CI reagent in PTR-MS. Contrary to H_3O^+, which is a soft ionizer, the O_2^+ ion appears to be a more aggressive CI reagent and the resulting CI "fingerprint" of the given molecule results in a more fragmented mass spectrum, albeit the mother ion may often be clearly identified and may, as a result, be quantified. Similar to the sitation listed above for the proton transfer reaction between the hydronium ion and the gas-phase reactant molecule, the O_2^+ electron exchange reaction can be applied only for exothermic reactions where the ionization energy (IE) of the gas-phase reactant molecule is lower than that of molecular oxygen, $IE(O_2) = 12.0697 \pm 0.0002$ eV.[21]

While the gas phase thermochemistry of methyl iodide (CH_3I) and iodoethane (C_2H_5I) is well known, proton affinity values of higher organic iodides, namely CH_2I_2, iso-C_3H_7I, n-C_3H_7I, n-C_4H_9I, 2-C_4H_9I and n-$C_5H_{11}I$ remain scant at best. The same may be said

concerning the dipole moment and polarizability data. That is, for the majority of the short chain organic iodides listed above, the thermochemistry, dipole moment and polarizability data is limited or nonexistent. This is unfortunate since a detailed comparison of analytical data using different analytical techniques is often needed to lower the incertitude in the reported values so that the accuracy of accepted values is not brought into question. Moreover, the accuracy of the accepted polarizability and dipole moment values is of central importance since these values are used in the theoretical calculations of the collision rate coefficients that are, in turn, used in PTR-MS to calculate atmospheric mixing ratios of gas-phase pollutants.

In this work, the theoretical CI rate coefficients of the concurrent reactions of hydronium ions (H_3O^+) and oxygen ions (O_2^+) with CH_3I, CH_2I_2, C_2H_5I, iso-C_3H_7I, n-C_3H_7I, n-C_4H_9I, 2-C_4H_9I, n-$C_5H_{11}I$, 2-$C_5H_{11}I$, 3-$C_5H_{11}I$ are determined. The listed neutral short chain VIOCs have been chosen because these compounds are of atmospheric and environmental importance in the field of nuclear energy and nuclear power plant safety. To the best of our knowledge, there are no thermochemical data and no rate coefficients listed in the literature for the proton transfer reaction and the electron exchange reaction between H_3O^+ ions and O_2^+ ions, respectively, and CH_2I_2, iso-C_3H_7I, n-C_3H_7I, n-C_4H_9I, 2-C_4H_9I, n-$C_5H_{11}I$, 2-$C_5H_{11}I$ and 3-$C_5H_{11}I$. As a result, proton affinity, ionization energy, dipole moment, polarizability and the rate constant values of the concurrent reactions of hydronium ions (H_3O^+) and oxygen ions (O_2^+) with selected organic iodides have been determined theoretically. Theoretical ion-molecule collision rates were determined using the Su and Chesnavich theory based on parametrized trajectory calculations. It is important to well determine the proton affinity and ionization energy of the given organic iodide because these values will shed light on the exothermicity of the given proton transfer or electron exchange reaction. Further, the dipole moment and polarizability values are needed because they are used to calculate the given theoretical rate coefficients for the proton transfer or electron exchange reactions. As a result, proton affinities, ionization energies, dipole moments and polarizabilities were determined from density functional theory (DFT) and coupled-cluster single, double and perturbative triple excitations (CCSD(T)) calculations. The newly calculated rate coeffficients facilitate the use of the CI mass spectrometry in the atmospheric quantification of selected VIOCs without prior CIMS instrument calibration.

2   Theoretical approaches

Lindinger and coworkers (1998) [22] have shown that the gas phase VIOC mixing ratios may be determined using the following general equation:

$$[RI]_{cm^{-3}} = \frac{1}{kt} \cdot \frac{[RIH]^+}{[Reagent]^+} \cdot \frac{Tr_{[Reagent]^+}}{Tr_{[RIH]^+}} \tag{1}$$

where, $[RIH]^+$ and $[Reagent]^+$ are total ion signal count rates of all the product ions and the H_3O^+ reagent ion, respectively, k is the rate coefficient of the proton transfer reaction between the H_3O^+ reagent ion and the given VIOC and t is the reaction time of the ion within the drift tube.[7] It is assumed that the observed ion count rates are linearly

