MOMENTUM TRANSFER RATE CONSTANTS FOR COLLISION OF Cl^- WITH TRANS- DICHLOROETHYLENE AND PARA-DIFLUOROBENZENE

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ABSTRACT: *A classical theory is developed which calculates the momentum transfer rate constant between an ion and a non-polar molecule. The model takes into consideration the effect of diffraction outside the capture limit on the rate constants. The theory is used to calculate momentum transfer rate constant for Cl^- with trans-dichloroethylene and para-difluorobenzene. Theoretical results are compared to those predicted by the Langevin model and also with the experimental data. It is shown that the inclusion of diffraction outside the capture limit increases the theoretical momentum transfer rate constants. It is suggested that other potential terms may be important in determining momentum transfer rate constants for these systems.*

KEY WORDS: *Classical, Nonreactive collisions, Momentum transfer, Capture limit, Langevin model.*

INTRODUCTION

The dynamics of ion-molecule nonreactive collisions has received considerable attention in recent years. This in part is due to the availability of accurate experimental data which can be used to evaluate the validity of different theoretical models. In this regard, some efforts have been directed toward extensive theoretical studies to satisfy experimental observations. Most recently, *Barker* and *Ridge* (BR) [1] developed a theory of ion-polar molecule collision to calculate the momentum transfer rate constants. The BR theory gives a good agreement with absolute values of some momentum transfer rate constants for collision of an ion with a polar molecule.

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From a practical point of view, momentum transfer rate constants are accurately obtained from ion cyclotron resonance spectra and can provide important information about diffusion cross sections and ion mobilities [2-4]. *Su* and *Bowers* [5] have used an ion cyclotron resonance line broadening technique to measure the momentum transfer rate constant for Cl^- with *trans*-dichloroethylene and *para*-difluorobenzene. In their studies, all experimental rate constants were consistently higher than theoretical predictions based on the Langevin theory. These authors concluded that a more sophisticated theoretical approach other than the Langevin theory is needed to explain the discrepancies between theoretical results and the measured momentum transfer rate constants.

In this work, we present a theoretical approach based on the Langevin model, but one which accounts for diffraction outside the capture limit. The theoretical results are then compared with the experimental momentum transfer rate constants.

THEORY

The model considered here consists of a point charge interacting classically with a polarizable molecule. The system Hamiltonian (with the motion of the center of mass removed) is given by [6]

$$H = \frac{P_r^2}{2\mu} + \frac{L^2}{2\mu r^2} - \frac{q^2\alpha}{2r^4} \qquad (1)$$

where p_r is the radial momentum of the collision partners, L is their orbital angular momentum, μ is the reduced mass of the colliding pair, r is the distance between the ion and the center of mass of the neutral, q is the electron charge, and α is the (angle-averaged) polarizability of the neutral.

In Hamiltonian form, the equations of motion for the canonical pair $\{p_i , q_i\}$ are [7,8]

$$\frac{\partial H}{\partial p_i} = \dot{q}_i \quad ; \quad \frac{\partial H}{\partial q_i} = -\dot{P}_i \quad (i= 1,2,...) \qquad (2)$$

Where p_i and q_i are momentum and coordinate of the ith component and $\dot{p}_i$ and $\dot{q}_i$ are their respective time derivatives. In the system considered here there are two coordinates (r, θ) and two corresponding momenta (p_r , L), that appear to require integration of four equations of motion in Hamiltonian form. These equations are given by

$$\frac{\partial H}{\partial p_r} = \frac{dr}{dt} = \frac{P_r}{\mu} \qquad (3)$$

$$\frac{\partial H}{\partial L} = \frac{d\theta}{dt} = \frac{L}{\mu r^2} \qquad (4)$$

$$\frac{\partial H}{\partial r} = \frac{-dp_r}{dt} = -\frac{L^2}{\mu r^3} + \frac{2\alpha q^2}{r^5} \qquad (5)$$

$$\frac{\partial H}{\partial \theta} = \frac{-dL}{dt} = 0 \qquad (6)$$

where θ is the angle formed by the neutral and r.

