THE INFLUENCE OF ION VIBRATIONAL EXCITATION ON ION MOLECULE REACTIONS

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ABSTRACT

The energy dependences of the reactions $O_2^+ + CH_4$, $CO_2^+ + O_2$, $CO_2^+ + H_2$ and $CO_2^+ + D_2$ were investigated in drift experiments. The results obtained in different buffer gases give evidence for a strong influence of the ion vibrational energies in these reactions.

INTRODUCTION

During the last decade, and especially since the existence of the NOAA flow-drift tube /1/, the dependences of many ion molecule reactions on the relative kinetic energy KE_{cm} between the reactants have been investigated in the energy range from thermal to about 2 eV Ke_{cm}.
Recently also evidence was found in drift experiments for strong dependences of ion molecule reactions on the internal

vibrational energies of the reactant ions /2-4/. In this contribution we present drift tube results on the reactions of $O_2^+ + CH_4$, $CO_2^+ + O_2$, $CO_2^+ + H_2$ and $CO_2^+ + D_2$, all of which are strongly dependent on the internal vibrational energy of the reactant ions.

EXPERIMENTAL

Two apparatuses have been used for the present investigation:

a) The Innsbruck Flow Drift Apparatus /5/ (IFDA), which is a "slow flow" drift tube with a hollow cathode ion source.
b) The NOAA-Flow Drift Tube /1/ (NOAA-FDT), a "fast flow" tube, being essentially a flowing after glow combined with a drift tube.

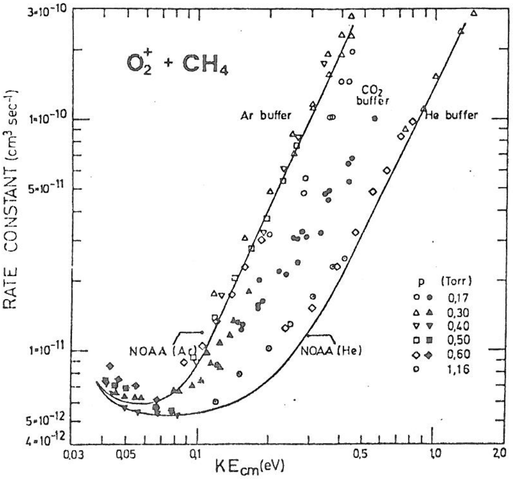
As both apparatuses have been described in the literature /1,5/ no details need to be repeated here.

The above mentioned reactions were measured as a function of E/N, from which the relative kinetic energy KE_{cm} of the reactants is calculated in the usual way /1/. Rate constants, measured in different buffer gases, and plotted as a function of KE_{cm}, show quite different dependences for each buffer gas, when the reactions are influenced by the internal ion vibrational energy. Generally in heavy buffer gases like Argon and N_2, ions get easier vibrationally excited than in a light buffer, like He. Thus we expect higher rate constants in argon than in helium for reactions that are promoted by vibrational energy of the reactant ion and vice versa.

RESULTS

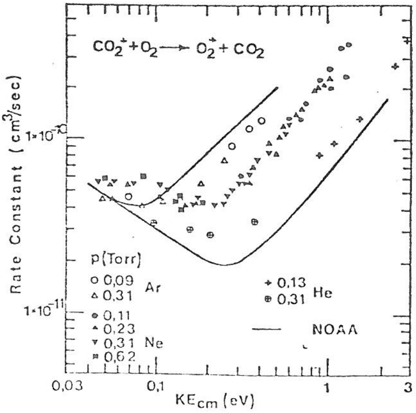
Fig. 1 shows the results for the reaction of $O_2^+ + CH_4$ obtained in Innsbruck (symbols) and Boulder (solid line, taken from Ref. 3). This reaction is slow at room temperature

Fig. 1



(k = $6x10^{-12}$ cm^3sec^{-1}) and has a main exothermic reaction channel into $O_2CH_3^+$, but at elevated energies the slightly endothermic reaction channels to CH_3^+ and CH_4^+ among others become available. According to theoretical considerations of Polanyi and coworkers /6, 7/ this type of reaction should be promoted by vibrational excitation. In fact the rate constant

