Proton transfer reaction rate constants between hydronium ion (H_3O^+) and volatile organic compounds

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Abstract

We report proton transfer reaction rate constants between the hydronium ion (H_3O^+) and selected atmospherically important volatile organic compounds (VOCs). The quantum chemical method was used to determine the structures of the organic species employing the density function theory-B3LYP. The ion–molecule reaction rates were determined using the average-dipole-orientation theory, along with the permanent dipole moment and polarizability of the organic species predicted from the quantum chemical calculations. The theoretical results are compared to available literature data of the permanent dipole moment, polarizability, and ion–molecule reaction rate. The newly calculated proton transfer rate constants facilitate the use of the proton transfer reaction mass spectrometry (PTR-MS) technique in applications of laboratory investigation of photochemical hydrocarbon oxidation reactions and field measurements of the abundance of VOCs.

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Keywords: Ion–molecule rate constants; Volatile organic compounds; Ambient air measurements; Tropospheric chemistry; Theoretical

1. Introduction

Volatile organic compounds (VOCs) play an important role in atmospheric chemistry (Seinfeld and Pandis, 1998). A major challenge in studying the hydrocarbon chemistry lies in the development of analytical instrumentation for detecting and quantifying the VOCs, their corresponding intermediate radicals and stable products under both laboratory and atmospheric conditions. Although various analytical methodologies have been developed for measurements of organic species (Guenther et al., 1995), the approach of proton transfer reaction mass spectrometry (PTR-MS) appears to offer the greatest advantage for detecting organic species for both field and laboratory applications (De Gouw et al., 2003; Zhao et al., 2004). For example, this method has been recently developed to measure atmospheric VOCs (Hansel et al., 1995; Lindinger et al., 1998; De Gouw et al., 2003). The PTR-MS method is based on proton transfer processes involving H_3O^+ ions, which do not react with any other neutral constitutes of clean air, but react with most VOCs in non-dissociative proton transfer reactions. With the exception of alkanes smaller than C5, most VOCs can be measured if their proton affinities are higher than that of water ($166.5\,kcal\,mol^{-1}$). It has been suggested that the PTR-MS technique allows for on-line measurements at levels as low as a few ppt (Hansel et al., 1995).

Within the drift tube of a PTR-MS, an organic gas, R, is ionized by undergoing a proton-transfer reaction with the hydronium ion (H_3O^+) as follows:

$$H_3O^+ + R \rightarrow RH^+ + H_2O. \tag{1}$$

Reaction (1) is exothermic and fast for the compounds that have a proton affinity (PA) higher than the PA of water. This includes most of the atmospheric anthropogenic and biogenic hydrocarbons and oxygenated

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VOCs (Lias et al., 1988). Proton-transfer reactions (1) between the H_3O^+ ions and the trace gases R take place and convert a small fraction of the reagent H_3O^+ ions into products RH^+ which are then detected by the MS system. The number concentration of product ions formed can be calculated using:

$$\Delta[RH^+] = -\Delta[H_3O^+] = k[H_3O^+]_t[R]\,\Delta t, \tag{2}$$

where k is the rate coefficients for the proton-transfer reaction (1) and Δt is the transient time for the reagent ions traversing the drift tube. If only a small fraction of H_3O^+ ions reacts (i.e., $\Delta[H_3O^+] \ll [H_3O^+]$), $[H_3O^+]_t$ can be assumed constant, and the number $\Delta[RH^+]$ of product ions formed is proportional to the neutral concentration [R],

$$\Delta[RH^+] \approx k[H_3O^+]_o[R]\Delta t. \tag{3}$$

If there is no mass-dependent proportionality in the MS detection efficiency, the densities of product ions $[RH^+]$ and the reagent ions $[H_3O^+]$ are proportional to their respective ion count signals measured by the mass spectrometer. It has been suggested that no change in detection efficiency was measured in the mass range of 19–250 Da (Lindinger et al., 1998). For the Δt term, the work by De Gouw et al. (2003) has shown that the reaction time can be calculated according to the ion drift velocity, which is excellent agreement with the measurement. Hence Eq. (3) allows for the calculation of gas phase concentrations without the necessity of calibration, if the proton transfer reaction rate constant is given. Our recent work has also demonstrated the application of the PTR-MS method in quantifying the product yields of hydrocarbon oxidation reactions (Zhao et al., 2004). This method allows product yield measurements without the necessity of calibration and hence is advantageous because of the general difficulty to obtain the authentic standards for products of many hydrocarbon reactions. Quantifying unidentified trace species is therefore possible, provided that the proton transfer rate constants for the reactant and product are known.

Hence the PTR-MS technique requires accurate knowledge of the ion–molecule reaction rate constants between H_3O^+ and the organic species, which can be determined according to experimental or theoretical procedures (Su and Chesnavich, 1982; Zhang and Lei, 2000). While investigation of ion–molecule reactions has been an area of intensive research (Harrison, 1992; Anicich, 1994), only limited results of proton transfer reactions relevant to atmospheric VOCs are presently available.

