Collision Rate Constants for Polarizable Ions

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Langevin described a model for the interaction between an ion and a neutral nearly a century ago and since then, many modifications have been introduced to adjust for specific circumstances. This work discusses the induced dipole–induced dipole interaction between an ion and a neutral without a permanent dipole and introduces an anisotropic adjustment. A point polarizable ion model (PPI) and an orientation dependent polarizable ion model (ODPI) are discussed and applied to systems where the ion is highly polarizable and the neutral is only weakly polarizable. Significant deviations from classical Langevin rate constants and significant differences between PPI and ODPI are observed.   (J Am Soc Mass Spectrom 2003, 14, 501–505) © 2003 American Society for Mass Spectrometry

Over the last century, many scientists have discussed the collisional rate of an ion with a polarizable neutral. Langevin began the discussion in 1905 [1] with work outlining the attractive potential between a point charge and a point-polarizable neutral. The result was an expression for the collisional rate constant, k_L, in terms of a few simple variables; e, the elementary charge, α_n, the polarizability of the neutral, and μ, the reduced mass of the ion-neutral pair.

$$k_L = 2\pi e \left(\frac{\alpha_n}{\mu}\right)^{1/2}$$

The approach is appealing in its simplicity, and has been used as a standard for ion–molecule and ion–atom collisions. This method has been used extensively to calculate collision rate constants in many environments, including the interstellar medium, where atomic hydrogen, molecular hydrogen, and atomic oxygen and nitrogen are the most abundant species.

Another major area of work involves the interaction of an ion and a neutral species with a permanent dipole moment. Several approaches have been taken, ranging from an orientation-fixed dipole approximation to orientation-dependent approaches which rigorously conserve angular momentum and energy. These methods have been discussed in detail [2, 3]. Additional work in this area involves parameterizing the theory to obtain a solution that is easily accessible to experimentalists [4, 5].

Deviations from a point charge model have been described by Su et al. [9, 10] and an induced dipole–induced dipole adjustment has been discussed by Su and Bowers [11]. The possibility for large deviation is mentioned with respect to anionic systems, but due to the difficulty of acquiring ionic polarizabilities, only the Cl^- and H^- anions are discussed. These systems afford less than 5% deviation from the classical Langevin rate constants. In this paper we highlight the importance of the anisotropy of the induced dipole–induced dipole interaction and introduce an orientation dependent polarizable ion model. We demonstrate that these interactions, especially when anisotropy is included, have significant impact on the collision rate constants of large molecular cations and anions.

Theory

The Langevin rate constant is derived from a potential that assumes the ion is a point charge. Two factors, the long-range nature of the potential involving ions and the way in which the random orientation of an ion causes the location of the charge to average to the center, make this approximation accurate in most cases. Deviation can occur, however, in the second of these two factors. If the charge is mobile within the ion, the average location of the charge can shift from the center, effectively increasing the critical impact parameter.

Traditionally, positive ions have been studied more frequently in laboratory experiments because of the wide range of their applicability and the relative ease with which they are made. In cation systems, ionic polarizability effects have not been observed in experiments where measured rate constants are compared

with theoretical collision rate constants. For negative ions that are similar in size to these cations, however, one would expect the mobility of the charge to be much larger.

The approach taken to assess the dependence of the collision rate on the polarizability of the ion was to adjust the Langevin potential in the following way:

$$V_{eff} = V_{Langevin} + V_\alpha \tag{1}$$

$$V_{Langevin} = E\left(\frac{b^2}{r^2}\right) - \frac{1}{2}\frac{\alpha_n e^2}{r^4} \tag{2}$$

Here, E is the relative kinetic energy, b the impact parameter, r the distance between the ion and the neutral, and α_n is the polarizability of the neutral. V_α is an additional term based on the attraction between a polarizable ion and a polarizable neutral.

