Moment of Inertia Influence on Ion-Molecule Reaction Rates

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The locked-dipole model for reactions between ions and polar molecules is modified by introducing the moment of inertia into the centrifugal term of the interaction potential. The resulting rate coefficients are compared with other models and experimental data.

Key words: Gases – ions – momentum of inertia – polar molecules – reaction kinetics

Introduction

In a series of recent papers [1–8] the theory of reactions between ions and (polar) molecules is under consideration for several reasons. On one hand there is no general theory up to now which describes all the physical aspects simultaneously, although the theoretical versions of the average dipole orientation (ADO) theory [9–11] and ADO with conservation of angular momentum (AADO) [12], and some further models [13–15] present – at least partially – sufficient agreement with the experimental data. On the other hand there are new experimental findings [16–20], e. g. with temperature-dependent measurements, partly at low temperatures in view of astrophysical questions [6, 16, 18, 21].

In this paper the predictions of a relatively simple model implying the molecular parameters polarizability α_M, dipole moment μ_M and moment of inertia I are compared with experimental results. The simplest models in this direction are the Langevin model [22, 23], the locked-dipole model (LD) [24, 25] and the free-rotator model [26]. The temperature dependence of the rate coefficient comes from a weighting of the reactive cross section with the Maxwell-Boltzmann distribution of relative velocities and integration over all the relative energies of the translational motion of the reactants.

The LD theory is characterized by the effective interaction potential

$$V_{\mathrm{eff}}^{\mathrm{LD}}(r) = \frac{L_{\mathrm{orb}}^2}{2mr^2} - \frac{\alpha_M q^2}{2r^4} - \frac{\mu_M q}{r^2}\cos\theta\Big|_{\theta=0}, \quad (1)$$

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where $L_{\mathrm{orb}} = m b v$ is the angular momentum of the orbital motion with m and v the reduced mass and the relative velocity of the reactants, respectively, b the impact parameter, q the charge of the ion and r the ion-molecule distance.

From (1) follows the reaction cross section between an ion and a molecule with their relative translational energy $E = m v^2/2$ as

$$\sigma^{\mathrm{LD}}(E) = \pi b_{\mathrm{LD}}^2(E) = \pi q\,[(2\alpha_M/E)^{1/2} + \mu_M/E], \quad (2)$$

where b_{LD} is the maximum impact parameter characterizing the "capture" in a successive reactive collision. The corresponding rate coefficient can be written in the well-known form

$$k^{\mathrm{LD}}(T) = 2\pi q m^{-1/2}[\alpha_M^{1/2} + (2/\pi k_B T)^{1/2}\cdot\mu_M], \quad (3)$$

k_B Boltzmann constant, T gas temperature.

The model here under consideration is in some respect a link between the LD-model and a model which regards the conservation of angular momentum (A). The latter theory was first presented as so-called AADO theory by Su, Su, and Bowers [12]. A similar procedure, considering the quadrupole part of the interaction potential, was carried out by Kosmas [27].

Theory

The AADO theory replaces the angular momentum L_{orb} of (1) by a generalized expression

$$L(r) = L_{\mathrm{orb}} - C_L(r), \quad (4)$$

where

$$C_L(r) = L_R(r' = r) - L_R(r' \to \infty), \quad (5)$$

i. e. the difference of angular momentum L_R of the rotating molecule for a fixed point $r' = r$ and the angu-

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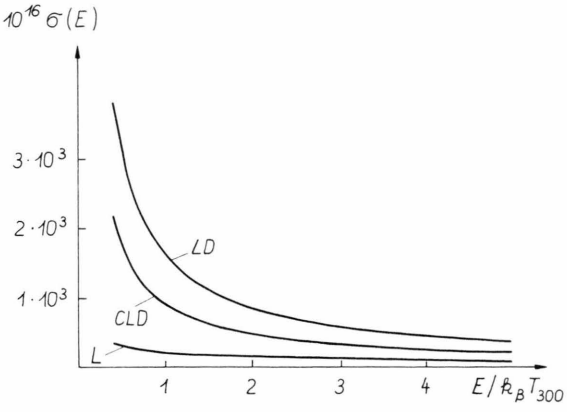

Fig. 1. Reaction cross sections σ (in cm^2) for the models L, LD and CLD of the reaction $CH_3CN + H^-$ vs. energy E (in units of $k_B T_{300}$).

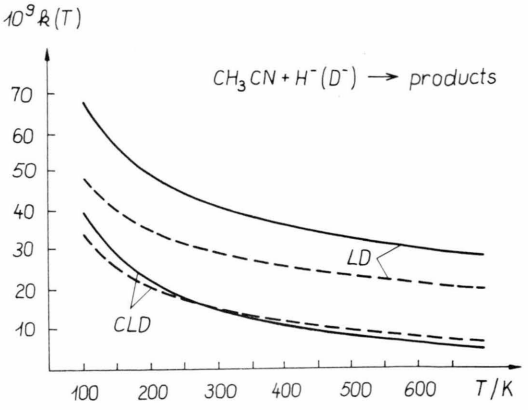

Fig. 2. Rate coefficients k (in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for the models LD and CLD of the reactions $CH_3CN + H^-$ and $CH_3CN + D^-$ (dashed) vs. temperature T (in K).

lar momentum L_R for $r = \infty$. It is assumed that

$$L_R(r) = (2 I \bar{E}_R(r))^{1/2} \tag{6}$$

and

$$L_R(\infty) = (I k_B T_R)^{1/2}, \tag{7}$$

where $\bar{E}_R(r)$ is the average rotational energy of the molecule and T_R the rotational temperature.