In this study, we present a study of ion–molecule reactions between the H_3O^+ and atmospherically important VOCs. We employed the quantum chemical method to determine the structures and the permanent dipole moment and polarizability of selected atmospherically important VOCs. The ion-molecule reaction rates were calculated using the average-dipole-orientation (ADO) theory. Our theoretical results are compared to available literature data of permanent dipole moment, polarizability, and ion–molecule reaction rate constants. The newly calculated proton transfer reaction rate constants are important in applying the PTR-MS technique for laboratory investigation of photochemical hydrocarbon oxidation reactions and field measurements of VOCs.

2. Methodology

The quantum chemical calculations were performed on an SGI Origin 3800 supercomputer using the Gaussian 98 software package. Recently, we have evaluated the quantum chemical theory which applies to organic species on the basis of computational accuracy and efficiency (Lei and Zhang, 2000; Lei et al., 2000; Suh et al., 2001, 2002, 2003; Zhang and Zhang, 2002; Zhang et al., 2002). For a set of organic species, we performed full geometry optimization and energy calculations using different basis sets and levels of electron correlation, and compared the results to limited available experimental data (Lei et al., 2000). The results indicated that electron correlation did not affect the geometries of the organic species appreciably. Better convergence behavior and considerably higher computational efficiency were achieved using the non-local gradient density functional (NLDFT) theory as the method of geometry and frequency calculations. It was also noticed that beyond the split valence polarized level of description there was little improvement in the molecular geometry when the size of the basis set was further increased (i.e., triple split, diffuse functions, expansion of the polarization portion of the basis sets, etc.). In the present study, geometry optimization of the organic species was executed using Becke's three parameter hybrid method employing the LYP correction function (B3LYP) in conjunction with the split valence polarized basis set 6-31G(d,p). Harmonic vibrational frequency calculations were performed using B3LYP/6-31G(d,p). The evaluation of the vibrational frequencies confirmed that all geometries obtained represented minima on the potential energy surfaces.

We calculated the ion–molecule reaction rate constants using three classic models of ion–molecule interactions involving polar molecules. The ADO theory predicts the ion–molecule collision rate constants determined by the expression (Su and Bowers, 1973a, b; Bass et al., 1975):

$$k_{ADO} = (2\pi q/\mu^{1/2})[\alpha^{1/2} + C\mu_D(2/\pi kT)^{1/2}], \tag{4}$$

where q is the charge of the ion, μ is the reduced mass of the reactants, α is the polarizability and μ_D the

permanent dipole moment of the neutral. C has been parameterized to have a value between 0 and 1, with the expression $C = f(\mu_D/\alpha^{1/2})$. Eq. (4) reduces to the locked-dipole (LD) limit, k_{LD}, when $C = 1$. The Langevin (L) expression, k_L, results when $C = 0$.

To determine the ion–molecule collision rate constant, we used the permanent dipole moment and polarizability of the organic species predicted from the quantum chemical calculations. The values of α and μ_D were determined at the B3LYP/6-31G(d,p) level of theory. Since the ion–molecule rate constant is related to the square root of the permanent dipole moment and polarizability, the uncertainty in the calculated rate constant due to uncertainties in the permanent dipole moment and polarizability is small. If we assume the uncertainty of $\pm 30\%$ for both quantities on the basis of comparisons between our calculated and previous experimental values, we estimated an uncertainty of less than $\pm 15\%$ in our calculated ion–molecule reaction rate constants.

3. Results and discussion

The majority of the initial structures of the molecules investigated in this study were taken from the NIST database (NIST, 2003). Geometry optimization was then performed at B3LYP/6-31G(d,p) level of theory based on the NIST initial structures. Some optimized geometries of organic molecules were obtained from our previous studies (Lei et al., 2000; Suh et al., 2002; Zhao et al., 2003). Frequency calculation was executed to confirm that all the optimized geometries were minima on the basis of zero negative frequency. The permanent dipole moment of the organics species was directly taken from the output files of the frequency calculations. The polarizability was averaged over the exact and approximate polarizability of their bonds, including three isentropic components.