The approach taken by Su et al. [9] assumes that the ion is a single massive point with a uniform polarizability. The V_α for a point-polarizable ion (PPI)-neutral pair takes the form [11]:

$$V_{PPI}(r) = -\frac{3}{2}a_0^{1/2}e^2\frac{\alpha_{ion}\alpha_n}{\left(\left(\frac{\alpha_{ion}}{N_{ion}}\right)^{1/2} + \left(\frac{\alpha_n}{N_n}\right)^{1/2}\right)r^6} \tag{3}$$

where a_0 is the Bohr radius, α_{ion} and α_n are the polarizabilities of the ion and the neutral, respectively. N_{ion} and N_n are the outer shell electrons of an atomic species or the number of electrons in the HOMO of molecular species. The r^{-6} dependence is typical of the attraction between two polarizable species.

We incorporate an adjustment to this approach, an orientation dependent polarizable ion (ODPI) model, which considers the ion as a tube of charge with an average orientation towards the approaching neutral. This model is useful when the polarizability along one axis differs greatly from the polarizability along the other two. In the longer of the negatively charged and highly conjugated chains we will discuss, the polarizability parallel to the chain is much larger than the polarizability perpendicular to the chain. Two polarizability values are needed, $\alpha_\perp$ and $\alpha_\parallel$. When the neutral approaches the chain at an angle θ (Figure 1), the following expression represents the potential V_α:

$$V_{ODPI}(r) =$$
$$-\frac{3}{2}a_0^{1/2}e^2\frac{(\alpha_\parallel cos\theta + \alpha_\perp sin\theta)\alpha_n}{\left(\left(\frac{(\alpha_\parallel cos\theta + \alpha_\perp sin\theta)}{N_{ion}}\right)^{1/2} + \left(\frac{\alpha_n}{N_n}\right)^{1/2}\right)r^6} \tag{4}$$

In Eq 4, an approach similar to the one taken in ADO theory is utilized to acquire the average value for θ. The

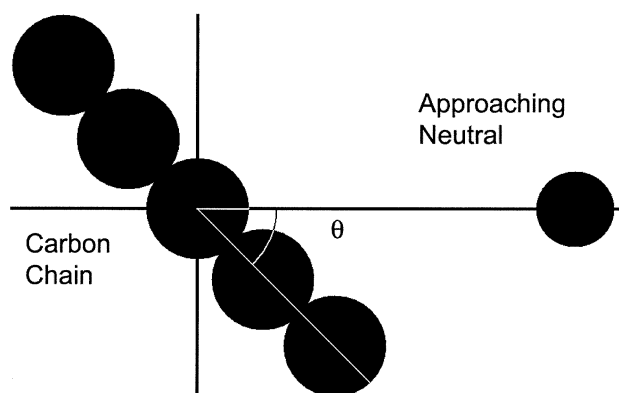**Figure 1.** θ is defined as the angle between the primary axis of the molecule and the approach vector of the neutral.

general expression for the average value of θ is:

$$\langle\theta\rangle = \frac{\int_0^{\pi/2}\theta P(\theta)d\theta}{\int_0^{\pi/2}P(\theta)d\theta} \tag{5}$$

The probability function for θ, $P(\theta)$, takes the form,

$$P(\theta) = \frac{sin\theta}{(E_{rot} + V_\alpha)^{1/2}} \tag{6}$$

as described in ADO theory, where E_{rot} is the rotational energy. Due to the r^{-6} dependence of V_α, however, $E_{rot} \gg V_\alpha$ at room temperature. Since E_{rot} is independent of θ, Eq 5 reduces to:

$$\langle\theta\rangle = \frac{\int_0^{\pi/2}\theta sin\theta d\theta}{\int_0^{\pi/2}sin\theta d\theta} = 1 \text{ radian} \tag{7}$$

ODPI addresses the case where there will be substantial deviation from PPI when considering the polarizabilities along the axes. In other cases, PPI is sufficient.