Fig. 2



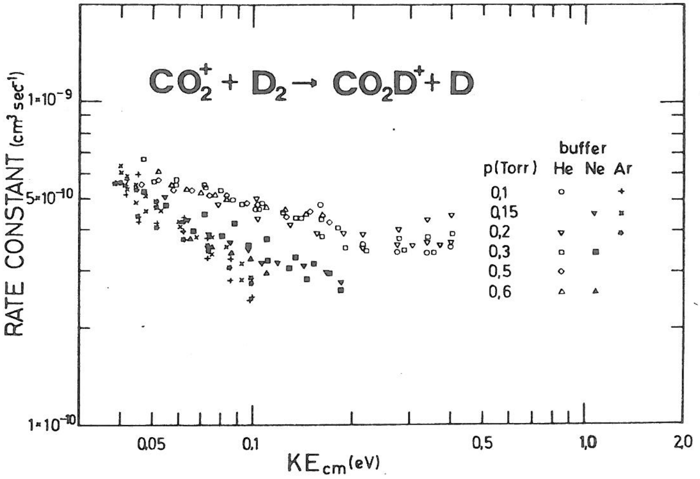


Fig. 3

for the reaction of O_2^+ with CH_4 shows a much stronger increase at elevated energies in an argon buffer where stronger vibrational excitation of the O_2^+ ions occurs than in a helium buffer. The CO_2 buffer is less efficient in vibrationally exciting O_2^+ ions than argon but more efficient than helium. The Innsbruck results for the reaction of CO_2^+ with O_2, which is also promoted by vibrational excitation of the reactant ion are shown in Fig. 2 together with data obtained in a helium and an argon buffer at NOAA /2/. $CO_2^+ + D_2$ on the other hand is a reaction, which is slowed down by vibrational excitation and our results are shown in Fig. 3. There is a stronger decline with increasing E/N and KE_{cm} the heavier the mass of the rare gas buffer is, which means that increasing the vibrational CO_2^+ energy leads to a decline of the rate constant for its reaction with D_2.

NOAA data on the reaction of $CO_2^+ + H_2$ are presented in Fig. 4. Here again the same dependence on the buffer mass is observed. Addition of CO_2 to the argon buffer leads to a decline of the "vibrational temperature" of CO_2^+ due to the

Fig. 4

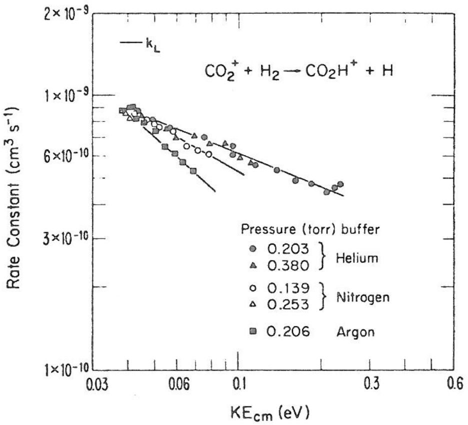
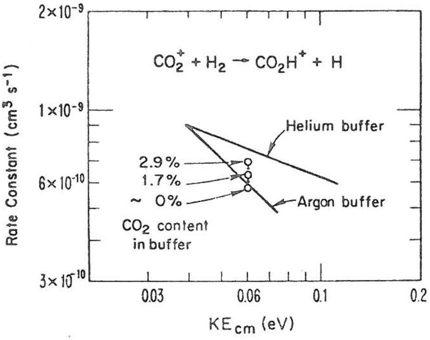


Fig. 5



charge transfer $CO_2^+(v\neq 0) + CO_2 \longrightarrow CO_2^+(v=0) + CO_2$. In fact this "cooling" effect is demonstrated by the results of Fig. 5, where it is shown, that the addition of only a few % of CO_2 to the Ar-buffer leads to a remarkable increase of the rate constant towards the helium buffer data.

CONCLUSION

The present results, together with earlier ones obtained at the NOAA-FDT /2, 3, 8/ and at IFDA /4/ show drift experiments to be an ideal tool to study the dependences of Ion Molecule Reactions on the ion vibrational energies.

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