J. Am. Chem. Soc. 1989, 111, 6015–6018

Effect of Temperature on the Mobility of Ions

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Abstract: The effect of temperature, between 87 and 250 °C, on the mobility of protonated amines in helium, air, CO_2, and SF_6 was studied by ion mobility spectrometry. In helium, the reduced mobility was found to decrease as the temperature was raised, due to an increase in the collision cross section, and was approximately proportional to $T^{-1/2}$. In CO_2, where clustering takes place at low temperatures, raising the temperature led to an increase in the reduced mobility, mainly due to breakdown of the clusters and a decrease in the effective mass of the ion. In air, where only little clustering was observed, the reduced mobility of light ions increases with the temperature, while for heavy ions the opposite was found. In SF_6, like in CO_2, the increase of the reduced mobility with temperature was attributed to breakdown of clusters. An expression for the temperature dependence of the reduced mobility in each of these drift gases was determined semiempirically.

The effect of temperature on the reduced mobility of ions has been the subject of some controversy in the literature.[1-5] According to the polarization limit model[6] there should be no dependence of the reduced mobility on temperature, while according to the rigid-sphere approximation (see, for example, ref 5) the reduced mobility should be proportional to $T^{-1/2}$. The two-temperature and three-temperature models[2] take into account the fact that the ions acquire energy from the electric field and are accelerated to a higher translational temperature than the drift gas molecules. The model most commonly used for ion mobility spectrometry (IMS) studies, and adopted here, is the one developed mainly by Mason and co-workers[4,5] that employs a hard-core potential to represent the interaction of the ions with the drift gas molecules.

According to this model,[5] the reduced mobility of an ion drifting through a buffer gas in an electric field is given by

$$K = (3q/16N)(2\pi/\mu kT)^{1/2}(1/\Omega_D) \quad (1)$$

where q is the charge of the ion and m its mass, N is the density of the neutral molecules and M their mass, μ is the reduced mass $\mu = mM/(m + M)$, k is the Boltzmann constant, T is the effective temperature, and Ω_D is the collision cross section. As noted previously,[7] if the drift gas molecules form clusters with the core ion, its mass will be altered to a new effective mass, given by $m_{eff} = m + nM$, where n is the number of clustered molecules. This may not necessarily be the true number of molecules clustered around each ion but represents the average number of clustered molecules.

The reduced mobility, Ko, is obtained by normalizing eq 1 to standard temperature (273 K) and pressure (760 Torr) conditions:

$$\mathrm{Ko} = K(273/T)(P/760) \quad (2)$$

Rearranging and substituting the appropriate constants and taking the inverse of the reduced mobility, one obtains[5]

$$\mathrm{Ko}^{-1} = 1.697 \times 10^{-4}(\mu T)^{1/2}\Omega_D \quad (3)$$

where Ko^{-1} is in V s cm^{-2}, μ in amu, T in degrees kelvin, and Ω_D in Å^2.

The collision cross section, Ω_D, is given by

$$\Omega_D = \pi r_m^2 \Omega^*(T^*) \quad (4)$$

where $\Omega^*(T^*)$ is the dimensionless collision integral, which depends on the ion–neutral interaction potential and is a function of the dimensionless temperature, $T^* = kT/\epsilon_0$. Here ϵ_0 is the depth of the potential minimum, and r_m is its position:[5]

