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Capture Collisions of Polyynide Anions with Hydrogen Atoms: Effect of the Ion Dipole, Quadrupole, and Anisotropic Polarizability

Kent M. Ervin *

Department of Chemistry and Chemical Physics Program, University of Nevada, Reno, 1664 N. Virginia St. MS 216, Reno, NV 89557-0216, USA

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Bierbaum 65th Birthday.

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Classical capture rate constants are calculated for a molecular ion with a dipole moment, quadrupole moment, and anisotropic polarizability colliding with a neutral polarizable atom. The free-energy effective potential method is used to average the potential energy over the interaction angle. Numerical methods are used to calculate the effective potential from the full anisotropic induction potential energy function, to solve for the position of the centrifugal barrier, and to determine the thermal rate constants. The capture collision model is applied to the reactions of polyynide anions, HC_4^-, HC_6^-, and HC_8^-, with atomic hydrogen, which are of interest in astrophysical environments, using calculated multipole moments and anisotropic polarizabilities. The dipole moment, quadrupole moment, and polarizability of the ion each contribute significantly toward the total predicted classical capture collision rates for these systems.

1. Introduction

Polyynide anions, HC_{2n}^- ($n = 2–4$), were the first anions to be observed by radio astronomy in interstellar environments [1–3], and they may also be of interest in planetary ionospheres [4]. The reactions of the anions with atoms that are abundant in these astrophysical environments are thus of interest for modeling the ion and neutral chemistry. Bierbaum and coworkers measured rate constants at 300 K for reactions of HC_{2n}^- ($n = 1–3$) anions with hydrogen atoms and other neutral reactants [5,6]. They calculated the reaction efficiencies relative to a collision rate model that included the charge and polarizability of the ion interacting with the polarizable atom [7]. For temperatures of 10 K and 100 K relevant to interstellar clouds and planetary ionospheres, respectively, Faure et al. [4] used a semi-empirical capture model to extrapolate the reaction rate constants from measured room-temperature values, using a locked-dipole collision model at 10 K for the case of reactions of anions with a polar neutral molecule. The HC_{2n}^- anions themselves possess large dipole moments, which is indeed why they can be observed by radio astronomy. The permanent dipole moments and the quadrupole moments, also large, of the HC_{2n}^- anions were not considered in the previous models for the collision rates these systems [4,6,7].

This work evaluates the importance of the higher-order electric moments of the polyynide anions on the rate constants for the classical capture collisions with hydrogen atoms. A collision model with an orientationally averaged potential energy is used as a computationally tractable method to estimate capture rates. Capture collisions between an anisotropically polarizable ion with permanent dipole and quadrupole moments and a neutral polarizable atom are considered. The case of a polar ion interacting with a polar neutral molecule has also been discussed [8,9].

Ion–neutral capture collisions have been treated extensively in the literature, with various approaches proposed for handling non-spherical potentials [8–29]. For the purpose of this work, the Helmholtz free energy effective potential approach of Ridge and coworkers [20,21] and Turulski and Foryś [22] has an appropriate balance of accuracy and computational effort. Celli et al. [20] demonstrated, by showing its equivalence with canonical variational transition state theory (also known as activated complex theory), that the calculated rate constants by this method are upper limits to the true classical capture rate constants. Marković and Nordholm [23,24] further developed the free energy effective potential method to eliminate classically bound states and include additional degrees of freedom, but the more basic method of Celli et al. [20] is used here. Potentially more accurate methods such as classical trajectory studies [24–29], microcanonical variational transition state theory [29], the adiabatic invariance method [13–16], or the statistical

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* Tel.: +1 775 784 6676; fax: +1 775 784 6804.
E-mail address: ervin@unr.edu (K.M. Ervin).

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adiabatic channel model [17,18] are significantly more involved computationally and are beyond the scope of this work.

2. Capture collision model

The long-range potential energy function for an anisotropically polarizable cylindrical molecular ion (A) with permanent dipole and quadrupole moments interacting with an isotropically polarizable neutral atom or molecule (B), each treated as a point particle, is represented by Eq. (1),

$$V(r,\theta_A) = -\Sigma_n \frac{C_n f_n(\theta_A)}{r^n} \tag{1}$$

where C_n is a constant coefficient and $f_n(\theta_A)$ is the angular dependence of the various components of the potential energy. The individual terms in the summation are given in Eq. (2) [30,31],

$$V_4 = -\frac{z_A^2 e^2 \alpha_B}{(4\pi\varepsilon_0)^2 2r^4}(\text{ion} + \text{charge} - \text{induceddipole}) \tag{2a}$$

$$V_5 = -\frac{2z_A e\mu_A \alpha_B}{(4\pi\varepsilon_0)^2 r^5}\cos\theta_A(\text{dipole} + \text{charge} - \text{induced dipole}) \tag{2b}$$

$$V_{6a} = -\frac{\mu_A^2 \alpha_B}{(4\pi\varepsilon_0)^2 2r^6}(3\cos^2\theta_A + 1)(\text{dipole} + \text{dipole} - \text{induced dipole}) \tag{2c}$$

$$V_{6b} = -\frac{3z_A e Q_A \alpha_B}{(4\pi\varepsilon_0)^2 2r^6}(3\cos^2\theta_A - 1) \quad (\text{quadrupole} + \text{charge} - \text{induced dipole}) \tag{2d}$$

$$V_7 \quad -\frac{6\mu_A Q_A \alpha_B}{(4\pi\varepsilon_0)^2 r^7}\cos^3\theta_A(\text{quadrupole} + \text{dipole} - \text{induced dipole}) \tag{2e}$$