In both cases, the derivation of the rate constant through the critical impact parameter does not afford a simple expression in terms of a few variables, as with the traditional Langevin theory. Values for E and the various α's and N's were substituted such that:

$$V(r) = xb^2r^{-2} - yr^{-4} - zr^{-6} \tag{8}$$

where x, y, and z are real, positive numbers. The derivative of V with respect to r was then taken and set to zero to calculate r*(b), the value of r in terms of b, where V is at a maximum. Substituting this result into

Table 1. Values of k_L and k_{PPI} for the reaction of C_n^- and C_nH^- with O, the percent increase in the collisional rate constant, and the reaction efficiencies for both theories.

	k_L	k_{PPI}	% Deviation	Efficiencies	
	$(cm^3/s) \times 10^{-10}$	$(cm^3/s) \times 10^{-10}$	PPI from Langevin	k_{exp}/k_L	k_{exp}/k_{PPI}
C_2^-	6.77	8.16	20.5	0.85	0.71
C_4^-	6.05	7.19	18.8	0.92	0.77
C_5^-	5.90	7.12	20.7	1.09	0.90
C_6^-	5.80	7.15	23.3	0.80	0.65
C_7^-	5.72	7.18	25.5	0.92	0.73
C_8^-	5.66	7.25	28.0		
C_2H^-	6.71	8.46	26.0	0.93	0.74
C_4H^-	6.04	7.75	28.3	0.88	0.68
C_6H^-	5.79	7.89	36.3	0.93	0.69

V(r), we obtain V*(b). Now taking V* as the value for the barrier to collision, E must satisfy the condition $E \geq V^*$. Setting $E = V^*(b)$, a value for b* can be obtained, where b* is the maximum impact parameter that results in a collision. Given this result, k was found using:

$$k = \left(\frac{2E}{\mu}\right)^{1/2} \pi b^{*2} \tag{9}$$

Results and Discussion

Because of their potential relevance in the interstellar medium, we have carried out comprehensive experimental studies of the reactions of aromatic cations and of carbon chain anions with H_2, H, N, and O [12–17]. In these unusual systems, the polarizability of the neutral is small and that of the ion is large, which accentuates the effect of the V_α term on the overall potential. To illustrate this, we have calculated the collisional rate constants for $C_n^- + O$ and $C_nH^- + O$ systems using Langevin theory, PPI and ODPI. [Ionic polarizability values were obtained from Gaussian 98 calculations at the B3LYP/aug-cc-pVDZ level [6–8]. This basis set gave the best polarizability value for neutral benzene and was necessary to obtain minimized structures for the C_n^- and C_nH^- anions.] Table 1 shows the results of the PPI approach, where significant deviations from Langevin theory are evident, ranging from ~19–36%.

While the PPI approach affords significant deviation, of specific interest to the reactions of C_n^- is the ODPI form of V_α. For C_2^-, $\alpha_\parallel$ is less than $\alpha_\perp$, but in all longer chains, $\alpha_\parallel$ is much larger than $\alpha_\perp$ (by more than a factor of 7 in the case of C_8^-). Because of this, we expect there to be a difference between the PPI results and the ODPI results. Figure 2 shows a plot of the potential, V_α, as a function of the angle θ for $C_6H^- + O$. At the average angle calculated, the potential has a greater value and therefore leads to a larger rate constant.

We expect this difference to increase as the chain length increases. As shown in Table 2, this is the case. With C_2^-, the change in deviation is less than 1% but as chain length increases, the change in deviation increases significantly and is greater than 7% in the longer chains.

This result illustrates that, for small ions, the PPI approximation gives reasonable results, but as the size of the ion increases, consideration of the unique orientation aspects of the system is essential.

The contribution of size to the collisional rate constant has been discussed previously by Su et al. [10]. In their work, an adjustment is added when the size of the ion is larger than the theoretical collisional cross section. In our systems, the impact parameter is defined with respect to the center of mass of each species. The largest of our molecules, C_8^-, has a distance from the center of mass to the end of the chain of ~4.55 Å. The impact parameter for this molecule is 5.6 Å for PPI and 5.7 Å for ODPI. When considering the atomic radii of oxygen, which is ~0.75 Å, it is clear that the ion–atom collisional cross section is larger than the rotationally averaged hard sphere collisional cross section for these systems. For this reason, the size consideration previously discussed by Su et al. it is not necessary in this case.

