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Experimental and theoretical study of the kinetic of proton transfer reaction by ion mobility spectrometry

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ABSTRACT

Rate constants of the proton transfer reactions $RH^+ + DMP \rightarrow R + DMP \cdot H^+$, where R was acetone (Ac), trimethyl amine (TMA) or H_2O and DMP was 2,4-dimethyl pyridine have been measured by ion mobility spectrometry (IMS). The Reactant R was injected into the ionization region of IMS to produce RH^+ while DMP was continuously delivered to the drift region to react with the RH^+ pulsed into the drift tube by a shutter grid. Since DMP.H⁺ was generated along the drift tube, a tail appeared in the IMS spectrum that contained kinetic information. To prevent proton-bound dimer formation, the reactions were carried out at elevated temperatures ($170-230 \circ C$). We measured rate constants of 1.17×10^{-9} , 0.90×10^{-9} and $0.68 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for proton transfer from H_3O^+ , Ac·H⁺ and TMA·H⁺ to DMP, respectively. The experimental rate constants were almost temperature independent, indicating that no activation energy was involved in those proton transfer reactions. The rate constants were also calculated by using average dipole orientation (ADO) theory at B3LYP and MP2 levels. The calculated values revealed acceptable agreement between the experimental and theoretical trends.

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21 Introduction

Proton transfer is one of the most important ion-molecule reactions which occur in atmosphere and bio-related environments
 [1,2]. It is also the main reaction in the ionization region of ion mobility spectrometry (IMS) as well as proton transfer reaction mass spectrometry (PTR-MS) [3].

$$_{27} \quad RH^+(g) + P(g) = PH^+(g) + R(g) \tag{1}$$

28 Thermodynamic and kinetics of such proton transfer reactions have been studied theoretically [4–6] and experimentally. The 29 experimental techniques include high pressure mass spectrometry 30 [7–9], ion trap mass spectrometry [10], time-of-flight (TOF) mass 31 spectrometry [11] and IMS [12,13]. Mass spectrometry techniques 32 give reliable results as the nature of the reactant (R) and product (P) 33 ions are known. However, the experiment needs to be done under 34 vacuum which is different from the real condition. Advantages of 35 IMS not only include its simplicity and low cost but also comprise 36 its capability to carry out the measurement in a more realistic con-37 dition in atmospheric pressure. Despite its simplicity, IMS has been 38

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http://dx.doi.org/10.1016/j.ijms.2014.04.011 1387-3806/© 2014 Published by Elsevier B.V. proved as a useful technique in kinetic and thermodynamic studies of ion-molecule reactions. Proton affinity of some chemicals and their corresponding equilibrium constants of the proton transfer reactions have already been determined by IMS [12,13]. Also, IMS has been used in study of electron capture reactions [14], proton transfer and proton-bound dimer formation reactions [15,16]. IMS can be used for kinetic study of both negative and positive charged ions. Sahlstrom et al. [17] determined the rate constants for the gas phase reaction of chloride ion with methyl bromide over the pressure range of 300–1100 Torr by IMS. They reported that the effect of pressure on the rate constants is negligible.

Kinetic studies of proton transfer with IMS and mass spectrometry often carried out on the proton transfer from H_3O^+ [5,18–22] so that the rate coefficients of proton transfer from H_3O^+ to many different classes of organic molecules are now available. In this work we applied the method presented in reference [15] to measure the rate constants of the proton transfer from species other than H_3O^+ , namely protonated acetone (Ac·H⁺), and protonated trimethyl amine (TMA·H⁺) by ion mobility spectrometry. Experimental measured rate constants were compared with those calculated from the theoretical methods of Langevin [23] and locked-dipole theory [24,25]. Polarizability and dipole moment of DMP were needed to use the Langevin and the locked-dipole methods. The values were calculated using quantum computational methods.