$$\epsilon_0 = q^2\alpha_p[3r_m^2(1 - a^*)^4]^{-1} \quad (5)$$

$$r_m = (r_0 + zm_{eff})[1 + (m_{eff}/M)^{1/3}] \quad (6)$$

where α_p is the polarizability of the neutral molecule, a^* is a parameter that represents the reduced core diameter, r_0 is a constant, and z is the correction factor suggested previously.[8] As seen in eq 3 and 5, the inverse reduced mobility depends directly on the temperature through $T^{1/2}$ and indirectly through Ω_D and, more subtly, through m_{eff}, which reflects the extent of clustering, which is a temperature-dependent phenomenon. Therefore, analysis of the temperature dependence of the mobility must take into account the interplay between these terms. The physical parameters to which the reduced mobility is proportional are, as given by eq 3, the collision cross section, the reduced mass, and the temperature. We shall try to analyze the effects of each of these parameters on the mobility, in view of the experimental data presented below, and try to build a comprehensive model of the factors that affect the motion of polyatomic ions in an atmospheric pressure drift gas. The approach adopted here was to look at the correlation between temperature and reduced mobility in a simple system like helium, where clustering is expected to be negligible, and compare the results with those obtained in more complex systems: air, CO_2, and SF_6. Then we analyze the temperature dependence of the cross section, Ω_D, and its components (r_m and Ω^*) and of the effective mass, m_{eff} (which depends on clustering). To remove artifacts that may arise from calculations based on a single type of ion and determine the effect of the ion mass on mobility, a series of protonated amines with masses varying from 46 to 522 amu was examined.

Experimental Section

The work was carried out on a Phemto-Chem 100 (PCP, Inc.) ion mobility spectrometer (IMS), described in detail previously.[9,10] The carrier and drift gas flow rates were set at 100 and 500 mL/min, respectively. The ambient pressure, P, was measured to within 0.1 Torr, and the cell temperature, T, to within 0.5 °C. The electric field was set between 50 and 64.3 V/cm for mobility measurements in helium at 224 and 87 °C, respectively, and at about 200 V/cm in air, SF_6, and CO_2. Thus, E/N varies from a minimum of 0.25Td for He at 87 °C to a

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Table I. Reduced Mobility Ko (in Units of $cm^2/(V\ s)$) of Several Protonated Aliphatic and Aromatic Compounds in Helium, Air, CO_2, and SF_6 at Different Temperatures

		Ko											
		helium[a]			air[a]			CO_2[b]			SF_6		
compound	MW	87 °C	200 °C	224 °C	87 °C	150 °C	250 °C	90 °C	154 °C	250 °C	91 °C	150 °C	250 °C
						Aliphatic							
ethylamine	45	11.0	12.1	11.8	2.16	2.25	2.41	1.06	1.24	1.31	0.62	0.68	0.72
isopropylamine	59	10.1	10.4	10.0	2.02	2.16	2.23		1.19	1.26		0.64	0.64
trimethylamine	59		10.6	10.1			2.38		1.19	1.28		0.65	0.65
diethylamine	73		9.1	8.7		2.11	2.16		1.16	1.25			
triethylamine	101	8.05	7.58	7.4	1.93	1.94	1.95	0.94	1.07	1.11	0.56	0.61	0.64
tripropylamine	143	6.33		5.6	1.65		1.62		1.04	1.08	0.49	0.53	0.56
tributylamine	185	5.16	4.78	4.6	1.42	1.40	1.35	0.89	0.93	0.95	0.43	0.48	0.49
tripentylamine	227	4.42		3.9	1.25		1.19		0.83	0.85	0.39	0.42	0.44
triheptylamine	311	3.47		3.0	1.02		0.95		0.69	0.69	0.33	0.34	0.36
trioctylamine	353	3.16	2.83	2.7	0.94	0.89	0.85	0.64	0.64	0.62	0.31	0.32	0.33
tridodecylamine	521		2.08	2.0	0.74	0.69	0.64		0.50	0.48		0.25	0.25
						Aromatic							
pyridine	79	10.3	10.1	9.7	2.08	2.18	2.24	1.07	1.16	1.29	0.61	0.67	0.69
2-picoline	93	9.35		8.5	2.04		2.10	1.08	1.18	1.26	0.58	0.62	0.66
4-picoline	93	9.35	8.87	8.5	2.02	2.08	2.08		1.15	1.24	0.58	0.63	0.65
2,4-lutidine	107	8.42	7.92	7.6	1.93	1.95	1.95	1.07	1.15	1.21	0.56	0.59	0.62
2,4,6-collidine	121	7.63	7.13	6.8	1.83	1.83	1.81	1.06	1.13	1.17	0.54	0.57	0.59
quinoline	129	8.05	7.54	7.3	1.78	1.85	1.84	1.02	1.10	1.15	0.52	0.52	0.57

[a] This work and ref 8 and 9. [b] This work and ref 7.