The ion–molecule collision rate constant was determined from Eq. (4) using the polarizability and permanent dipole moment obtained from the quantum chemical calculations. Table 1 lists the ion–molecule collision rate constant between the H_3O^+ and the selected VOCs, along with their corresponding PA, polarizability and permanent dipole moment. The proton affinities of the VOCs were taken from the NIST database (NIST, 2003). The ion–molecule collision rate constants range from $(1–5) \times 10^{-9}\, cm^3\, s^{-1}$, depending on the individual proton transfer reaction of the organic compound. As reflected by Eq. (4), the collision rate coefficient is related to the reduced mass of the collision ion–molecule pair and the polarizability and permanent dipole moment of the neutral species. If the permanent dipole moment is small, the collision rate constant is close to (within 10%) the Langevin limit, because of the

Table 1
Ion-molecule reaction rate constants (k) for proton transfer reactions between H_3O^+ and VOCs, along with the corresponding PA, polarizability (α), and permanent dipole moment (μ_D)[a]

Substance	Formula	PA	α	μ_D	k
Hydrocarbons					
1,2-Propadiene	C_3H_4	185.3	5.71	0	1.56
Cyclopropene	C_3H_4	195.6	5.05	0.515	1.60
Propyne	C_3H_4	178.8	4.98	0.715	1.71
Propene	C_3H_6	179.6	5.62	0.368	1.58
1,3-Butadiyne	C_4H_2	176.2	7.81	0.000	1.76
1,2-Butadiene	C_4H_6	186.2	7.82	0.413	1.81
1,3-Butadiene	C_4H_6	187.2	8.39	0.000	1.81
2-Butyne	C_4H_6	185.4	7.20	0.001	1.68
Cyclobutene	C_4H_6	187.5	7.19	0.121	1.69
1-Butene	C_4H_8		7.52	0.347	1.73
2-Butene	C_4H_8	178.5	7.71	0.001	1.73
2-Methylpropene	C_4H_8	191.7	7.66	0.526	1.82
Cis-2-Butene	C_4H_8	179.0	7.64	0.200	1.72
Trans-2-Butene	C_4H_8		7.71	0.001	1.73
1,3-Cyclopentadiene	C_5H_6	196.4	8.64[b]	0.419[b]	1.83
2-Pentyne	C_5H_8	193.6	8.77	0.663	1.95
Cyclopentene	C_5H_8	183.2	8.84	0.175	1.81
Isoprene	C_5H_8	197.5	10.22	0.250	1.94
Trans-1,3-pentadiene	C_5H_8	199.4	10.0[b]	0.585[b]	2.02
1-Pentene	C_5H_{10}		9.41	0.360	1.87
2-methyl-1-butene	C_5H_{10}	193.3	9.47	0.513	1.94
2-Methyl-2-butene	C_5H_{10}		9.72	0.192	1.89
3-Methyl-1-butene	C_5H_{10}		9.38	0.379	1.88
Cis-2-pentene	C_5H_{10}		9.56	0.211	1.87
Trans-2-pentene	C_5H_{10}		9.64	0.045	1.88
Benzene	C_6H_6	179.3	10.78	0.000	1.97
1-Hexyne	C_6H_{10}	191.2	10.69	0.828	2.16
2-Hexyne	C_6H_{10}	192.7	11.03	0.131	1.98
Cyclohexene	C_6H_{10}	187.5	10.77	0.243	1.96
1-Hexene	C_6H_{12}	192.4	11.33	0.392	2.02
Methylcyclopentane	C_6H_{12}	181.6[c]	10.78	0.067	1.95
Trans-2-hexene	C_6H_{12}		11.53	0.073	2.05
3-Methylpentane	C_6H_{14}		11.33	0.047	2.00
Hexane	C_6H_{14}		11.29	0.017	2.00
Toluene	C_7H_8	187.4	12.90	0.343	2.12
Cycloheptene	C_7H_{12}		12.59	0.273	2.09
1-Heptene	C_7H_{14}		13.22	0.394	2.14
Methylcyclohexane	C_7H_{14}		12.80	0.069	2.10
Trans-2-heptene	C_7H_{14}		13.44	0.074	2.15
3-Methylhexane	C_7H_{16}		13.27	0.041	2.14
Heptane	C_7H_{16}		13.25	0.040	2.14
Styrene	C_8H_8	200.6	15.86	0.186	2.33
Ethylbenzene	C_8H_{10}	188.3	14.85	0.297	2.25
m-Xylene	C_8H_{10}		15.03	0.271	2.26
o-Xylene	C_8H_{10}	214.8	14.99	0.582	2.32
p-Xylene	C_8H_{10}	189.9	15.08	0.081	2.27
1-Octene	C_8H_{16}		15.05	0.400	2.26
Cyclooctane	C_8H_{16}	181.6[c]	14.54	0.061	2.22
Octane	C_8H_{18}		15.08	0.021	2.25
Indene	C_9H_8	202.9	17.08	0.681	2.49
1,2,3Trimethylbenzene	C_9H_{12}		17.09	0.660	2.47
1,2,4Trimethylbenzene	C_9H_{12}		17.17	0.291	2.40
1,3,5Trimethylbenzene	C_9H_{12}	199.9	17.16	0.047	2.40

Table 1 (*continued*)