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Theory

Exothermic proton transfer reactions are faster than the neutral-neutral reactions [26], since long-range attractive forces of ion-molecule reactions increase the reaction cross-section beyond the maximum cross section of the hard sphere [3]. A number of theoretical methods have been proposed to estimate the rate con-60 stant of ion-molecule reactions. In case the proton transfer reaction 70 involves a non-polar neutral molecule, the Langevin theory could 71 be a proper method for calculating the rate constant, k_{I} [23]

$$k_L = q \sqrt{\frac{\pi\alpha}{\mu\varepsilon_o}} \tag{2}$$

where q is the ion charge, μ is the reduced mass of the system, α is 74 the polarizability of the neutral reactant, and ε_0 is the permittivity 75 of the free space. The only component in Eq. (2), which remains 76 to be computationally calculated, is α . Since, in derivation of Eq. 77 (2), the interaction between the positive charge of the protonated 78 molecule and the permanent electric dipole moment of the neutral 79 molecule is neglected, this equation is not valid for calculating the 80 rate constant of reactions involving polar neutrals. To add the effect 81 of the permanent electric dipole moment, Su and Bowers [24,25] 82 proposed a theoretical rate constant which is known as the average 83 dipole orientation (ADO) theory 84

$$k_{\rm ADO} = q \sqrt{\frac{\pi\alpha}{\mu\varepsilon_o}} + \frac{C\mu_D q}{\varepsilon_o} \sqrt{\frac{1}{2\pi\mu kT}}$$
(3)

where μ_D is the dipole moment of the neutral molecule and C is a 86 locking parameter that accounts for the average orientation of the 87 neutral molecule's dipole moment. If C = 1, Eq. (3) is equivalent to 88 the locked-dipole theory [24,25] and when C=0, it is equivalent to 89 the Langevin theory [23]. We used Eq. (3) at two extreme limits of 90 C=0 and C=1 to calculated the rate constant of Reaction 1. 91

Computational details 92

For calculating the rate constants, the polarizibility (α) and 93 dipole moment (μ_D) of DMP were needed. For this purpose, the 94 geometry of DMP was separately optimized at the B3LYP and MP2 95 levels of theory. The frequency calculations were also performed at 96 the same level of theory to obtain the nature of optimized geome-97 tries. Theoretical rate constants were separately calculated using 98 Eq. (3) and the calculated values of α and μ_D at the B3LYP/aug-cc-99 PVDZ and MP2/6-311++G(d,p) levels of theory. To compute proton 100 affinities and gas phase basicities, the neutral and protonated forms 101 of H₂O, acetone, trimethylamine and DMP were also optimized and 102 frequency calculations were then performed. Gaussian 09 quantum 103 chemistry package [27] was used in all calculations. 104

Experimental 105

Instrumentation and chemicals 106

The stand alone ion mobility spectrometer used in this work was 107 manufactured in our laboratory at Isfahan University of Technol-108 ogy [28]. The corona discharge ionization source and the drift tube 109 consisted of 4 and 11 aluminum rings, respectively which were sep-110 arated with a Bradbary-Nielson shutter grid. The whole assembly 111 made a total length of 15 cm and was mounted in a thermostated 112 oven with a temperature control up to $250 \,^{\circ}$ C within $\pm 2 \,^{\circ}$ C. The 113 shutter grid opening time was about 100 µs in 20 ms intervals. 114 Nitrogen (99.5%) was used as the drift gas after the removal of the 115 residual water and other contaminants with a 13× molecular sieve 116 117 (Fluka) trap. The flow rates of the drift and the carrier gas were typically 900 and, 500 mL/min, respectively. 118



Fig. 1. Concentration profiles of reactant (RH⁺) and proton acceptor (PH⁺) ions in the drift tube and at different evolution times.

Acetone, trimethyl amine (TMA) and 2,4-dimethyl pyridine (DMP) from Fluka were used without further purification. Experiments were performed at ambient pressure and a temperature range of 170–230 °C.