proportional to the respective number concentrations in the drift tube.[11] The reaction time t is calculated using given instrumental parameters (or constant factors) that include the drift tube length, ion mobility, reduced mobility, electric potential applied to the drift tube (U_drift) and drift tube temperature (T_drift) and pressure (p_drift). If hydronium H_3O^+ ions are used as CI reagent ions, the equation (1) may be rewritten by including the given instrument constant factors listed above to obtain the following equation (2):

$$[RI]_\text{ppbV} = \frac{10^9}{k} \cdot \frac{V_\text{m} \cdot \mu_0 \cdot U_\text{drift}}{N_A \cdot l^2} \cdot \frac{T_\text{drift}^2}{T_0^2} \cdot \frac{p_0^2}{p_\text{drift}^2} \cdot \frac{[RIH]^+}{[H_3O]^+} \cdot \frac{Tr_{[H_3O]^+}}{Tr_{[RIH]^+}} \tag{2}$$

or

$$[RI]_\text{ppbV} = 1.657 \times 10^{-11} \cdot \frac{U_\text{drift} \cdot T_\text{drift}^2}{k \cdot p_\text{drift}^2} \cdot \frac{[RIH]^+}{[H_3O]^+} \cdot \frac{Tr_{[H_3O]^+}}{Tr_{[RIH]^+}} \tag{3}$$

where $k(\text{cm}^3\text{s}^{-1})$ is the ion-molecule rate coefficient, $V_\text{m} = 22400\,\text{cm}^3\text{mol}^{-1}$ is the molar volume, $\mu_0 = 2.8\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ is the reduced mobility, $p_0 = 1013.25\,\text{mbar}$ is the standard pressure, $p_\text{drift}(\text{mbar})$ is the pressure in the drift tube, $T_0 = 273.15\text{K}$, $l = 9.3\,\text{cm}$ is the drift-tube length, $N_A(\text{mol}^{-1})$ is the Avogadro number and $Tr_{[H_3O]^+}$ and $Tr_{[CH_3IH]^+}$ are the transmission efficiencies for H_3O^+ and $[CH_3IH]^+$ ions, respectively. The transmission efficiency values are mostly mass dependent and range between 0 and 1. More precisely, to correct mass dependence losses of the selected ions between the drift tube and the mass analyzer, the detected ion count rates are normalized by their corresponding transmission factors.[11] If the rate coeffficient k of the proton transfer reaction between the H_3O^+ ion and the given RI is known, the gas phase mixing ratio of the VIOC of interest may be determined using the PTR-MS technique without prior calibration by simply using the MS signal ion counts and given instrument operating parameters listed above.

Similar to the situation described above and using O_2^+ as the CI reagent, the organic iodide gas phase concentration may be calculated using the following equation (4):

$$[RI]_\text{ppbV} = 1.657 \times 10^{-11} \cdot \frac{U_\text{drift} \cdot T_\text{drift}^2}{k \cdot p_\text{drift}^2} \cdot \frac{[RI]^+}{[O_2]^+} \cdot \frac{Tr_{O_2^+}}{Tr_{RI^+}} \tag{4}$$

where $Tr_{O_2^+}$ and Tr_{RI^+} are the transmission efficiencies for O_2^+ and organic iodide ions, respectively. Similar to the situation described above for the ion-molecule reaction between the hydronium ion and a reactant molecule, if the rate coeffficients k for the electron exchange reaction between the O_2^+ ion and the given RI is known, the gas phase mixing ratio of the VIOC of interest may be determined using the PTR-MS technique without prior calibration by simply using MS signal ion counts and given instrument operating parameters as mentioned before.

2.1   Theoretical determination of k

Historically, three prevailing mathematical approaches used to determine the collision rate coeffficients between a given reagent ion and a neutral reactant molecule in PTR-

MS include (1) the Langevin theory [19], (2) the average-dipole-orientation (ADO) theory [39, 40] and (3) the Su and Chesnavich parametrized trajectory calculations [42, 37, 36].

The Langevin collision rate coeffficient k_{L} [19] that is based on the Langevin theoretical approach [19] gives only a good initial value for the reaction rate coeffficient between the given CI reagent and the neutral reactant molecule in the high temperature limit [7] because it assumes that the neutral reactant molecule has no permanent dipole and that the interactions proceed through an induced dipole. Consequently, the Langevin theory alone cannot be applied to polar molecules studied in this work.