Substance	Formula	PA	α	μ_D	k
Isopropylbenzene	C_9H_{12}	189.2	17.2[b]	0.79[b]	2.54
Azulene	$C_{10}H_8$	221.1	24.13	1.054	3.04
Napthalene	$C_{10}H_8$	191.9	20.18	0.000	2.59
p-Cymene	$C_{10}H_{14}$		18.99	0.086	2.50
2-Carene	$C_{10}H_{16}$		18.39	0.313	2.46
3-Carene	$C_{10}H_{16}$		18.11	0.193	2.44
α-Phellandrene	$C_{10}H_{16}$		18.67	0.060	2.48
α-Pinene	$C_{10}H_{16}$		18.07	0.149	2.44
β-Pinene	$C_{10}H_{16}$		18.03	0.639	2.50
d-Limonene	$C_{10}H_{16}$		18.57	0.651	2.54
Myrcene	$C_{10}H_{16}$		20.02	0.423	2.57
Sabinene	$C_{10}H_{16}$		18.17	0.911	2.63
Terpinolene	$C_{10}H_{16}$		19.09	0.192	2.51
Decane	$C_{10}H_{22}$		19.1[b]	0.058[b]	2.50
1-Methylnaphthalene	$C_{11}H_{10}$	199.5	22.31	0.318	2.70
2-Methylnaphthalene	$C_{11}H_{10}$	198.8	22.52	0.443	2.72
Undecane	$C_{11}H_{24}$		20.82	0.028	2.60
Acenaphthylene	$C_{12}H_8$		25.18	0.324	2.86
Acenaphthene	$C_{12}H_{10}$	203.6	23.87	0.848	2.91
Fluorene	$C_{13}H_{10}$	198.7	25.62	0.502	2.87
Anthracene	$C_{14}H_{10}$	209.7	29.30	0	3.06
Phenanthrene	$C_{14}H_{10}$	197.3	29.67	0.034	3.08
Fluoranthene	$C_{16}H_{10}$	198.0	34.79	0.329	3.32
Pyrene	$C_{16}H_{10}$	207.7	36.78	0.000	3.41
Anphthacene	$C_{18}H_{12}$		23.87	0.848	2.91
Oxygenated VOCs					
Formaldehyde	CH_2O	170.4	2.41	2.183	2.92
Formic acid	CH_2O_2	177.3	3.05	1.443	2.02
Methanol	CH_4O	180.3	2.67	1.662	2.33
Ketene	C_2H_2O	197.3	4.04	1.493	2.21
Glyoxal	$C_2H_2O_2$		4.71	0.004	1.34
Acetaldehyde	C_2H_4O	183.7	4.30	2.648	3.36
Acetic acid	$C_2H_4O_2$	187.3	4.80	1.605	2.27
Ethanol	C_2H_6O	185.6	4.53	1.529	2.26
2-Propenal	C_3H_4O	190.5	6.15	2.636	3.35
Glyoxylicacid	$C_3H_4O_2$		5.25	1.276	2.00
2-Propen-1-ol	C_3H_6O		7.65[b]	1.600[b]	2.52
Acetone	C_3H_6O	194.1	6.09	2.289	3.00
Oxetane	C_3H_6O	191.5	5.77	1.974	2.69
Propanal	C_3H_6O	187.9	6.13	2.748	3.44
1-Propanol	C_3H_8O	188.0	6.38	1.646	2.44
2-Propanol	C_3H_8O	189.5	7.29[b]	1.580[b]	2.47
Isopropylalcohol	C_3H_8O	189.5	6.41	1.530	2.35
Furan	C_4H_4O	192.0	7.21	0.630	1.78
2-Butenal	C_4H_6O	198.6	8.78	3.917	4.66
Crotonaldehyde	C_4H_6O		8.43	3.109	3.84
Methacrolein	C_4H_6O	193.3	8.41	2.800	3.55
Methyl vinyl ketone	C_4H_6O	199.5	8.19	3.110	3.83
2,3-Butanedione	$C_4H_6O_2$	191.7	8.30	0.003	1.71
2-Butanone	C_4H_8O	197.7	7.90	2.764	3.38
2-Methyl-propanal	C_4H_8O	190.6	7.97	2.616	3.35
Butanal	C_4H_8O	189.5	7.97	2.768	3.49
Isobutanal	C_4H_8O	190.6	7.97	2.616	3.35
Methyl ethyl ketone	C_4H_8O	197.7	7.90	2.764	3.48
1,3-Dioxane	$C_4H_8O_2$	197.3	8.33	1.984	2.77
1,4-Dioxane	$C_4H_8O_2$	190.6	8.42	0.000	1.72
1-Butanol	$C_4H_{10}O$	188.6	8.22	1.563	2.47

Table 1 (*continued*)