Table II. Parameters a^*, r_0, z, and n, Defined and Explained in Text, Obtained from the Fitting Procedure in Helium, Air, CO_2, and SF_6 and the Effect of Clustering (Increasing the Mass of the Core Ion) on the Reduced Mass for Core Ions of Mass 46 and 522 Amu

						$(\mu_{eff}^{1/2} - \mu^{1/2})/\mu^{1/2}$	
drift gas	temp, °C	a^*	r_0, Å	z, Å/amu	n, molecules	m = 46 amu	m = 522 amu
helium	87	0.2	1.33	0.001 73	0 ± 3.02	0	0
helium	200	0.2	1.27	0.001 69	0 ± 0.94	0	0
helium	224	0.2	1.32	0.001 68	0 ± 0.77	0	0
air	87	0.2	2.39	0.001 85	0.64 ± 0.07	0.06	0
air	150	0.2	2.37	0.002 00	0.17 ± 0.01	0.01	0
air	200	0.2	2.29	0.002 19	0 ± 0.35	0	0
air	250	0.2	2.23	0.002 29	0 ± 0.26	0	0
CO_2	90	0.3	2.17	0.002 03	3.37 ± 0.02	0.25	0.01
CO_2	154	0.3	2.58	0.001 84	0.49 ± 0.02	0.09	0
CO_2	250	0.3	2.45	0.002 04	0.12 ± 0.03	0.02	0
SF_6	91	0.3	3.57	0.003 29	0.36 ± 0.01	0.32	0.01
SF_6	150	0.3	3.65	0.002 33	0.21 ± 0.01	0.22	0.007
SF_6	250	0.3	3.23	0.002 71	0.14 ± 0.01	0.16	0.004

maximum of 1.5*Td* for air, CO_2, and SF_6 at 250 °C.

The reduced mobility, Ko, was determined from the equation[10]

$$Ko = (d/Et)(273/T)(P/760) \tag{7}$$

where P, T, and E were defined above, and t is the measured drift time of the ion traversing the distance, d. The error in these measurements is estimated as being below 2%.

Results and Discussion

The reduced mobility of protonated aliphatic and aromatic amines in helium was determined at cell temperatures of 87, 200, and 224 °C. These results are compared with reduced mobilities of these or similar ions in air, CO_2 (ref 7), and SF_6 at temperatures of approximately 90, 150, and 250 °C.

As the results, summarized in Table I, clearly show, the general trend of the reduced mobility in helium is of a negative temperature dependence, i.e., it decreases as the temperature is raised. In air the temperature dependence is positive for ions with masses below 90 amu, namely, increasing by about 2% for each 50 °C, but negative for ions with masses above 180 amu, while for ions of intermediate mass it is almost unchanged in the temperature range of this study. In CO_2 the temperature dependence is much more pronounced, increasing in some cases, like pyridine, by 11% between 154 and 250 °C, although the biggest relative change was observed for raising the temperature from 90 to 154 °C. However, the very large aliphatic ions, like protonated trioctylamine (354 amu), show little or no temperature dependence in CO_2. In SF_6 a positive temperature dependence was also observed, although not as pronounced as in CO_2.

The procedure used for fitting the reduced mobilities calculated from eq 3, to the experimental data points, was described in detail previously.[7] Four parameters, defined above, were used in the fit: a^*, r_0, z, and n. Table II summarizes the values of these parameters obtained from the fitting procedure for each drift gas at each of the temperatures investigated here. The value of a^* was incremented from 0 to 0.4 in steps of 0.1, and the value that gave the least χ^2 was chosen. The errors in r_0 and z are small and vary from 0.5 to 2% and to 3%, respectively. The errors in n are listed in Table II. Note that for helium the value of n is zero, but the error in the calculated number of clustered molecules is large. This is an outcome of the insensitivity of the reduced mass to changes in the ion mass when helium is the drift gas. The errors in the parameters obtained from this fitting procedure are generally larger for helium than for the heavier drift gases. Thus the effects of varying the temperature or changing the drift gas and of clustering, on the collision cross section and the reduced mass can be analyzed independently. From these, the reasons underlying the observed changes in the reduced mobility with temperature can be evaluated.