A somewhat better approximation of the rate coefficient for the concurrent reactions between the O_2^+ reagent ion or the H_3O^+ reagent ion and the polar organic iodide neutral molecule that has been used until fairly recently is the average-dipole-orientation (ADO) theory.[39, 40] That is, contrary to k_{L}, the k_{ADO} rate coeffficient based on the ADO theory [39, 40] accounts for a permanent dipole in the reactant molecule. It has been shown that the ADO collision rate coeffficient values for the reaction between the reagent ion and the neutral molecule compare within 10 to 20% of the experimentally determined ones, k_{exp}.[7, 39, 24]

Today, the theoretical approach most widely used to determine the ion-polar molecule rate coeffficients is based on the extensive parametrized trajectory calculations carried out by Su, Chesnavich and Bowers.[42, 37, 36] In their work, Su (1982, 1994), and Chesnavich (1980) [42, 38, 8] showed that k_{CAP} can be parametrized using polarizability α, permanent dipole moment μ_{D}, and the center-of-mass kinetic energy KE_{cm} values as shown in the following equation [32]:

$$k_{\text{CAP}}\left(T, KE_{\text{cm}}\right) = k_{\text{L}} K_{\text{CAP}}\left(\tau, \varepsilon\right) \tag{5}$$

where k_{CAP} is the reagent ion - polar molecule collision rate coefficient, K_{CAP} is the parametrized locking coefficient, and k_{L} is the Langevin collision rate coefficient. In equation (5) above,

$$k_{\text{L}} = q\sqrt{\frac{\pi\alpha}{\mu_m \varepsilon_0}} \tag{6}$$

where α is the polarizability of the neutral molecule, q is the ion charge, ε_0 is the permittivity of the free space, μ_m is the reduced mass of the colliding partners (here, O_2^+ or H_3O^+ and organic iodide).[19]

Also, in the equation 5 above,

$$K_{\text{CAP}}\left(\tau, \varepsilon\right) = 1 + c_1 \cdot \tau^{0.4} \cdot \varepsilon^2 \cdot S + c_2 \cdot (1 - S) \cdot \sin[c_3 \{c_4 + \ln\left(\tau\right)\}] \cdot \tau^{0.6} \cdot \sqrt{\varepsilon - 0.5} \tag{7}$$

In the equation (7) above, $c_1 = 0.727143$, $c_2 = 3.71823$, $c_3 = 0.586920$, $c_4 = 4.97894$.[32] Also, the parameter $\tau = \frac{\mu_D}{\sqrt{\alpha T}}$ and the parameter $\varepsilon = \frac{\mu_D}{\sqrt{\alpha \cdot KE_{\text{cm}}}}$. The center-of-mass kinetic energy KE_{cm} used to obtain ε is calculated as shown in the following equation [32]:

$$KE_{\text{cm}} = \frac{3}{2} \cdot k_{\text{B}} \cdot T + \left(\frac{M_{\text{R}}}{M_{\text{R}} + M_{\text{ion}}}\right) \cdot \frac{1}{2} \cdot (M_{\text{ion}} + M_{\text{buffer}}) \cdot v_{\text{d}}^2 \tag{8}$$

where M_{buffer} is the mass of the buffer gas (here, nitrogen + oxygen), M_{ion} is the mass of the reagent ion (here, O_2^+ or H_3O^+), M_R is the mass of the neutral reactant molecule (given organic iodide) and v_d=930 m $\cdot$ s^{-1} and is the drift velocity of the ion within the drift tube of the PTR-MS. In equation (7) above, $S = e^{[-2(\varepsilon-1.5)]}$ if $\varepsilon > 1.5$ or $S = 1$ if $\varepsilon \leq 1.5$.

Proton affinity, ionization energy and geometry optimization structure calculations of selected organic iodides that were used to calculate the k_{CAP} values were determined using quantum chemical methods as described below.