Substance	Formula	PA	α	μ_D	k
2-Methyl-1-propanol	$C_4H_{10}O$	189.7	8.24	1.423	2.37
2-Furaldehyde-anti	$C_5H_4O_2$		10.88	4.152	4.83
2-Furaldehyde-syn	$C_5H_4O_2$		10.86	3.580	4.28
1,5-Pentanedial	$C_5H_8O_2$		10.21	3.680	4.14
Acetylacetone	$C_5H_8O_2$	208.8	10.36	1.486	2.51
2-Pentanone	$C_5H_{10}O$	199.0	9.78	2.631	3.41
3-Pentanone	$C_5H_{10}O$	200.0	9.73	2.565	3.35
Pentanal	$C_5H_{10}O$	190.4	9.84	2.543	3.34
p-Benzoquinone	$C_6H_4O_2$	191.0	13.58	0.002	2.15
Phenol	C_6H_6O	195.3	11.73	1.335	2.52
Cyclohexanol	$C_6H_{12}O$		11.32	1.512	2.59
Hexanal	$C_6H_{12}O$		11.78	2.942	3.74
2-Methylpentane	$C_6H_{14}O$		11.36	0.067	2.00
Hexanol	$C_6H_{14}O$		12.04	1.449	2.60
Benzoic acid	$C_7H_6O_2$	198.2[d]	14.33	1.915	3.02
Benzaldehyde	C_7H_6O	199.3	14.06	3.282	4.12
Benzylalcohol	C_7H_8O	186.0	13.54	1.681	2.84
m-Cresol	C_7H_8O		13.83	1.033	2.45
k-Cresol	C_7H_8O		13.84	1.045	2.46
p-Cresol	C_7H_8O		13.89	1.301	2.61
Heptanal	$C_7H_{14}O$		13.52	2.378	3.34
Acetophenone	C_8H_8O	205.8	15.00b	3.020b	3.91
Octanal	$C_8H_{16}O$		15.48	2.535	3.53
Nonanal	$C_9H_{18}O$		17.41	2.839	3.84
Decanal	$C_{10}H_{20}O$		19.20	2.501	3.67
Other VOCs					
Acetonitrile	C_2H_3N	186.2	4.29	3.828	4.74
Dimethyl sulfide	C_2H_6S	198.6	6.80	1.718	2.53

[a] *PA*, in kcal mol^{-1} was taken from NIST (2003), except specification. The polarizability (α, in 10^{-24} cm^3) and permanent dipole moment (μ_D, in D) were obtained from frequency calculations at B3LYP/6-31G(d,p) level, except specification. ==The ion–molecule rate constant (*k*, in 10^{-9} cm^3 s^{-1}) was calculated using ADO theory according to Eq. (4).==
[b] The values of α and μ_D were taken from the *CRC Handbook of Chemistry and Physics, 2002–2003, 83rd Edition*.
[c] The proton affinity was taken from Nourse and Cooks (1991).
[d] The proton affinity was taken from Midey et al. (2003).

small value of the dipole locking constant, *C*. In this case, there is little contribution to the collision rate from the second item on the right-hand side of Eq. (4). This is indeed the case for all the hydrocarbons studied in this work. For example, the collision rate constants are 1.58, 1.94, 1.97, 2.12×10^{-9} cm^3 s^{-1} for propene, isoprene, benzene and toluene, respectively, very close or equal to the corresponding values of the Langevin limit (1.54, 1.94, 1.97 and 2.12×10^{-9} cm^3 s^{-1} for propene, isoprene, bezene, and toluene, respectively). The collision rate constants, however, are much smaller than the locked dipole limit values, i.e., 0.50, 0.73, and 0.69 of the corresponding locked dipole limit values for propene, isoprene, and toluene, respectively. For benzene, the

three rate constants (i.e., the Langevin limit, locked dipole limit and ADO rate constants) are nearly identical because of the zero value of the permanent dipole moment of this compound. The permanent dipole moment of the hydrocarbons investigated in this study is smaller than 1.0 D, except for azulene which has a value of 1.054 D. Since the reduced mass of the collision ion–molecule pair typically ranges from 11 to 18 a.u. for the proton transfer reaction between H_3O^+ and VOCs, the collision rate constant is proportional to the square root of the polarizability of the hydrocarbons because of their negligible permanent dipole moment. In general, the polarizability increases with the carbon number of the hydrocarbons and thus the collision rate constant also increases with the carbon number for the proton transfer reaction with H_3O^+.

For oxygenated volatile organic compounds, the permanent dipole moment is much greater than 1.0 D and thus the permanent dipole moment contributes significantly to the collision rate constant. For example, the collision rate constants are 2.92, 2.02 and 2.33×10^{-9} cm^3 s^{-1} for formaldehyde, formic acid, and methanol, respectively, while the corresponding values of the Langevin limit are 1.07, 1.12, 1.11×10^{-9} cm^3 s^{-1}. Those collision rate constants are hence greater than the Langevin limit values, by about a factor of three for formaldehyde and by about a factor of two for formic acid and methanol. The collision rate constants of those molecules, however, are smaller than their corresponding locked dipole limit values, 0.33, 0.35, and 0.34 of the locked dipole limit rate constants for formaldehyde, formic acid, and methanol, respectively.