The reduced mass, μ, depends on the masses of the ion and drift gas and formally should not depend on the temperature or on the polarizability of the drift gas. However, the mass of the ion may be altered by clustering, a process that does depend on the temperature and the polarizability of the drift gas. As shown in Figure 1 and Table II, the calculations indicate that helium does not cluster with the protonated amines under the IMS conditions even at 87 °C, although, as mentioned above, there is a large uncer-

Table III. Calculated Dimensionless Collision Cross Section, $\Omega^*(T^*)$, the Distance Parameter, r_m, and the Product $\Omega_D T^{1/2}$ in Helium, Air, CO_2, and SF_6 at Different Temperatures, for Some Protonated Aliphatic Amines

Helium

ion mass, amu	87 °C			154 °C			250 °C		
	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$
46	4.57	0.69	858	4.37	0.68	886	4.51	0.66	939
60	4.96	0.65	952	4.73	0.64	977	4.89	0.63	1054
102	5.93	0.59	1236	5.67	0.58	1273	5.85	0.57	1365
144	6.79	0.55	1510				6.69	0.53	1660
186	7.59	0.52	1784	7.27	0.51	1858	7.47	0.50	1972
228	8.36	0.50	2081				8.22	0.48	2270
312	9.86	0.46	2664				9.69	0.45	2957
354	10.6	0.44	2945	10.2	0.44	3126	10.4	0.43	3261
522				13.0	0.39	4549	13.3	0.39	4929

Air

ion mass, amu	87 °C			150 °C			250 °C		
	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$
46	5.81	0.92	1850	5.42	0.97	1840	4.47	1.62	2265
60	6.10	0.87	1928	5.74	0.89	1893	4.76	1.42	2252
102	6.84	0.76	2118	6.55	0.76	2105	5.04	1.08	2303
144	7.50	0.71	2379				6.18	0.92	2459
186	8.10	0.67	2618	7.88	0.66	2646	6.79	0.83	2678
228	8.68	0.64	2872				7.38	0.77	2935
312	9.78	0.60	3419				8.51	0.68	3574
354	10.32	0.58	3680	10.2	0.57	3829	9.07	0.68	3915
522	12.41	0.53	4862	12.4	0.52	5163	11.28	0.62	5486

CO_2

ion mass, amu	90 °C			154 °C			250 °C		
	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$
46	6.77	1.07	2933	5.81	1.30	2847	5.22	1.46	2856
60				6.07	1.20	2868	5.51	1.31	2855
102	7.47	0.92	3087	6.77	1.00	2973	6.26	1.05	2954
144				7.36	0.90	3163	6.88	0.91	3093
186	8.44	0.81	3451	7.92	0.83	3378	7.46	0.84	3356
228				8.45	0.78	3613	8.01	0.79	3639
312				9.46	0.72	4209	9.06	0.72	4243
354	10.3	0.70	4494	9.94	0.70	4487	9.58	0.70	4613
522				11.8	0.64	5866	11.5	0.64	6162

SF_6

ion mass, amu	91 °C			150 °C			250 °C		
	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$	r_m, Å	$\Omega^*(T^*)$	$\Omega_D T^{1/2}$, Å^2 deg$^{1/2}$
46	7.29	1.19	3783	6.89	1.23	3770	6.03	1.44	3759
60				7.13	1.16	3808	6.27	1.33	3754
102	8.21	0.98	3951	7.77	1.00	3898	6.92	1.11	3816
144	8.85	0.89	4170	8.34	0.91	4087	7.50	0.98	3958
186	9.47	0.83	4453	8.87	0.85	4318	8.04	0.89	4131
228	10.00	0.78	4722	9.38	0.81	4602	8.56	0.84	4419
312	11.2	0.73	5497	10.3	0.75	5178	9.57	0.76	4998
354	11.7	0.71	5904	10.8	0.73	5509	10.1	0.74	5420
522				12.6	0.67	6928	12.0	0.67	6923