2.2 Thermochemistry and electronic structure calculations

Density functional theory (DFT) calculations to investigate the electronic structure of neutral compounds (and their protonated or ionized counterparts) were performed using Quadruple-Zeta-Valence basis set + Polarization + Diffuse basis functions (def2-QZVPD) at the Becke-Lee-Yang-Parr three-parameter functional (B3LYP) level of theory. The B3LYP functional is a hybrid functional mostly used to study gas phase systems. The def2-QZVPD basis set was chosen because it contains polarization and diffuse functions that are important in order to accurately calculate polarizabilities. For iodine, an effective core potential (ECP) was used along with the def2-QZVPD basis set. The ECP allows to reduce the number of electrons to be treated explicitly[30] : in this work, the inner 28 electrons of iodine ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$) are replaced by an effective potential and the 25 other electrons are explicitly taken into account in the electronic structure calculations. This allowed to reduce the computation time without sacrificing accuracy. The geometries of all compounds in this study have been optimized and their ground state minima have been properly characterized by harmonic vibrational frequency calculations. Dipole moments and polarizabilities were determined from these geometries, as well as proton affinities and vertical ionization energies including zero point energy (ZPE) corrections. All calculations were performed using the Turbomole [14, 1] software.

3 Results and discussion

The theoretical rate coeffficient calculations for the ion-molecule reactions between the given CI reagent and the selected neutral organic iodide molecule were calculated using the capture rate coefficient k_{CAP} [42, 37, 36] trajectory calculations. As shown in equations (5) - (8) , the calculated k_{CAP} values are based on given constant parameters and the electronic structure of the given organic iodide, namely its polarizability and the dipole moment values. While the electronic structure information for CH_3I is available in the NIST database [16], to the best of our knowledge the geometries of neutral CH_2I_2, iso-C_3H_7I, n-C_3H_7I, n-C_4H_9I, 2-C_4H_9I, n-$C_5H_{11}I$, 2-$C_5H_{11}I$ and 3-$C_5H_{11}I$ molecules are not available in the literature. Further, the available literature data on the electronic structure and thermochemistry of C_2H_5I is very limited. As a result, the def2-QZVPD basis set at the B3LYP level of theory was used to calculate the geometries of the neutral organic iodide molecules listed above. This level of theory was employed because it

gave good accord with the quantum chemical calculations obtained in the literature for similar molecules, namely CH_3I, C_2H_5I and CH_3OH. Moreover, benchmark calculations were performed at the CCSD(T) level for the three smallest iodide molecules and allowed us to confirm the validity of the DFT calculations. The obtained theoretical results for polarizabilities and dipole moments were then used to calculate the reagent ion - polar molecule collision rate coefficients (k_{CAP}). The list of literature and calculated polarizability, dipole moment, proton affinity and electronegativity values for selected organic iodides are shown in Table 1. Theoretical k_{CAP} values for the proton transfer reaction between the given organic iodide and the H_3O^+ reagent ion are shown in Table 2. Theoretical k_{CAP} values obtained in this work for the electron exchange reaction between the given organic iodide and the O_2^+ reagent ion are shown in Table 3.

Table 1: Theoretical and referenced dipole moment (μ), polarizability (α), proton affinity (PA) and ionization energy (eV) values obtained in this work using the def2-QZVPD basis set at the B3LYP level of theory. Literature data (where available) are listed in brackets.

RI	μ_D (Debye)	α (Å^3)	PA (kJ mol^{-1})	IE (eV)
CH_3OH	1.65 [1.70[†], 1.66[‡]]	3.21 [3.21[†], 2.67[‡]]	748.0 [754.3[†]]	10.51 [10.84[†]]
CH_3I	1.67 [1.620[†]]	7.52 [7.33[†], 7.22[§]]	694.4 [691.7[†], 690.8[§]]	9.54 [9.54[†],9.72[§]]
CH_2I_2	1.12	12.9 [12.3[§]]	691.8 [680.5[§]]	8.93 [9.46[†], 9.64[§]]
C_2H_5I	2.07	9.53 [9.05[§]]	716.7 [724.8[†], 706.2[§]]	9.35 [9.35[†], 9.57[§]]
iso-C_3H_7I	2.31	11.5	742.4	9.12 [9.19[†]]
n-C_3H_7I	2.14	11.3	727.0	9.17 [9.26[†]]
n-C_4H_9I	2.12	13.0	727.5	9.10 [9.23[†]]
2-C_4H_9I	2.32	13.2	751.0	9.00 [9.10[†]]
n-$C_5H_{11}I$	2.38	15.3	736.6	9.01 [9.20[†]]
2-$C_5H_{11}I$	2.53	15.3	757.3	8.95
3-$C_5H_{11}I$	2.44	15.1	763.6	8.90

[†] Electronic structure and thermochemistry data obtained from NIST [16].
[‡] Electronic structure data obtained by Zhao and Zhang (2004) [44] and were determined from frequency calculations at the B3LYP/6-31G(d,p) level of theory.
[§] This work : CCSD(T) level, with the de2-QZVP basis for C and H, def2-QZVPPD basis for I. Values are corrected with B3LYP ZPE.