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The experimental method

The experimental method to measure the rate constant has been described in ref [15]. DMP as proton acceptor (P) was allowed to enter the drift tube. A package of protonated reactant ion, RH⁺ $(R = acetone, TMA \text{ or } H_2O)$ already formed in the ionization region is released from the shutter grid to react with the neutral DMP present in the drift region. RH⁺ ions transfer their proton to DMP while traveling along the drift tube. Consequently, the number density of RH⁺ decreased as it is consumed on its way to the detector. Consumption of the reactant ion, RH⁺ resulted in generation of the product ion, DMPH⁺ via the reaction $RH^+ + P \rightarrow R + PH^+$. The amount of generated PH⁺ in each part of the drift tube depends on the number density of RH⁺ in that part. Because of reaction, the amount of RH⁺ at the point near the shutter grid is larger than that close to the detector. Consequently, the amount of produced PH⁺ in the shutter grid side is larger than that in the detector side. The electric field, existing in the drift tube, causes all ions to move towards the collector. By the time when the first group of survived RH⁺ ions reach the collector, the first produced PH⁺, near the shutter grid, are on their midway to the detector. This is depicted in Fig. 1. The new PH⁺ ions travel with the same velocity as those PH⁺ ions formed in the ionization region, behind the shutter grid. The PH⁺ ions formed between the shutter grid and the collector arrive at a time between the two RH⁺ and PH⁺ peaks, depending on where the proton transfer took place in

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the tube. As the collector registers a mirror image of the distributed
ions in the drift tube, the described manifest appears as a tail on the
ion mobility spectrum starting from the RH⁺ peak, extending to the
PH⁺ peak. This is schematically illustrated in Fig. 1 and experimentally in Fig. 3. The rate constant of the proton transfer reaction can
then be derived from this tail [15].

¹⁵³ We have previously derived a mathematical expression for ¹⁵⁴ the formation of dimer in the drift region for the reaction ¹⁵⁵ $MH^+ + M \rightarrow MH^+M$ [15].

¹⁵⁶
$$[D]_t = (k[MH^+]_o[M]t_g) \exp\left(\frac{-k[M]t_M(t-t_D)}{t_M - t_D}\right)$$
 (4)

where D stands for the MH⁺M dimer. $[D]_t$ represents the distribu-157 tion of the dimer over drifting time. [MH⁺]₀ is the initial number 158 density of the monomer ions released from the shutter grid and 150 [M] is the stationary concentration of the sample M in the drift 160 region. t_M and t_D are the drift time for the monomer and dimer, 161 respectively. t_g is the width of the MH⁺ swarm passing through the 162 drift region, and t is the drift time. In Eq. (4), since the monomer 163 ions are converted to dimer ions, the coordinate t, starts from t_M , 164 and ends to t_D , i.e. a tail from the monomer peak to dimer peak. 165 Maximum intensity of the tail is $t = t_D$ where the exponential term 166 becomes unity. The rise time of such a function, taken by the signal 167 to change from 10% to 90% of maximum height, is 0.8 t_D . Thus, any 168 factor changing the drift times will affect the slope of the tail. 169

Eq. (4) can also be used for proton transfer between two species. If, the RH⁺ is produced from the primary reactant ion of H_3O^+ in the ionization region and then reacts with the acceptor in the drift region, i.e.

 $_{174}$ $H_3O^+ + R \rightarrow RH^+$ inthereactionregion

$_{175}$ RH⁺ + P \rightarrow PH⁺ inthedriftregion,

M and D in Eq. (4) should be replaced by RH⁺ and PH⁺, respectively, Eq. (4) may be simplified by taking logarithm from both sides
 and set all constants to C;

⁷⁹
$$\ln [PH^+]_t = C_{(t_{RH})} + \frac{k[P]t_{RH^+}}{t_{PH^+} - t_{RH^+}}t$$
 (5)

where $[PH^+]_t$ represents the signal intensity of the tail between the 180 RH^+ and PH^+ peaks at drift time *t*, *k* is the rate constant, [P] is the 181 concentration of the proton acceptor in the drift region and $t_{\rm RH}^+$ 182 and $t_{\rm PH}^+$ are the drift times of RH⁺ and PH⁺, respectively. $C_{(t_{\rm RH})}$ is a 183 184 constant which is a function of the reactant or the product ion drift times which are themselves dependent on the electric field and 185 186 temperature. Thus, at constant temperature and electric field, a plot of the logarithm of the ion current intensity versus the drift time of 187 the tail is expected to be a straight line with a slope proportional 188 to the rate constant, k. 189