The $C_n^- + O$ system has two factors that accentuate the induced dipole–induced dipole interaction. The first is the large polarizabilities of the anions, as discussed above. The second factor is the low polarizability of O atom. Because the Langevin rate constant depends directly on α_n, the question arises, for diverse systems,
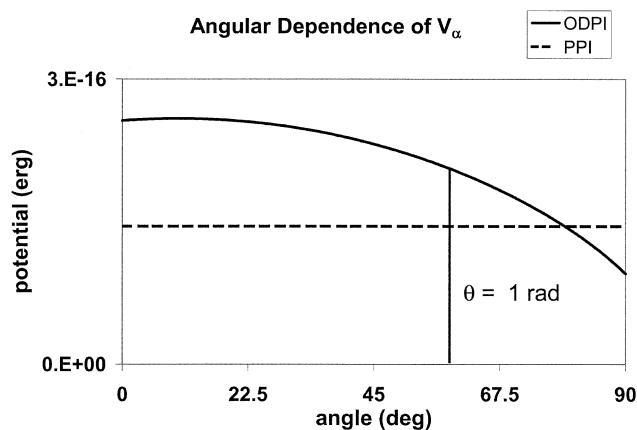

Figure 2. At a value of $\theta = 1$ radian, the contribution of ODPI to the overall potential is greater than PPI. Data taken from an intermolecular distance of 10 Å.

Table 2. Values of k_L and k_{ODPI} for the reaction of C_n^- and C_nH^- with O, and the percent deviation of k_{ODPI} from k_L and k_{PPI}.

	k_L	k_{ODPI}	% deviation	% deviation
	$(cm^3/s) \times 10^{-10}$	$(cm^3/s) \times 10^{-10}$	(from Langevin)	(from PPI)
C_2^-	6.77	8.18	20.8	0.2
C_4^-	6.05	7.39	22.1	2.8
C_5^-	5.90	7.36	24.7	3.4
C_6^-	5.80	7.34	26.6	2.7
C_7^-	5.72	7.44	30.0	3.6
C_8^-	5.66	7.53	33.0	3.9
C_2H^-	6.71	8.89	32.4	5.1
C_4H^-	6.04	7.97	32.0	2.8
C_6H^-	5.79	8.46	46.1	7.2

at what α_n does the ion-neutral dispersion interaction become significant? Two more common ions were evaluated, OH^- and H_3O^+, and, using PPI, the value for α_n below which deviation from k_L becomes more than 5% was determined. For OH^-, values of α_n must be <4.3 Å^3 and for H_3O^+, values must be <1.0 Å^3 for the polarizability of the ion to be important. This clearly illustrates that the effect must be considered for most negative ions unless α_n is quite high, whereas positive ions of similar size will only be affected by neutrals with very low polarizabilities (atomic species). For C_6H^-, the values of α_n must be <22.3 Å^3 for the polarizability of the ion to be important using PPI, and <42.6 Å^3 when using ODPI. These relatively large values suggest that, for reactions of most negative ions, there is a strong dependence of the collision rate on the polarizability of the ion.

This calculation was also done for the benzene cation, whose larger analogs may have relevance to interstellar chemistry, specifically to the unidentified DIBs. In this case the polarizability of the ion is important when $\alpha_n < 9.5$ Å^3 using PPI and when $\alpha_n < 26.9$ Å^3 using ODPI. This result is quite interesting since collisions with H atom, for which $\alpha_n = 0.667$ Å^3, are extremely important in the interstellar medium. An increase in the theoretical collision rates will have an impact on models of interstellar chemistry and physics.

Conclusions

While most ion-neutral reactions can be reasonably approximated as point charge systems, in reactions where either the polarizability of the ion is high or the polarizability of the neutral is low, the attractive potential between the two polarizable species must be considered. Ionic species in this category include most anions and large, π-system cations.

Implications of this consideration range from laboratory experiments to the interstellar medium. In the laboratory, many reactions that were previously thought to have efficiencies close to unity may have significantly lower efficiencies, indicating that new dynamic considerations may be warranted. Most models of the processes and interactions in the ISM use the Langevin theory to describe the collision frequency between ions and neutral molecules and atoms. In these

environments, the significance of the induced dipole–induced dipole adjustment may be substantial.

Acknowledgments

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