To check the reliability and validity of our work, the calculated molecular structure, thermochemistry and rate coefficeint values for methanol, methyl iodide and iodoethane were compared with the available literature data.

As shown in Table 1, the NIST dipole moment (μ_D = 1.70 Debye [16]) and the NIST polarizability (α = 3.21 Å^3 [16]) values for methanol compare very well with the calculated values obtained in this work (μ_D = 1.65 Debye and α = 3.21 Å^3). Further, the proton affinity (748.0 kJ mol^{-1}) and ionization energy (10.51 eV) values for methanol calculated in this work compare very well the NIST database values (PA = 754.3 kJ mol^{-1} and IE = 10.84 eV) [16].

As may be seen in Table 2, the proton transfer reaction theoretical rate coefficient calculated using NIST electronic structure information for CH_3OH (k_{CAP} = 2.59×10^{-9} cm^{3}s^{-1})

Table 2: Reference experimental and theoretical K_{CAP} and k_{CAP} values obtained in this work for the proton transfer reaction between the given RI and the H_3O^+ reagent ion. For comparison, the available literature data are listed in brackets.

RI	K_{CAP} $(10^{-9}cm^3s^{-1})$	k_{CAP} $(10^{-9}cm^3s^{-1})$	k_{exp} $(10^{-9}cm^3s^{-1})$
CH_3OH	2.06 [2.13[†]]	2.50 [2.59[†], 2.7[‡]]	[3.8[§], 2[♯], 2.7[∥], 2.1[♭], 2.8[&]]
CH_3I	1.29 [1.26[†]]	2.02 [1.95[†], 2.5[$]]	[1.2[$]]
CH_2I_2	1.04	2.08	
C_2H_5I	1.10	2.67 [2.9[$]]	[2.5[$]]
iso-C_3H_7I	1.48	2.58	
n-C_3H_7I	1.30	2.50	
n-C_4H_9I	1.23	2.58	
2-C_4H_9I	1.31	2.77	
n-$C_5H_{11}I$	1.26	0.82	
2-$C_5H_{11}I$	1.32	0.86	
3-$C_5H_{11}I$	1.30	0.84	

[†] Value calculated using NIST [16] electronic structure data (see Table 1).

[‡] Theoretical value obtained by Su and Chesnavich (1982) [42].

[§] Experimental value was taken from Lee at al. (1992) [20].

[♯] Experimental value was taken from Fehsenfeld et al. (1978) [12] and was determined using a flowing afterglow and flow drift reaction system.

[∥] Experimental value was taken from Spanel and Smith (1997) [34] and was determined using the selected ion flow tube (SIFT) technique.

[♭] Experimental value was taken from Španěl and Smith (1995) [43] and was determined using the selected ion flow tube (SIFT) technique.

[&] Experimental value was taken from Mackay et al (1979) [23] and was determined using the flowing afterglow technique.

[$] Theoretical and experimental values determined by Španěl and Smith (1999) [35]. The experimental value was determined using the SIFT technique and the theoretical value is based on the parametrized trajectory calculations [42].

compares well with the calculated rate coefficient that uses the dipole moment and polarizability values for methanol obtained in this work ($k_{CAP} = 2.50 \times 10^{-9}cm^3s^{-1}$). Similarly, as may be seen in Table 3, the electron exchange reaction theoretical rate coefficient calculated using NIST electronic structure information for CH_3OH ($k_{CAP} = 2.22 \times 10^{-9}$ cm^3s^{-1}) compares well with the calculated rate coefficient that uses the dipole moment and polarizability values for methanol obtained in this work ($k_{CAP} = 2.15 \times 10^{-9}cm^3s^{-1}$).

In a similar manner, the NIST value for dipole moment ($\mu_D = 1.62$ Debye [16]) and the NIST polarizability value ($\alpha = 7.33$ Å^3 [16]) for methyl iodide compare well the calculated values obtained in this work : $\mu_D = 1.696$ Debye and $\alpha = 7.52$ Å^3 (DFT) or 7.22 Å^3 (CCSD(T)).