tainty involved in this particular calculation. In air, the average number of clustered molecules is $n = 0.64$ at 87 °C and drops to zero at 215 °C. In CO_2, the number of clustered molecules drops steeply from $n = 3.37$ at 90 °C to zero at 245 °C, while in SF_6 the number of clustered molecules is surprisingly small, $n = 0.36$ at 91 °C, and drops gradually until it reaches zero (by extrapolation) at 335 °C. Below 220 °C, clustering in CO_2 is larger than in SF_6. When considering the effect of clustering on the reduced mass, one must bear in mind not just the value of n but also the molecular weight of the drift gas and the mass of the core ion. The last two columns of Table II show the relative change in the reduced mass, $(\mu_{eff}^{1/2} - \mu^{1/2})/\mu^{1/2}$, calculated for core ions of masses 46 and 522 amu. Evidently, the addition of a fixed mass to a small ion will affect it relatively more than addition of the same mass to a heavy ion, i.e., the effect of clustering on the reduced mobility depends on the ion mass. Furthermore, as the results in Table II show, the relative shift of the reduced mass, for a fixed mass increment to the ion, is larger in SF_6 than in the other gases. This is an outcome of the fact that in the lighter drift gases the reduced mass term is dominated by the molecular weight of the drift gas for these amine ions, while in SF_6 (MW 146 amu) the ion mass also plays an important role in determining the reduced mass. The effect of clustering on the collision cross section can be estimated by analyzing the components of Ω_D. The dimensionless collision cross section, $\Omega^*(T^*)$, for each ion in each drift gas at any given temperature, was obtained from calculations based on the experimental data and the tables in ref 4. The ion mass was corrected by substituting the value of n obtained from the fitting procedure, in the expression for effective ion mass given above. The value of r_m was calculated

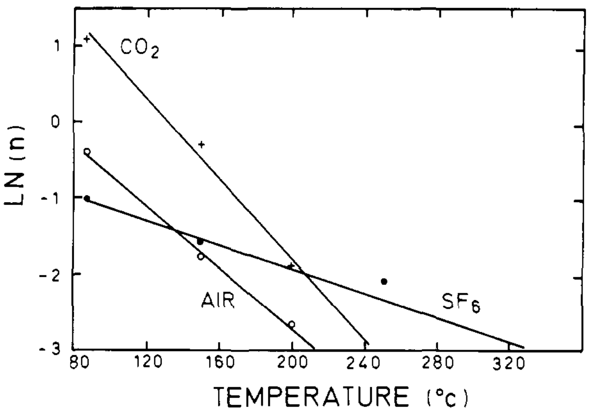

Figure 1. Natural logarithm of the number of clustered drift gas molecules, n, as a function of temperature in air, CO_2, and SF_6.

from eq 6 by use of the parameters r_0, z, and m_{eff}, obtained from the fitting procedure. The collision cross section was then calculated from eq 4. The values thus obtained for r_m and $\Omega^*(T^*)$ are summarized in Table III. To normalize the effect of the temperature, the product $\Omega_D T^{1/2}$ is shown in the last column of Table III.

The value of r_m increases with ion mass and with the size of the drift gas molecules, although for the heavy ions it is almost independent of the type of drift gas. On the other hand, r_m decreases with temperature, except in helium, where it is almost constant for a given ion. The dimensionless collision cross section increases with temperature, except in helium, and decreases with ion mass. For a given ion it is much smaller in helium than in the other gases and is almost equal in CO_2 and SF_6. The product $\Omega_D T^{1/2}$ increases with ion mass in all drift gases and for a given ion with the molecular weight of the drift gas. It also increases with the temperature in helium and air but is almost constant in CO_2 and actually decreases with temperature in SF_6.