The reactant R is not allowed to enter the drift tube, since it is prevented by the counter flowing drift gas. Hence, further reactions of species with R in the drift region rule out. However, other reactions may happen in the drift region. These include the proton bound dimer formation for P, i.e. formation of PH⁺P (Reaction 6) and proton transferring between product ion and its un-protonated form (Reaction 7).

$$PH^+ + P \to PH^+P \tag{6}$$

$$PH^+ + P \rightarrow P + PH^+$$
(7)

If the dimer is formed in the drift region, another tail should
 appear after the PH⁺ peak. This tail affects the first tail as dimer
 ions may be formed all the way in the drift region. Since a second
 rate constant will be involved, the situation becomes complicated.
 We are currently working on driving another expression to include



Fig. 2. IMS spectra of (a) reactant ions, (b) acetone at low concentration and (c) acetone at high concentration which quenches the reactant ion peaks.

such second consecutive reaction. For simplicity we chose a substance as the proton acceptor (DMP), and condition (temperature range of 170-230 °C) in which the dimer formation becomes negligible. This condition is practically achieved when no tail was observed after the PH⁺ peak. Reaction 7 would not disturb the tail since the proton transfer is very fast and any newly produced PH⁺ ion moves with the same velocity as the annihilated one.

Another reaction that may need to be considered is the reaction between the acceptor and water molecule presents in the drift region, i.e. $PH^+ + H_2O \rightarrow H_3O^+ + P$. If this happens, a tail resulting from the newly born H_3O^+ ions, starting from the H_3O^+ peak appears. Again to simplify the problem we chose a substance (DMP) with high proton affinity, that this reaction is negligible. Generally, an ideal condition is that a spectrum is observed with no tail before the RH⁺ peak or after the PH⁺ peak but a nice exponential curve tail in between.

As corona discharge ionization source is used, primary reactant ions other than H_3O^+ such as NO^+ and NH_4^+ also existed. However, these ions disappeared when reactant was added to the ionization region. This is clear from Fig. 2c.

Sample introduction and recording spectra

Since the purpose of this work is to measurement the rate coefficients of proton transfer from protonated species other than H_3O^+ by IMS, to assess and confirm the accuracy of our method, we chose TMA and acetone as an amine and a ketone, respectively. In addition, the species should be selected so that the reactant (RH⁺) and product (PH⁺) ion peaks are well separated to observe a clear tail in between. Furthermore, as discussed above, the reactant and product ion should fulfill the condition that dimer PH⁺P is not formed.

Pure acetone or TMA were continuously injected into the ionization region of IMS with a syringe pump (New Era Pump System Inc. USA). Direct infusion of excess amount of acetone or 227

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Fig. 3. IMS spectra of (a) DMP and (b) acetone (in high concentrations) injected into the ionization region; and (c) DMP introduced into the drift gas while acetone was injected into the ionization region.

237 TMA suppressed the reactant ion peaks ensuring that the proton transfer occurred exclusively from the protonated acetone or TMA 238 to DMP (Fig. 2c). 239

DMP was introduced by a second syringe pump (New Era Pump 240 System Inc. USA) into the drift gas and entered the drift tube from 241 the detector side, instead of a normal entrance form the ioniza-242 tion source. Transferring proton along the drift tube generated a 243 tail between IMS peaks of protonated acetone or TMA and DMP, 244 which was used to find the underlying kinetic data. A syringe was 245 filled with the DMP vapor from the liquid head space and the DMP 246 injection flow rate was finely adjusted $(30-60 \,\mu L \,min^{-1})$ to observe 247 a clear tail between the two peaks. The actual concentration was 248 determined from the DMP vapor pressure at standard conditions, 249 and the flow rates of the syringe pump and the drift gas. Stable 250 stationary condition was reached by direct infusion of the sample 251 for about 30 min prior to data acquisition. We used the averaged 252 spectra after two minutes of data acquisition for further analysis. 253