To evaluate the accuracy of the calculated values of the polarizability and permanent dipole moment of the organic species, we compared our calculated values with available literature results which were obtained mostly from experimental studies. Table 2 contains the available literature values of the polarizability and permanent dipole moment (Lide, 2003), along with our calculated results. For polarizability, the calculated values are in good agreement with the experimental results within ±30%. For example, the calculated polarizabilities of 1,3-butadiene, isoprene, methacrolein, and toluene are 8.39, 10.22, 8.41 and 12.90×10^{-24} cm^3, respectively, in excellent agreement with the respective experimental values (8.64, 9.99, 8.30, and 12.2×10^{-24} cm^3). For those four compounds, the deviation of the theoretical values from the experimental results is only a few percent. The calculated values of permanent dipole moment are also consistent with the experimental value within ±30%. For example, the values of the calculated permanent dipole moments are 0.368, 0.25, 1.66 and 0.63 D for propene, isoprene, methanol, and furan, respectively, which are nearly identical to those of the corresponding experimental values (0.366, 0.25, 1.70 and 0.63 D). Only one compound exhibits a significant deviation in the

Table 2
Comparison of the calculated polarizability (α) and permanent dipole moment (μ_D) of VOCs with the experimental results[a]

Substance	α		μ_D	
	Literature	This work	Literature	This work
Cyclopropene		5.05	0.454	0.515
Propyne	6.18	4.98	0.784	0.715
Propene	6.26	5.62	0.366	0.368
1,2-Butadiene		7.82	0.403	0.413
1,3-Butadiene	8.64	8.39		0
2-Butyne	7.41	7.20		0.663
Cyclobutene		7.19	0.132	0.121
1-Butene	7.97, 8.52	7.52	0.438, 0.359	0.347
2-Methylpropene	8.29	7.66		0.526
Cis-2-Butene		7.64	0.253	0.20
Trans-2-Butene	8.49	7.71		0.001
2-Pentyne	9.12	8.77		0.663
Cyclopentene			0.20	0.175
Isoprene	9.99	10.22	0.25	0.25
1-Pentene	9.65	9.41	0.5	0.360
2-Methyl-1-butene		9.47	0.398, 0.320	0.513
Benzene	10, 10.32, 10.74	10.78		0
1-Hexyne	10.9	10.69		0.828
Cyclohexene	10.7	10.77		0.243
1-Hexene	11.7	11.33		0.392
Hexane	11.9	11.29		0.017
Toluene	11.8, 12.26, 12.3	12.90	0.375	0.343
1-Heptene	13.5	13.22		0.394
Methylcyclohexane	13.10	12.80		0.069
Styrene	15.0, 14.4	15.86	0.123	0.186
Ethylbenzene	14.2	14.85		0.297
m-Xylene	14.2	15.03		0.271
o-Xylene	14.9, 14.1	14.99	0.640	0.582
p-Xylene	13.7, 14.2, 14.9	15.08		0.081
Octane	15.09	15.08		0.021
Azulene		24.13	0.80	1.054
Napthalene	16.5, 17.5	20.18		0
Undecane	21.0	20.82		0.028
Acenaphthylene	20.6	23.87	0.85	0.848
Fluorene	21.7	25.62		0.502
Anthracene	25.4, 25.9	29.30		0
Phenanthrene	24.7, 36.8	29.67		0.034
Pyrene	28.2	36.78		0
Anphthacene	32.3	23.87		0.848
Formaldehyde	2.8, 2.45	2.41	2.332	2.183
Formic acid	3.4	3.05	1.425	1.12
Methanol	3.29, 3.23, 3.32	2.67	1.70	1.66
Ketene	4.4	4.04	1.4225	1.493
Acetaldehyde	4.6, 4.59	4.30	2.75	2.648
Acetic acid	5.1	4.80	1.70	1.605
Ethanol	5.41, 5.11	4.53	1.69	1.529
Acetone	6.33, 6.4, 6.39	6.09	2.88	2.289
Oxetane		5.77	1.94	1.974
Propanal	6.50	6.13	2.72	2.748
1-Propanol	6.74	6.38	1.58, 1.55	1.646
Furan		7.21	0.66	0.63
Crotonaldehyde	8.5	8.43		3.109
Methacrolein	8.3	8.41		2.80
Butanal	8.2	7.97	2.72	2.768
Isobutanal		7.97	2.67, 2.86	2.616
Methyl ethyl ketone	8.13	7.90		3.110
1,3-Dioxane		8.33	2.06	1.984
1,4-Dioxane	10.0	8.42		0
1-Butanol	8.88	8.22	1.66	1.563

Table 2 (*continued*)