As may be seen in Table 2, the proton transfer reaction theoretical rate coeffficients that are calculated using the NIST database electronic structure information for CH_3I

Table 3: Theoretical K_{CAP} and k_{CAP} values obtained in this work for the electron exchange reaction between the given RI and the O_2^+ reagent ion. For comparison, literature data (where available) are listed in brackets.

RI	K_{CAP} $(10^{-9} cm^3 s^{-1})$	k_{CAP} $(10^{-9} cm^3 s^{-1})$	k_{exp} $(10^{-9} cm^3 s^{-1})$
CH_3OH	2.05 [2.12[†]]	2.15 [2.22[†]]	
CH_3I	1.22 [1.19[†]]	1.54 [1.48[†], 2.0[$]]	[2.0[$], 1.72[◇]]
CH_2I_2	1.05	1.66	
C_2H_5I	1.05	2.03 [2.3[$]]	[2.3[$]]
iso-C_3H_7I	1.41	1.96	
n-C_3H_7I	1.23	1.88	
n-C_4H_9I	1.15	1.87	
2-C_4H_9I	1.23	2.01	
n-$C_5H_{11}I$	1.19	2.07	
2-$C_5H_{11}I$	1.24	2.16	
3-$C_5H_{11}I$	1.22	2.13	

[†] Theoretical rate constants calculations based on the electronic structure data obtained from NIST.[16]
[$] Theoretical and experimental values determined by Španěl and Smith (1999) [35].
[◇] Experimental rate constant determined by Strekowski and coworkers [29].

($k_{CAP} = 1.95 \times 10^{-9}$ cm^{3}s^{-1}) compares well with the calculated rate coefficient that uses the dipole moment and polarizability values for CH$_3$I obtained in this work ($k_{CAP} = 2.02 \times 10^{-9}$cm^{3}s^{-1}). Similarly, as may be seen in Table 3, the electron exchange reaction theoretical rate coeficient calculated using NIST electronic structure information for CH$_3$I ($k_{CAP} = 1.48 \times 10^{-9}$ cm^{3}s^{-1}) is in good agreement with the calculated rate coefficient that uses the dipole moment and polarizability values for CH$_3$I obtained in this work ($k_{CAP} = 1.54 \times 10^{-9}$cm^{3}s^{-1}).

Further, the proton affinity and ionization energy values of iodoethane (C$_2$H$_5$I) calculated in this work compare well with the available NIST literature values (see Table 1). Only one study reports on the theoretical and experimental rate coeffficients for the proton transfer reaction between the H$_3$O$^+$ reagent ion and the iodoethane neutral molecule and the electron transfer reaction between the O$_2^+$ molecular oxygen ion and C$_2$H$_5$I. As shown in Table 2 the proton transfer reaction theoretical rate coeffficient ($k_{CAP} = 2.67 \times 10^{-9}$ cm^3 s^{-1}) for the reaction H$_3$O$^+$ + C$_2$H$_5$I calculated using the dipole moment and polarizability obtained in this work compares well with the theoretical ($k_{CAP} = 2.9 \times 10^{-9}$ cm^3 s^{-1} [35]) and experimental ($k_{exp} = 2.5 \times 10^{-9}$ cm^3 s^{-1} [35]) rate coeffficient values obtained by Šaněl and Smith [35]. Similarly, the theoretical rate coeffficient ($k_{CAP} = 2.03 \times 10^{-9}$ cm^3 s^{-1}) for the electron exchange reaction O$_2^+$ + C$_2$H$_5$I calculated using the dipole moment and polarizability information obtained in this work compares well with the theoretical ($k_{CAP} = 2.3 \times 10^{-9}$ cm^3 s^{-1} [35]) and experimental ($k_{exp} = 2.3 \times 10^{-9}$ cm^3 s^{-1} [35]) rate coeffficient values obtained by Šaněl and Smith [35].

From the above discussion on the calculated rate coeffficients for the benchmark molecules (CH$_3$OH, CH$_3$I and CH$_2$I$_2$) with H$_3$O$^+$ and O$_2^+$ reagents, one can draw the following

conclusions : first, the k_{CAP} values agree within a $\approx 10\%$ error, which is in line of Su's estimation of the accuracy of capture models [41]. Second, the errors on the rate constants originating from a difference in the values of the molecular properties (dipole moments and polarizabilities) fall below ($\approx 5\%$) the above mentioned errors inherent of the models. For larger iodide molecules, one can expect the same trend.