Results and discussions 254

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Experimental rate constants 255

Fig. 3 shows the ion mobility spectra of (a) DMP and (b) acetone 256 injected into the ionization region in high concentration and (c) 257 DMP introduced into the drift region while acetone was injected 258 into the ionization region. When DMP is introduced into the IMS cell, it entered into both drift and ionization region. 260

Ion mobility spectra were recorded at several drift fields (Fig. 4) 261 and various temperatures, while DMP was running into the drift 262 tube and acetone or TMA were continuously injected into the 263 ionization chamber. Fig. 4 shows typical examples of spectra for 264 acetone and DMP at given drift fields at 230 °C. The peak positions 265 vary with the drift field while the tail keeps its exponential shape 266 with increasing slope. This behavior is predicted by Eq. (4). Electric 267 268 field decreases the drift times, hence lowering the rise time and making the tail steeper. 269



Fig. 4. Ion mobility spectra of acetone and DMP for several drift fields while the DMP was introducing into the drift tube.



Fig. 5. Logarithm of the signal intensity of the tail between the protonated acetone peak and the DMP peak at various electric fields. Points are experimental data and solid lines are linear fitting.

Fig. 5 shows the logarithm of the tail intensity versus drift time at various electric fields. As Eq. (5) predicts, the logarithm of the tails versus the drift time are all linear with similar slopes, but different intercepts, $C_{(t_{RH})}$. Experimental data are shown as points while the solid lines are linear fitting results. Based on Eq. (5), the slopes are expected to be equal $k[P]t_{RH^+}/(t_{PH^+}-t_{RH^+})$.

Rate constants, determined at different drift fields, were in good agreement among themselves. This proved the independency of the rate constant to the drift field as expected from Eq. (5). An averaged value for the rate constant was therefore reported for each temperature. Table 1 summarizes the measured rate constants of proton transfer from protonated acetone, TMA and H₂O to DMP from the corresponding IMS spectra.

A fast ion-molecule reaction has a rate constant of $\sim 10^{-9}$ cm³ s⁻¹ or more [3]. Measured rate constants of the proton transfer from H₃O⁺, AcH⁺ and TMA·H⁺ to DMP indicate that these reactions are in fact fast ion-molecule reactions. Activation energy, E_a of the proton transfer can be determined from the Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT}$$

(8)

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Table 1

Experimental measured rate constants for proton transfer from H₃O⁺, AcH⁺ and 03 (TMA)H⁺ to DMP at given temperatures.

Temperature (°C)	Rate constant, k (cm ³ s ⁻¹)					
	H ₃ O ⁺ + DMP	AcH ⁺ + DMP	(TMA)H ⁺ + DMP			
170	1.10×10^{-9}	0.76×10^{-9}	0.65×10^{-9}			
180	$1.10 imes 10^{-9}$	$0.77 imes 10^{-9}$	$0.65 imes 10^{-9}$			
190	1.16×10^{-9}	$0.88 imes 10^{-9}$	$0.71 imes 10^{-9}$			
200	$1.17 imes 10^{-9}$	$0.90 imes 10^{-9}$	$0.68 imes 10^{-9}$			
210	1.19×10^{-9}	$0.85 imes 10^{-9}$	$0.67 imes 10^{-9}$			
220	$1.20 imes 10^{-9}$	$0.84 imes 10^{-9}$	$0.72 imes 10^{-9}$			
230	0.97×10^{-9}	0.79×10^{-9}	0.68×10^{-9}			



Fig. 6. Arrhenius plots of the proton transfer reaction between H_3O^+ , $Ac \cdot H^+$ or TMA·H⁺ and DMP.

The Arrhenius plots for the three proton transfer reactions from 290 H₃O⁺, Ac·H⁺ and TMA·H⁺ to DMP are illustrated in Fig. 6.

It is clear that the natural logarithm of the rate constant is invariant to the temperature. This implies that there is no activation energy for the corresponding proton transfer reactions, which agrees with the general understanding of the ion-molecule reactions [3].