Since the total energy of the system is $\frac{1}{2}\mu V_0^2$ where V_0 is the relative velocity at infinite separation, for our purpose, it is convenient to rewrite Eq. (1) as:

$$\frac{1}{2}\mu V_0^2 = \frac{\mu V_r^2}{2} + \frac{L^2}{2\mu r^2} - \frac{\alpha q^2}{2r^4} \qquad (7)$$

At a given ion-molecule separation r, the relative velocity vector V is resolved into two components: the velocity component along the line of centers of collision V_r and the normal component $V_\perp$, as shown in Fig. 1. Solving Eq.(7) for V_r gives

$$V_r^2 = V_0^2 - \frac{L^2}{\mu^2 r^2} + \frac{\alpha q^2}{\mu r^4} \qquad (8)$$

the orbital angular momentum of the colliding particles is given by

$$L = V_0 \mu b = \mu b(\frac{2E}{\mu})^{1/2} = b(2E\mu)^{1/2} \qquad (9)$$

or

$$L = V_\perp r \mu \qquad (10)$$

Where b is the impact parameter.

Combining Eq. (9) and Eq. (10) and solving it for the normal component of the relative velocity yields

$$V_\perp = \frac{V_0 \mu b}{\mu r} = \frac{V_0 b}{r} \qquad (11)$$

Fig. 1 shows the ion-molecule closest approach, r_b , which is the smallest ion-molecule separation for a given trajectory. At this point, there is no radial momentum of the collision partners (p_r= 0) and $V_\perp$ is given by

$$V_\perp = \frac{V_0 b}{r_b} \qquad (12)$$

The closest approach (r_b) can be calculated using Eq. (1) by setting p_r= 0

$$\frac{1}{2}\mu V_0^2 = \frac{L}{2\mu r_b^2} - \frac{q^2\alpha}{2r_b^4} \qquad (13)$$

the total energy of the system and the orbital angular

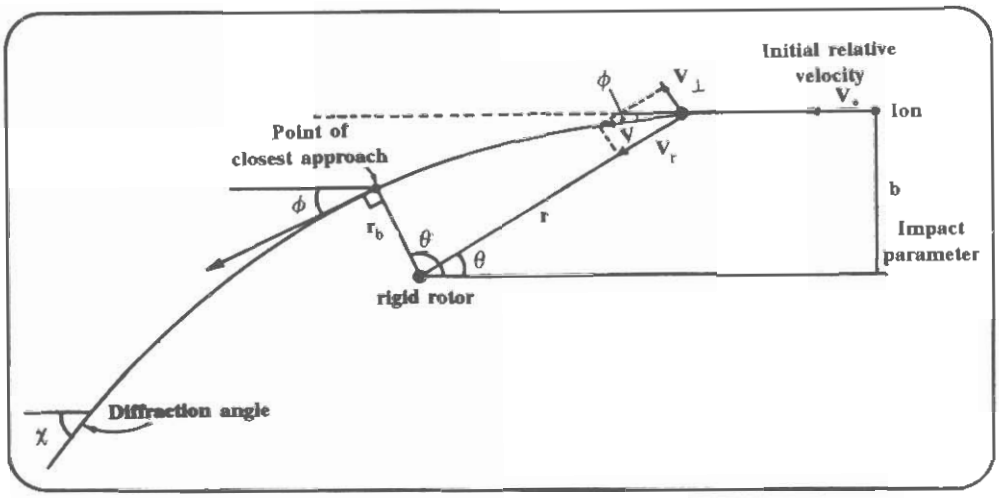

Fig. 1: Schematic diagram of the momentum transfer showing the diffraction angle and the point of closest approach

momentum of the two particles are given by $E= 1/2\ \mu V_0^2$ and $L= V_0\ \mu b$, respectively. Thus Eq. (13) can be rewritten as

$$E = \frac{Eb^2}{r_b^2} - \frac{q^2\alpha}{2r_b^4} \tag{14}$$

The solution to Eq. (14) is the closest approach r_b .

$$r_b = \left[\frac{b^2E + (b^4E^2 - 2E\alpha q^2)^{1/2}}{2E}\right]^{1/2} \tag{15}$$

The momentum transfer rate constant [9] at a given total energy is given by

$$K(E)= [2\pi q(\frac{\alpha}{\mu})^{1/2} + 2\pi \int_{b_c}^{\infty}(1-\cos\chi)b\ db](\frac{M}{M+m}) \tag{16}$$

Where M is the mass of the neutral, m is the mass of the ion and b_c is the critical impact parameter which is given by

$$b_c = (\frac{2q^2\alpha}{E})^{1/4} \tag{17}$$

and χ is the diffraction angle shown in Fig. 1 and is defined as

$$\chi= 2\phi = 2(\theta - \frac{\pi}{2})= 2\theta-\pi \tag{18}$$

where ϕ is the intermediate diffraction angle at the point of closest approach. The first term in Eq. (16) is the familiar Langevin rate constant, the second term represented the momentum transfer rate constant contributed by diffraction outside the capture limit.

