MOBILITIES AND LONGITUDINAL DIFFUSION COEFFICIENTS OF CH_x^+ IONS IN He. REACTIONS OF CH_3^+ WITH NH_3

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ABSTRACT

We have used a drift tube mass spectrometer with selective introduction (T.D.S.M.) to measure the mobilities and longitudinal diffusion coefficients of positive ions C^+, CH^+, CH_2^+, CH_3^+, CH_4^+ and CH_5^+ in helium at a gas temperature of 300 K, in the 5-100 Td range of the parameter E/N (1 Td = 10^{-17} V.cm^2). The reaction $CH_3^+ + NH_3$ have been studied in the 0.04 eV to 1 eV energy range.

1. EXPERIMENTAL

A drift tube apparatus (T.D.S.M.) with selective introduction of ions has been used for measurements of the mobilities and longitudinal diffusion coefficients. The T.D.S.M. apparatus has previously been described (1). The CH_x^+ ions are generated in an electron impact ion source containing CH_4. The ions are mass selected using a magnetic analyser and injected at low energy (2-3 eV) into the drift tube containing a buffer gas (Helium) After transiting the drift region some of the ions in the swarm effuve through the exit orifice into a quadrupole mass filter and channel electron multiplier. The ion source operates in a repetitive pulsed mode and the spectrum of arrival of the ions is measured electronically with a multichanel analyser. The condition for obtaining a suitable drift velocity is that the experimental arrival time spectrum from which the drift velocity is derived must closely resemble the spectrum calculated by solving the transport equation for the ion in the apparatus (2).
In the general case the transport equation for ions is written:

$$J(r,t) = v_d\, n(r,t) - D\, \nabla\, n(r,t) \qquad |1|$$

Here J (r,t) is the ionic flux density, v_d the drift velocity and D the diffusion tensor. This equation is solved for our apparatus by using the analysis of Moseley et al. reported in ref.2, p.84:

$$\phi(\ ) = \frac{\alpha}{\sqrt{D_L t^3}}\left(v_d + \frac{1}{t}\right) \exp\left[-\frac{1 - v_d\, t^{\ 2}}{4\, D_L\, t}\right] \qquad |2|$$

here α is a numerical coefficient of normalisation. Equation |2| was used to calculate the expected shapes of the arrival time spectra used for comparison with experimental data. The best values for v_d and D_L are obtained by the least squares method.

For kinetic study the reactant neutral gas is added and mixed preliminary with helium. A multiscaler sweep is triggered by a mass selector to obtain kinetic parameters. Rate coefficients, k, are determined in the conventional manner by observing the decrease in the reactant ion counts as a function of time.

2. RESULTS.

a) Ions mobilities

The ions mobilities were computed from the measured drift velocities and corresponding electric field strength E using the relation:

$$v_d = K\,E \qquad |3|$$

and converted to the conventional reduced mobilities K_o by:

$$K_o = K \frac{p}{760} \times \frac{273,16}{T} \qquad |4|$$

p is the helium pressure in Torr and T is the temperature in Kelvin.

Figure 1 presents the reduced mobilities for CH^+, CH_2^+, CH_3^+, CH_4^+ and CH_5^+ in helium, as a function of E/N, where N is the buffer gas number density The unit of E/N used is the Townsend (1 Td = 10^{-17} $V.cm^2$). For the addition of one H atom the change of mobility is larger than predicted by the Langevin theory.

b) Diffusion Coefficients

The Wannier equation expressed in terms of the variable v_d may be put into the form (2):

$$N\,D_L = N\,D(O) + \frac{(M + 3.72m)}{3(M + 1.908m)e} \cdot \frac{v_d}{E/N} \qquad |5|$$

D(O) is the zero-field value of the diffusion coefficient D.
D is calculated by the Einstein equation:

$$K = \frac{e\,D}{k\,T} \qquad |6|$$

m and M are the ion and neutral masses, e is the electronic charge and k the Boltzmann constant.

The products $N\,D_L$ are represented in figure 2. Experimental results are in good agreement with the predictions of Wannier's theory.

c) Rate coefficient

Using the drift velocities of CH_3^+, the reaction times are calculated from the relation:

$$t = \frac{L}{v_d} \quad (L = \text{tube's length})$$

The reaction rate coefficients and products distribution for the $CH_3^+ + NH_3$ reaction are studied at different values of E/N, they remain independent of pressure over the range accessible to the experiment (0.2 - 0.7 torr).

The present results are obtained from ions distribution, studied as a function of NH_3 concentration and extrapolated to $|NH_3| = 0$, in order to consider only the three primary reactions:

$$CH_3^+ + NH_3 \xrightarrow{k^{18}} NH_4^+ + CH_2$$
$$\xrightarrow{k\,32} CH_3NH_3^+$$
$$\xrightarrow{k\,30} CH_2NH_2^+ + H_2$$

Figure 3 gives the graph of the rate coefficients as a function of the collisional kinetic energy in the mass center system.

The mass center kinetic energy is given by:

$$W_{MC} = \frac{M}{M+m} (W - \frac{3}{2} kT) + \frac{3}{2} kT \qquad |7|$$

Here w is the ion kinetic energy given by the Wannier's relation:

$$W = \frac{1}{2} m v_d^2 + \frac{1}{2} M_f v_d^2 + \frac{3}{2} kT \qquad |8|$$

(m = ion mass ; M = neutral gas mass ; M_f = buffer gas mass).

The global mechanism which take into account the reactions between initial products and NH_3, is discussed elsewhere (3).