Theoretical rate constants 297

Based on the experimental results which proved that the pro-298 ton transfer reactions are fast with no activation energy, the ADO 299 theory (Eq. (3)) may be used to calculate the rate constants. Polariz-300 ability (α) and electric dipole moment (μ_D) of DMP were calculated 301 302 using B3LYP and MP2 methods. Results are summarized in Table 2. Calculated values with different basis set produced comparable 303 results. 304

Rate constants were calculated using Eq. (3) and the computed α and μ_D presented in Table 2. Table 3 shows the proton transfer rate

Table 2

Calculated polarizability (α) and dipole moment (μ_D) for DMP using different computational methods.

Method	α (A ³)	μ_D (D)
B3LYP/6-31G(d)	11.042	2.221
B3LYP/6-311++G(2df,p)	13.287	2.404
B3LYP/aug-cc-PVDZ	13.751	2.393
MP2/6-311G(d,p)	11.731	2.403
MP2/6-311++G(d,p)	12.889	2.538

constants calculated by B3LYP and MP2 computational methods with aug-cc-PVDZ and 6-311++G(d,p) basis sets, respectively.

According to Eq. (3), the calculated rate constants from Langevin theory (C=0) are temperature independent while those obtained from the lock-dipole theory (C=1) slightly decrease with temperature. Furthermore, the calculated values are larger, when the interaction between the positive charge of the protonated molecules and the permanent electric dipole moment of DMP is fully considered (C=1) compared to neglecting the permanent electric dipole moment (C=0). In fact, the value of locking parameter should be chosen based on the condition (temperature) and dipole moment as well as the polarizability value of the neutral molecule $(\mu_D/\alpha^{1/2})$. Su and Bowers [29] published C values at different temperatures and $\mu_D/\alpha^{1/2}$ values. From the data presented in Table 2 the value for $\mu_D/\alpha^{1/2}$ is obtained to be in the range of 0.66–0.7. By using the data reported in ref. [29] the values of C in the temperature range of 170–230 °C are 0.175–0.165. Table 4 summarized the calculated rate constants using the ADO theory (Eq. (3)) with C = 0.17.

The theoretical and experimental values for rate constants are comparable with similar trends. Both two theoretical methods produced comparable data. Furthermore, both theoretical and experimental rate constants for the R+DMP reaction decreases in the order $H_3O^+ > AcH^+ > (TMA)H^+$ for R. However, the theoretical rate constants are generally bigger than the experimental ones. This discrepancy could be due to the hydration of protonated molecules which is neglected in the theoretical calculations. Hydration causes all ions to be bigger and heavier than their intrinsic size and mass, hence slower reaction and decreasing the rate constants, though we carried out the experiments in high temperature range (170-230 °C) to decrease the effect of hydration. Moreover, the rate constants were measured at atmospheric pressure, in the presence of carrier gas which may affect the experimental results. Nevertheless, the discrepancy is not very significant and can also be attributed to errors in the computational methods or the experimental set up.

Proton affinity

Proton affinity (PA) and gas phase basicity ($-\Delta G$ of protonation reaction) of H₂O, acetone, TMA and DMP, calculated at B3LYP level of theory with 6-311++G(2df,p) basis set are presented in Table 5.

Table 3

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Calculated proton transfer rate constants (10 ⁹ k/cm ³ s ⁻¹) from Eq. (3) for C = 0 and	C = 1 (locked dipole theory).
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T (°C)	B3LYP/au	B3LYP/aug-cc-PVDZ					MP2/6-311++G(d,p)					
$H_3O^+ + DMP$		MP	AcH ⁺ + DMP		(TMA)H ⁺ + DMP		H ₃ O ⁺ + DMP		AcH ⁺ + DMP		(TMA)H ⁺ + DMP	
	<i>C</i> = 0	<i>C</i> =1	<i>C</i> =0	C=1	<i>C</i> =0	C=1	<i>C</i> =0	C=1	C=0	C=1	<i>C</i> = 0	C = 1
170	2.16	6.65	1.41	4.33	1.40	4.31	2.09	6.86	1.36	4.47	1.35	4.44
180	2.16	6.61	1.41	4.30	1.40	4.28	2.09	6.81	1.36	4.43	1.35	4.41
190	2.16	6.56	1.41	4.27	1.40	4.25	2.09	6.75	1.36	4.40	1.35	4.38
200	2.16	6.51	1.41	4.24	1.40	4.22	2.09	6.71	1.36	4.37	1.35	4.35
210	2.16	6.46	1.41	4.21	1.40	4.19	2.09	6.66	1.36	4.34	1.35	4.31
220	2.16	6.42	1.41	4.18	1.40	4.16	2.09	6.61	1.36	4.31	1.35	4.28
230	2.16	6.38	1.41	4.15	1.40	4.13	2.09	6.57	1.36	4.28	1.35	4.25