Substance	α		μ_D	
	Literature	This work	Literature	This work
2-Methyl-1-propanol	8.92	8.24		1.423
Acetylacetone	10.5	10.36		1.486
p-Benzoquinone	14.5	13.58		0.002
Phenol	11.1	11.73	1.224	1.335
Cyclohexanol	11.56	11.32		1.512
Benzaldehyde		10.06	3.0	3.282
Benzylalcohol		13.54	1.71	1.681
m-Cresol		13.83	1.48	1.033
o-Cresol		13.84	1.45	1.045
p-Cresol		13.89	1.48	1.301
Acetonitrile	4.40, 4.48	4.29	3.925	3.828
Dimethyl sulfide		6.80	1.554	1.718

[a] The literature values of polarizability (α, in 10^{-24} cm^3) and permanent dipole moment (μ_D, in D) were taken from the *CRC Handbook of Chemistry and Physics, 2002–2003, 83rd Edition.*

calculated permanent dipole moment. For styrene, the calculated value exceeds the experimental value by about 51%. Hence the good agreement between the present theoretical predictions and previous experimental results of the polarizability and permanent dipole moment validates the reliability of quantum chemical calculations which can be further employed for calculations of the proton transfer collision rates between H_3O^+ and VOCs.

For exothermic proton transfer reactions, the ion–molecule reaction always proceeds near or equal to the collision rate constant as predicted by Eq. (4). This has been validated extensively by comparing theoretical collision rate constants with experimental measurements of proton transfer reactions (Bohme, 1975; Ikezoe et al., 1987; Spanel and Smith, 1997). There are several experimental techniques available to measure the ion–molecule rate constant; the most common technique uses the selected ion flow tube (SIFT) coupled to the mass spectrometry. The SIFT method has been employed to investigate numerous ion–molecule reactions for several classes of organic species, including alcohol (Spanel and Smith, 1997), aldehydes and ketones (Spanel et al., 1997, 2002a; Midey et al., 2000), hydrocarbons (Spanel and Smith, 1998c; Diskin et al., 2002; Tani et al., 2003), diols (Spanel et al., 2002b), carboxylic acids and esters (Spanel and Smith, 1998a), and sulfides (Spanel and Smith, 1998b; Williams et al., 1998). The SIFT technique has hence provided experimental data for ion–molecule reactions which are valuable to validate the theoretical results for a wide range of organic compounds on the basis of their optical properties.

Table 3 compares the calculated ion–molecule rate constants with the literature results. Some of the literature data are experimental values, while the others

are theoretically predicted based on the experimental or estimated polarizability and permanent dipole moment. The rate constants obtained in this study are in very good agreement with the experimental values for alkenes, alkynes, aromatics, and oxygenated organic compounds. For those types of VOCs, the calculated ion–molecule collision rate constants are within $\pm 25\%$ of the literature values. For example, the calculated collision rate constants are 1.97, 2.12, and

Table 3
Comparison the calculated ion–molecule rate constants for proton transfer reactions between H_3O^+ and VOCs with the available literature values

Substance	k (10^{-9} cm^3 s^{-1})	
	Literature	This work
Propyne	1.8[a]	1.71
Propene	1.7[a], 1.5[b,c]	1.58
2-Butene	1.6[a]	1.73
Isoprene	2.0[d,b], 1.3[b]	1.94
1-Pentene	1.9[d], 2.0[e]	1.87
2-Methyl-1-butene	1.9[d]	1.89
Trans-2-pentene	1.9[e]	1.88
1-Hexene	2.1[e]	2.02
Trans-2-hexene	2.0[e]	2.05
Benzene	1.3[a], 1.8[f], 1.9[d], 2.1[b]	1.97
Toluene	1.3[a], 2.2[b,d,g], 2.3[f,h]	2.12
1-Heptene	2.3[e]	2.14
Methylcyclohexane	0.7[f], 0.8[i]	2.10
Trans-2-heptene	2.0[e]	2.15
Ethylbenzene	2.4[d], 2.5[h]	2.25
m-Xylene	2.3[d]	2.26
o-Xylene	2.4[d]	2.32
p-Xylene	2.2[d]	2.27
1-octene	2.4[e]	2.26
Cyclooctane	0.5[i]	2.22
Octane	0.9[d]	2.25
1,2,3Trimethylbenzene	2.5[d]	2.47
1,2,4Trimethylbenzene	2.4[d]	2.40
1,3,5Trimethylbenzene	2.3[d]	2.40
3-Carene	2.2[g]	2.44
d-Limonene	2.3[g]	2.54
Á-Pinene	2.2[g]	2.44
Â-Pinene	2.3[g]	2.50
Decane	1.6[d]	2.50
Formaldehyde	3.0[b,j], 3.3[k]	2.92
Formic acid	2.5[j], 2.7[b]	2.02
Methanol	2.1[f], 2.2[l], 2.5[j], 2.7[m], 2.8[c], 3.8[n]	2.33
Ketene	2.0[j]	2.21
Acetaldehyde	3.55[j], 3.6[b,c], 3.7[k]	3.36
Acetic acid	3.0[b,j]	2.27
Ethanol	2.7[m,f], 2.8[b,c,j], 3.8[n]	2.26
Acetone	3.9[b,n], 4.1[f]	3.0
1-Propanol	2.3[b], 2.7[m]	2.44
Isopropylalcohol	2.8[b]	2.35
2-Butenal	4.8[o]	4.66