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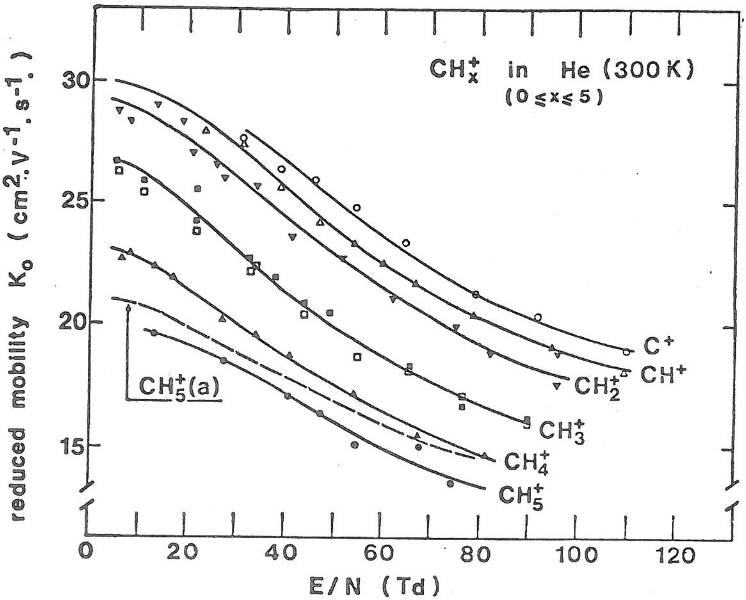

Figure 1

The reduced mobilities of CH_x^+ ions in He at 300 K plotted as function of E/N. (a) Values of W. LINDINGER and D.L. ALBRITTON. J. Chem. Phys. 62, (1975), 3517.

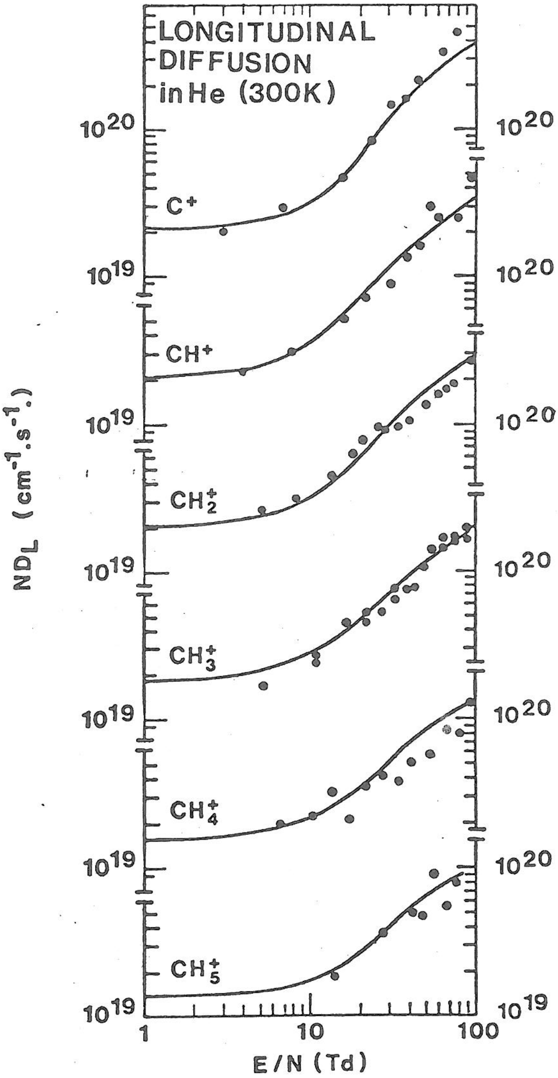

Figure 2
The solids curves are plots of the Wannier equation |5|

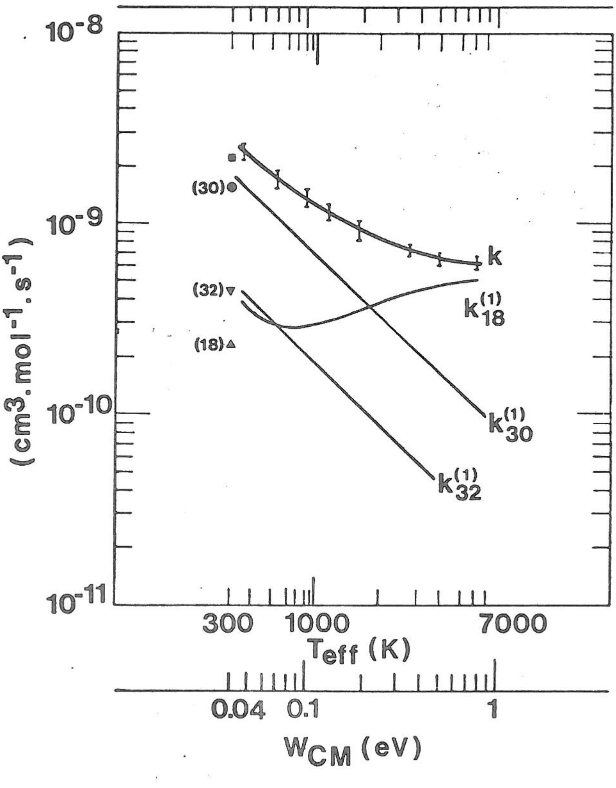

Figure 3

Variation of rate coefficients as a function of the center of mass collisional kinetic energy.