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Table 4 The calculated rate constants from the average dipole orientation (ADO) theory (Eq. (3)) and considering locking parameter equals to 0.17 (C = 0.17).

<i>T</i> (°C)	B3LYP/aug-cc-PVE	DZ		MP2/6-311++G(d,p)		
	$H_3O^+ + DMP$	AcH ⁺ + DMP	(TMA)H ⁺ + DMP	$H_3O^+ + DMP$	AcH ⁺ + DMP	(TMA)H ⁺ + DMP
170	2.923	1.906	1.894	2.900	1.888	1.875
180	2.916	1.901	1.889	2.892	1.881	1.870
190	2.908	1.896	1.884	2.882	1.876	1.865
200	2.899	1.891	1.879	2.875	1.871	1.860
210	2.891	1.886	1.874	2.866	1.866	1.853
220	2.884	1.880	1.869	2.858	1.861	1.848
230	2.877	1.875	1.864	2.851	1.856	1.843

Table 5

The calculated proton affinity (PA) and gas phase basicity of H₂O, acetone, TMA and DMP by B3LYP/6-311++G(2df,p) method. Δ PA = PA(DMP) – PA (R).

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	Molecule	PA (kJ/mol)	Gas phase basicity (kJ/mol)	ΔPA
	H_2O	686.83	658.53	285.10
	Acetone	819.07	789.32	152.86
	TMA	942.06	913.49	29.87
	DMP	971.93	942.37	0.0

The right column of Table 5 shows the proton affinity difference (Δ PA) between the reactant (R) and DMP. Both proton affinity and gas phase basicity of DMP are larger than those of H₂O, acetone and TMA. This makes the proton transfer to DMP thermodynamically favorable. Furthermore, the observed trend in the proton affinity and Δ G values reveals the tendency of loosing proton in the order of H₃O⁺ > AcH⁺ > (TMA)H⁺, confirming the experimental results.

354 Conclusion

A simple and cost effective method was introduced to mea-355 sure proton transfer rate constant of protonated molecules other 356 than H_3O^+ , at atmospheric pressure by ion mobility spectrometry. 357 Measured rate constants were about 10^{-9} cm³ s⁻¹ which indicates 358 a fast reaction rate for the proton transfer. Arrhenius plot of the 359 reactions showed a zero activation energy for the correspond-360 ing proton transfer reactions. Based on the experimental results, 361 fast reaction with no activation energy, the average dipole ori-362 entation (ADO) theory seemed to be useful for calculating the 363 theoretical rate constants of the reactions. Theoretical results pre-364 dicted an increase in the rate constants of the proton transfer 365 from $H_3O^+ > AcH^+ > (TMA)H^+$ which was in good agreement with 366 the experimental results. Since, no activation energy is involved, 367 the increasing trend in the rate constants can be attributed to a 368 decreasing trend in the proton affinities of the neutral reactant 369 370 species H₂O < Ac < TMA. The small difference between the exper-371 imental and calculated rate constants was assumed to be due to the difference between experimental and theoretical conditions. 372 Hydration of the protonated molecules was also mentioned as a 373 possible source for such a discrepancy. Hydration slows down reac-374 tions due to imposing a steric hindrance to the reactants. However, 375 the rate constants determined by the proposed method are more 376 realistic and applicable to ion-molecule reactions happening in real 377 environment. 378

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