Table 3 (*continued*)

Substance	k (10^{-9} cm^3 s^{-1})	
	Literature	This work
2-Methyl-propanal	3.8[o]	3.35
Butanal	3.8[o]	3.49
1-Butanol	2.7[m]	2.47
1,5-Pentanedial	3.9[p]	4.14
Phenol	2.7[m]	2.52
Heptanal	3.7[o]	3.34
Octanal	3.8[o]	3.53
Decanal	3.9[o]	3.67
Acetonitrile	4.50[j]	4.74
Dimethyl sulfide	1.7[q], 2.1[r,b], 2.5[s]	2.53

[a] From Milligan et al. (2002).
[b] From Lindinger et al. (1998).
[c] From Fehsenfeld et al. (1978).
[d] From Spanel and Smith (1998a, b, c).
[e] From Diskin et al. (2002).
[f] From Spanel et al. (1995).
[g] From Tani et al. (2003).
[h] From Midey et al. (2002).
[i] From Midey et al. (2003).
[j] From Anicich (1994).
[k] From Midey et al. (2000).
[l] From Mackay et al. (1979).
[m] From Spanel et al. (1997).
[n] From Lee et al. (1992).
[o] From Spanel et al. (2002a).
[p] From Spanel et al. (2002b).
[q] From Williams et al. (1998).
[r] From Passarella et al. (1987).
[s] From Arnold et al. (1998).

2.33×10^{-9} cm^3 s^{-1} for benzene, toluene, and methanol, respectively, which fall into the range of the reported experimental values, i.e., 1.3–2.1×10^{-9} cm^3 s^{-1} for benzene, 1.3–2.3×10^{-9} cm^3 s^{-1} for toluene, and 2.1–3.8×10^{-9} cm^3 s^{-1} for methanol.

For alkanes, however, the calculated collision rate constants are higher than the experimental ion–molecule reaction rate constants. For example, the experimental ion–molecule rate constants are 35% for methylcyclohexane, 23% for cyclocotane, 40% for octane, and 65% for decane of the theoretical collision rates. Alkanes typically behave differently from other classes of organic species in the proton transfer reactions with H_3O^+. Most small alkanes have proton affinities smaller than that of water so proton transfer is endothermic and unlikely occurs at thermal energies. The proton transfer reactions between H_3O^+ and larger alkanes are expected to be exothermic, although limited data are available for the proton affinities of large alkanes (Lias, 1988). The proton affinities of cyclooctane and methylcyclohexane have been recently estimated by Midey et al. (2003), with

a value of 181.6 kcal mol^{-1} for both species. The smaller values for the experimental ion–molecule reactions of the two compounds have been explained because of dissociation of the protonated product ions (Midey et al., 2003). In general, no direct proton transfer product ion larger than protonated propane has been observed, which suggests that the dissociation channel may be favorable or protonated product ions undergo immediately significant fragmentation if the proton transfer reaction does occur (Arnold et al., 1998; Spanel and Smith, 1998c). For cyclooctane and methylcyclohexane, the proton transfer reactions involve significant rearrangement and a ring-breaking mechanism is the likely reason that exothermic proton transfer reactions do not proceed at the collision rate (Midey et al., 2003).

Hence for alkanes, the collision rate constant does not represent the real ion–molecule rate. For many other types of organic species, the collision rate constants are in the range of the experimental data. It has been suggested by Lindinger and co-workers that because there are usually larger errors associated with the experimental determinations of the ion–molecule rate constants, the calculated collision rate coefficients using the ADO theory are more preferential in the applications of PTR-MS to measure the concentrations of VOCs in the air (Lindinger et al., 1998).

4. Conclusions

The proton transfer reactions of H_3O^+ with selected VOCs have been investigated. Our study contains 78 hydrocarbons including alkane, alkene, alkyne and aromatic hydrocarbon and 58 non-hydrocarbons including alcohol, aldehyde, ketone and other organic species important to atmospheric chemistry. The quantum chemical method of B3LYP/6-31G(d,p) was used to determine the equilibrium structures and permanent dipole moment and polarizability of the organic species. The ion–molecule reaction rates were determined using the ADO theory. The calculated permanent dipole moment and polarizability are in good agreement with available literature results. For alkenes, alkynes, aromatics, and oxygenated organic compounds, the calculated ADO collision rate constants agree with available experimentally measured ion–molecule reaction rates. For alkanes, the calculated collision rate constants are higher than the experimental values, probably because of dissociation of the protonated product ions. The newly calculated proton transfer rate constants facilitate the use of the PTR-MS technique in applications of laboratory investigation of photochemical hydrocarbon oxidation reactions and field measurements of the abundance of VOCs.

Acknowledgements

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