In the LD model the strong simplification is made that the dipole moment of the molecule is always "locked in" in the ion-molecule direction. In the framework of our model, $\bar{E}_R(r) = 0$ is assumed, i.e.

$$L_R(r) = 0. \tag{8}$$

From the (1) and (4)–(8) follows an effective potential of the form

$$V_{\text{eff}}^{\text{CLD}}(r) = \frac{(m b v + \sqrt{I k_B T_R})^2}{2 m r^2} - \frac{\alpha_M q^2}{2 r^4} - \frac{\mu_M q}{r^2}, \tag{9}$$

CLD means LD with enlarged centrifugal term.

It can be seen from (9) that the centrifugal term is indead enlarged (against the term in (1)). This leads to an increase of the centrifugal barrier and therefore to a decrease of the microscopic cross section $\sigma^{\text{CLD}}(E)$. This makes clear that the rate coefficient $k^{\text{CLD}}(T)$ is smaller than $k^{\text{LD}}(T)$.

From the equation $dV_{\text{eff}}/dr = 0$, determining the position $r_{\max}$ of the maximum of the centrifugal barrier, and the condition $V_{\text{eff}}(r_{\max}) = E$ for a successful reaction the following expression for the microscopic reaction cross section can be calculated:

$$\sigma^{\text{CLD}}(E) = \pi (b^{\text{LD}} - b^{\text{C}})^2 \tag{10}$$

Table 1. Rate coefficients k (T_{300}) in 10^{-9} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for reactions between CH_3CN and different ions ($\varkappa = k/k_{\text{exp}}$).

XH^+	k_{exp} [a]	k^{L}	k^{LD}	k^{CLD}	$\varkappa^{\text{LD}}$	$\varkappa^{\text{CLD}}$	$\varkappa^{\text{AADO}}$ [b]
H_3^+	10.0	2.98	24.4	14.5	2.4	1.4	1.1
H_3O^+	4.7	1.38	11.4	9.07	2.4	1.9	1.1
N_2H^+	4.1	1.21	9.94	8.16	2.4	2.0	1.2
HCO^+	4.1	1.21	9.94	8.16	2.4	2.0	1.2
N_2OH^+	3.8	0.78	6.40	5.65	1.7	1.5	1.1
CO_2H^+	4.1	0.78	6.40	5.65	1.6	1.4	1.0

[a] data from [29]. [b] values from [12].

with

$$b^{\text{C}} = [I k_B T_R/(2 E m)]^{1/2} \text{ and } b^{\text{LD}} \text{ according to (2).}$$

In Fig. 1 reaction cross sections σ^{LD}, σ^{CLD}, and σ^{L} are presented, where σ^{L} corresponds to the first term of (2) (Langevin model).

In what follows, the rotational temperature T_R is regarded to be equal to the gas temperature T.

Under the assumption of Maxwellian distribution of the velocities of both reactants, rate coefficients $k^{\text{CLD}}(T)$ on the basis of (10) were calculated:

$$k^{\text{CLD}}(T) = [8/\pi m (k_B T)^3]^{1/2} \int_0^\infty dE\, \sigma^{\text{CLD}}(E)\, E \cdot \exp(-E/k_B T). \tag{11}$$

Discussion

The relation $\sigma^{\text{L}} < \sigma^{\text{CLD}} < \sigma^{\text{LD}}$ (Fig. 1) is paralleled by the relation $k^{\text{L}} < k^{\text{CLD}} < k^{\text{LD}}$ (see Figure 2). In so much, this result is physically reasonable.

A pecularity of Fig. 2 is the crossing of the CLD curves for the reacting ions H^- and D^-. This comes from the fact that k depends in two ways on the reduced mass m (and therefore on m_{ion}): The "normal" m-dependency gives a decrease of k with increasing m_{ion} (see the factor in front of the integral in (11)) while the m-dependency of $\sigma^{CLD}(E)$ in (4) leads according to (10) to an increase of k with increasing m_{ion}. Concerning the absolute values of k^{CLD}, these theoretical values exceed in general the experimental ones by a factor lying between 1.4 and 2 (see Table 1) [28, 29]. For this reason the CLD model cannot be preferred for an interpretation of experimental data, as can be seen from a comparison with the k-values for the AADO model in Table 1. Nevertheless, the influences of the moment of inertia in the centrifugal term of the interaction potential is substantial and should be included in the models [12].

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