Dividing Eq. (3) by Eq. (4) gives

$$\frac{dr}{d\theta} = \frac{P_r r^2}{L} = \frac{\mu V_r r^2}{L} \tag{19}$$

or

$$d\theta = \frac{Ldr}{\mu V_r r^2}$$

Substituting Eq. (8) into Eq. (19) and integrating within proper limits, yields

$$\theta = \int_0^{\theta} d\theta= \frac{L}{\mu}\int_{\infty}^{r_b} \frac{dr}{(V_0^2r^4 - \frac{L^2r^2}{\mu^2} + \frac{\alpha q^2}{\mu})^{1/2}} \tag{20}$$

The thermal energy momentum transfer rate constant is obtained by averaging K(E) over a three-dimensional Boltzmann energy distribution,

$$K(T)= \int_0^{\infty} P(T,E)K(E)\ dE \tag{21}$$

where

$$p(T,E) = \frac{2}{\sqrt{\pi}}(\frac{1}{K_BT})^{3/4}(E)^{1/2}\exp(-E/K_BT)$$

K_B is the Boltzmann constant and T is the system temperature. Eq. (21) is numerically integrated by the Gauss Quadrature method [10]. In the above integration the impact parameter ranges from b_c to b_c + 10Å, the ion-molecule separation ranges from r_b + 55Å to r_b , and the total energy ranges from zero to 20 KT. It is important to mention that a serious effort at analytical evaluation (including a search of available integral tables) of Eq. (21) was made but failed.

RESULTS

Table 1 lists the experimental and theoretical momentum transfer rate constants for Cl^- with *trans*-dichloroethylene and *para*- difluorobenzene. Theoretical rate constants calculated by the induced dipole theory of Langevin [11]

$$K_{nonpolar} = 2\pi\, q(\frac{\theta}{\mu})^{1/2}[\frac{M}{M+m}]$$

where α is the angle average polarizability of the molecule, μ is the reduced mass, and M is the mass of the neutral, are also included in Table 1 for comparison.

Table 1: Experimental and theoretical momentum transfer rate constants at 300 K (All rate constants $\times 10^9$ Cm^3 $molecule^{-1}S^{-1}$)

Ion-molecule collision system	K_{Exp}	$K_{Langevin}$	$K_{present\ theory}$
Cl^- + *trans*-$C_2H_2Cl_2$	1.45	0.94	1.06
Cl^- + *para*-$C_6H_4F_2$	1.91	1.07	1.21

DISCUSSION AND CONCLUSIONS

Table 1 compares the thermal energy momentum transfer rate constant calculated from this approach with the Langevin theory and experimental results at 300 K for the collision of Cl^- with *trans*-$C_2H_2Cl_2$ and *para*-$C_6H_4F_2$.

It is apparent, from the data in Table 1 that the experimental rate constants [5] for both ion-molecule systems are considerably higher than those predicted by the charge induced dipole theory. The large rate constants for the non-polar molecules compared to the charge induced dipole theory are not well underestood. One possible explanation may be that momentum transfer could take place due to diffraction outside the capture limit. The results of this study clearly reveal that the inclusion of diffraction outside the capture limit raises the theoretical momentum transfer rate constants by about 13% . However, calculated rate constants are still much lower than the experimental values. It is suggested that the discrepancy may result from attractive forces other than ion-induced diople potential. It is thus likely that the inclusion of the ion-quadrupolar and the induced dipole-induced dipole terms in the potential function will increase the theoretical momentum transfer rate constants and make them more consistent with the experimental data. Negative ions usually have large polarizabilities. It is believed that the large polarizability of Cl^- (α=2.96Å^3) [12] might make a substantial contribution to momentum transfer rate constants.

Overall, the present approach properly accounts for the effect of diffraction outside the capture limit and raises the theoretical momentum transfer rate constants closer to the exprimental data. Further investigation is required to find out the cause of the relatively small theoretical rate constants compared to experimental data.

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