As Ω_D is proportional to r_m and Ω^* (eq 4), both of which are mass dependent (eq 5 and 6), any change in the ion mass that arises from clustering will affect the collision cross section.

The picture that emerges from these results is interesting. For a given ion drifting in helium, r_m and $\Omega^*(T^*)$, and therefore Ω_D, are almost independent of the temperature, so that the product $\Omega_D T^{1/2}$ increases with temperature. Clustering does not play a role in helium under our experimental conditions, so the reduced mass does not vary with temperature. Thus, the overall effect of raising the temperature for mobility measurements in helium is a decrease in the reduced mobility that arises from the $T^{1/2}$ term in eq 3. Quantitatively, the decrease is not quite as large as $T^{1/2}$, which is indicative of some slight temperature dependence of Ω_D.

In air, r_m decreases with temperature more than the increase in $\Omega^*(T^*)$, so that there is a net decrease in Ω_D. However, $\Omega_D T^{1/2}$ increases with temperature, due to the $T^{1/2}$ term.

Clustering also plays a role, with the cluster size decreasing with rising temperature, leading to a small decrease in the reduced mass. The overall effect of temperature on the reduced mobility of a given ion in air depends on the ion mass. For light ions, the reduction in clustering as the temperature is raised offsets the decrease in mobility due to the increase in $\Omega_D T^{1/2}$, while for heavy ions the reduced mass is hardly altered by clustering, and the term $\Omega_D T^{1/2}$ is dominant. Thus, in air, the reduced mobility of light ions increases with the temperature, that of heavy ions decreases, and for intermediate mass ions, the mobility is only slightly affected by temperature changes.

In CO_2, the decrease in r_m and increase in $\Omega^*(T^*)$ result in a decrease in Ω_D, but this is offset by the increase in $T^{1/2}$, so that the overall result is that $\Omega_D T^{1/2}$ is almost independent of the temperature. Thus, the observed pronounced increase with temperature of the reduced mobility in CO_2 is mainly a result of the dramatic decrease in cluster size. Namely, the increase in reduced mobility is attributed to the change of reduced mass.

In SF_6, like in CO_2, the overall effect of decreasing r_m and increasing $\Omega^*(T^*)$ leads to only slight changes in $\Omega_D T^{1/2}$ and the observed increase of the reduced mobility with temperature is attributed to decreasing cluster size. As the dependence of the cluster size on temperature in SF_6 is not as strong as in CO_2, the temperature dependence of the reduced mobility is also weaker.

The extent of clustering is not proportional directly to the polarizability, as evident from Figure 1, so it probably depends also on the shape of the drift gas molecule. A plausible explanation is that the large spherical SF_6 molecules cannot arrange around the ion as compactly as the cylindrical CO_2 molecules.

At elevated temperatures the internal state distribution of the ions may be altered, a fact that may affect their mobility.[11] However, under the low E/N conditions of our experiment and relatively narrow temperature range employed, most of these large polyatomic ions are expected to spend most of their time in their ground state.

Summary

The temperature dependence of the reduced mobility of a series of ions in helium, air, CO_2, and SF_6 varies considerably, both quantitatively as well as qualitatively. A negative temperature dependence was observed in helium, where clustering does not take place, and the $T^{1/2}$ term was dominant. On the other hand, in CO_2 the observed positive temperature dependence was predominantly a result of clustering that affected the reduced mass of the ion. In air and SF_6 where the average cluster size does not depend on the temperature as strongly, the increase in mobility was relatively small. Furthermore, the overall effect depended also on the mass of the core ion, so that heavy ions were not as affected as light ions.

Thus, when using the currently accepted mobility theory for predicting the temperature effect on mobility, one must consider the nature of the drift gas and its tendency to cluster with the core ions of interest. As clustering is strongly temperature dependent, the average cluster size must first be determined and then used to correct the ion mass. Subsequently, the mass–mobility correlation curve in the appropriate drift gas at the given temperature can be used to predict the reduced mobility.

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