$$V_8 = -\frac{9Q_A^2 \alpha_B}{(4\pi\varepsilon_0)^2 8r^8}(5\cos^4\theta_A - 2\cos^2\theta_A + 1) \quad (\text{quadrupole} + \text{quadrupole} - \text{induced multipole}) \tag{2f}$$

$$V_{6c} = -\frac{C_{\text{dis}}}{r^6}(\text{induceddipole} + \text{induced dipole}) \tag{2g}$$

where $z_A e$ is the charge of the ion, μ_A is the permanent dipole moment of the ion, Q_A is the permanent quadrupole moment of the ion, α_B is the polarizability of the neutral atom, ε_0 is the permittivity of vacuum, r is the distance between the particles, and θ_A is the angle between the dipole vector of A pointing from negative to positive and the vector between the particles pointing from A to B, as shown in Fig. 1. The dispersion constant, C_{dis}, is described further below. The induction terms, Eqs. (2a)–(2f), include all of the interactions of a charge, dipole, and quadrupole with a polarizable species, obtained by extending the derivation given by Maitland et al. [31] to higher order. Eq. (2) expresses the potential energy in SI units, where the charge is in units of Coulomb, the dipole moment in C m, the quadrupole moment in C m^2, and the polarizability in $\text{C m}^2\,\text{V}^{-1}$ or $\text{C}^2\,\text{m}^2\,\text{J}^{-1}$. The polarizability in electrostatic units is $\alpha' = \alpha/(4\pi\varepsilon_0)$, where the polarizability α' has traditional volume units (cm^3 or Å^3). The conversion to SI units for dipole moments μ' in Debye (statcoulomb Ångstrom) is $\mu = (\mu'/\text{Debye}) \times (10^{-21}\,\text{C m}^2\,\text{s}^{-1})/c$, where c is the speed of light. The traditional unit for quadrupole moments is the Buckingham or Debye Ångstrom, and the scalar quadrupole moment is defined here as the signed Q_{zz} component of the traceless quadrupole tensor [30,31].

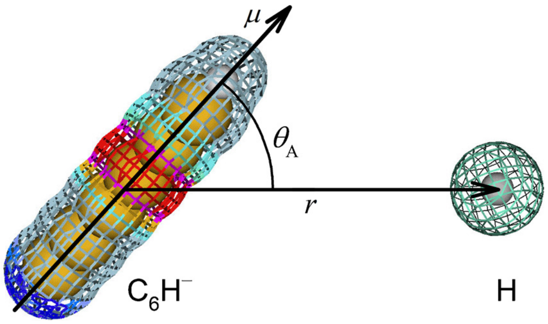

Fig. 1. Coordinate system for the example C_6H^- + H, with a representation of the electrostatic potential surface.

The Langevin–Gioumousis–Stevenson [32] collision-capture model of ion–neutral reactions accounts for the interaction between the charge of A and the charge-induced-dipole of B given by Eq. (2a). This interaction is always attractive ($V < 0$) with no angular dependence. The ion–induced-dipole potential alone yields the temperature-independent rate constant, k_{LGS}, in Eq. (3) [32,33],

$$k_{\text{LGS}} = 2\pi\left(\frac{z_A^2 e^2 \alpha_B}{(4\pi\varepsilon_0)^2 M_{AB}}\right)^{1/2} \tag{3}$$

where M_{AB} is the reduced mass of the A + B colliding pair. The higher induction potential terms in Eqs. (2b)–(2f) depend on the orientation of the dipole or quadrupole of the ion A relative to the A and B axis and several can be either attractive or repulsive. The attractive London dispersion forces are fundamentally quantum mechanical in nature, but the coefficient C_{dis} in Eq. (2g) may be approximated by the Slater-Kirkwood model, Eq. (4) [30],

$$C_{\text{dis}} = \frac{3}{2}\frac{a_0^{1/2}e^2}{(4\pi\varepsilon_0)^{5/2}}\left(\frac{\alpha_A\alpha_B}{(\alpha_A/N_A)^{1/2} + (\alpha_B/N_B)^{1/2}}\right) \tag{4}$$

where α_A is the polarizability of the ion A, a_0 is the Bohr radius, and N_A and N_B are the numbers of valence electrons of the two species ($N_A = 8n + 2$ for $C_{2n}H^-$ and $N_B = 1$ for H atom). To take into account the anisotropy of the polarizability of A, the substitution of Eq. (5a) or equivalently Eq. (5b) is used [30],

$$\alpha_A(\theta_A) = \alpha_A^{\|}\cos^2\theta_A + \alpha_A^{\perp}\sin^2\theta_A \tag{5a}$$

$$\alpha_A(\theta_A) = \alpha_A\left[1 + \delta_A\left(\cos^2\theta_A - \frac{1}{3}\right)\right] \tag{5b}$$

where $\alpha^{\perp}$ and $\alpha^{\|}$ are the perpendicular and parallel components of the polarizability, the angle-averaged isotropic polarizability is $\alpha_A = (1/3)\alpha_A^{\|} + (2/3)\alpha_A^{\perp}$, and the anisotropy is $\delta_A = (\alpha_A^{\|} - \alpha_A^{\perp})/\alpha_A$. The polarizability of the neutral B is treated here as isotropic, as is appropriate for hydrogen atoms.

The classical capture cross section [12,32,33] for ion–neutral collisions is determined by the ability of the collision partners to pass over the centrifugal barrier, which is the maximum of the effective potential, Eq. (6),

$$V_{\text{eff}}(r,\theta) = \frac{Eb^2}{r^2} - \Sigma_n \frac{C_n f_n(\theta)}{r^n} \tag{6}$$

where E is the relative collision energy and b is the impact parameter. The position of the centrifugal barrier at $r = r^*$ is given by Eq. (7),