The theoretical dipole moment, polarizability, proton affinity and ionization energy values for iso-C_3H_7I, n-C_3H_7I, n-C_4H_9I, 2-C_4H_9I and n-C_5H_{11} calculated in this work are listed in Table 1. The theoretical k_{CAP} values for the proton transfer reaction between the given organic iodide and the hydronium reagent ion obtained in this work are shown in Table 2 and the theoretical collision rate coefficeint values for the electron exchange reaction between the given RI molecule and the O_2^+ reagent ion are shown in Table 3.

All the proton affinities shown in Table 1 of the organic iodides that were studied in this work are greater than the PA of water. This is important since the PTR-MS technique is often used for sensitive detection and quantification of volatile organic compounds and it is usually applied to gas-phase compounds where the ion-molecule reaction between the CI reagent ion and the neutral molecule is exothermic. For example, in the case of a proton-transfer reaction between the H_3O^+ reagent ion and a neutral molecule, the PTR-MS may be applied only to gas-phase compounds with PA values higher than that of water, PA(H_2O) $= 691 \pm 3$ kJ mol^{-1} [17, 16]. Further, it has been argued that the proton-transfer reaction between the H_3O^+ ion and the analyte is efficient only if the difference in the proton affinity is greater than ~ 35 kJ mol^{-1} [5]. That is not to say that if ΔPA < 35 kJ mol^{-1}, PTR-MS may not be used to detect and quantify a given gas-phase compound. Two recent studies (among many others) show that PTR-MS may still be used to detect and quantify gas-phase species even if the reported CI reactions are inefficient and the experimental rate coeffficients are far below the collision rate (1.4×10^{-9} cm^{3}s^{-1}).[27, 6] With the exception of CH_3I, CH_2I_2 and C_2H_5I, ΔPA > 35 kJ mol^{-1} for all the other organic iodides listed in Table 1. This is important because it implies that the proton-transfer reaction experimental rate constant for the ion-molecule reaction in the PTR-MS will likely approach the theoretical value. As a result, the PTR-MS technique is potentially a very good analytical method of choice to measure and quantify rapid changes in gas-phase analyte concentrations without prior calibration using hydronium ions as a CI reagent.

All the ionization energy values listed in Table 1 are much less than the ionization energy of O_2^+ ion (IE= 12.0697 ± 0.0002 eV [21]). Similar to the situation described above, this is important since this implies that the electron exchange reactions between the O_2^+ reagent ions and the organic iodides listed in Table 1 are exothermic. Therefore, similar to the situation listed above for hydronium reagent ions, this invokes the PTR-MS technique as an ideal tool for online detection and quantification of relatively fast changing concentrations of given organic iodides in the atmosphere without prior calibration.

Given the exothermicity of the proton transfer reaction between the H_3O^+ and the given organic iodide and the electron exchange transfer reaction between the O_2^+ ion and the given organic iodide, the calculated rate coeffficient values obtained in this work may be used to calculate gas phase mixing ratios of the selected organic iodides. That is, all the theoretical rate constant values listed in Table 2 and 3 may be used in equation

(2) (proton transfer reaction) and equation (4) (electron exchange reaction) to calculate atmospheric concentrations of selected organic iodides as a function of given PTR-MS instrument parameters.

4 Concluding remarks and future work

The aim of the work presented here was to obtain theoretical ion-molecule rate coefffi-cients for selected organic iodides that are of interest in the atmospheric science community and in the nuclear industry safety field. The obtained theoretical rate coefffi-cients can be used in the PTR-MS or SIFT-MS quantitative analyses of the selected compound or a matrix of compounds without prior calibration. However, the calculated k_{CAP} values obtained in this work do not reflect an energy dependence of the collision rate coefficient. The actual rate coefficient for the ion-molecule reaction does, indeed, depend on the reagent ion drift velocity that will change with the experimental conditions within the drift tube that include the drift tube voltage and E/N ratio. Consequently, the obtained k_{CAP} rate coefffi-cients should be compared with the experimental values obtained under "real" conditions within the drift-tube of the PTR-MS. Clearly, more work is warranted.

Acknowledgement

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