Beam Studies of the Ion-Molecule Reaction $CO_2^+ + D_2 \rightarrow DCO_2^+ + D$

Hiroshi TOCHIHARA* and Yoshitada MURATA*

Department of Chemistry, Faculty of Science, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171

(Received September 19, 1977)

Reaction cross sections of the reaction $CO_2^+ + D_2 \rightarrow DCO_2^+ + D$ have been measured over the range of the collision energies $E = 0.4$ to 4 eV in the center of mass system. The cross section was obtained from relative values of the reaction $Ar^+ + D_2 \rightarrow DAr^+ + D$ by using the mixed ion beam method. The observed cross sections are about half of the Langevin-Gioumousis-Stevenson cross sections and show approximately $E^{-1/2}$ dependence.

Since the molecular beam technique has been used with great success, the ion beam technique has also been employed for ion-molecule reactions. This method has enabled the study of collision energy dependence of the reaction cross section. The following reactions have been studied extensively:[1-5)]

$$Ar^+ + D_2 \longrightarrow DAr^+ + D, \quad \Delta E = -1.2\ \text{eV}, \quad (1)$$

$$CO^+ + D_2 \longrightarrow DCO^+ + D, \quad \Delta E = -2.0\ \text{eV}, \quad (2)$$

and

$$N_2^+ + D_2 \longrightarrow DN_2^+ + D, \quad \Delta E = -2.5\ \text{eV}, \quad (3)$$

where ΔE denotes the heat of reaction. These reactions are exothermic. The cross sections in these reactions are in proportional to $E^{-1/2}$ at low energies (below 1 eV in the center of mass system**) and decrease more steeply with increasing collision energy. The cross section, σ, of Reactions 1 and 2 is in good agreement with the Langevin-Gioumousis-Stevenson (LGS) cross section[6)] below 1 eV.[2-4)] For Reaction 3 σ is about twice as large as the LGS cross section.[1,4,5)]

In this paper, the reaction

$$CO_2^+ + D_2 \longrightarrow DCO_2^+ + D, \quad \Delta E = -1.1\ \text{eV}, \quad (4)$$

was investigated. Since the incident ion of this reaction is more complex than those of Reactions 1—3, a different energy dependence of σ can be expected. This reaction has been studied by several methods such as flowing afterglow,[7)] mass-spectrometry,[8,9)] ion cyclotron resonance mass-spectrometry,[10,11)] and energy analysis of product ions.[12)] In these studies except for the last method, reaction rate constants were observed only at thermal or a little higher energies. Recently, Mahan and Schubart investigated the velocity vector distribution of DCO_2^+ in detail.[13)]

Experimental

An apparatus for the study of the ion-molecule reaction was constructed chiefly to determine the collision energy dependence of σ. The beam-collison chamber method was employed and a schematic diagram of the apparatus is shown in Fig. 1. The main chamber was evacuated to a pressure around 10^{-4} Pa and operated at around 10^{-3} Pa during the experiment.

The ion source used was a Bayard-Alpert gauge type. The impact energy of the electrons was about 33 eV. The electron current was 1×10^{-5} A and the pressure of the gas introduced into the ion source was about 5×10^{-3} Pa. An attenuation experiment[14)] ensured that the CO_2^+ ion beam produced by 33 eV electron impact in the present experiment did not contain any appreciable amount of metastable ions.

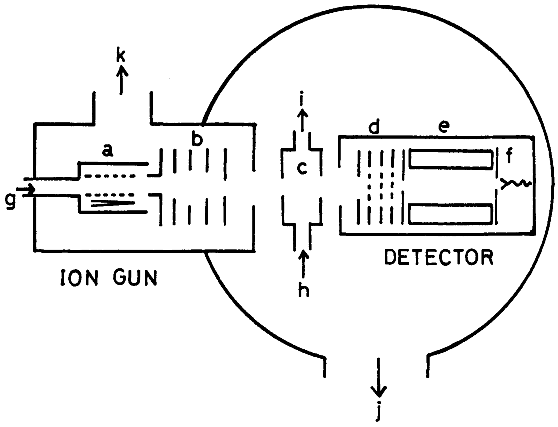

Fig. 1. Schematic diagram of the apparatus. a: Ion source, b: extracting electrode, einzel lens, and aperture, c: collision chamber, d: detection aperture and three-fold plane grids, e: quadrupole mass filter, f: channel electron multiplier, g: gas inlet to ion source, h: gas inlet to collision chamber, i: to ionization gauge, j: to 10 in. oil diffusion pump, k: to 2 in. oil diffusion pump.

The collision chamber was 15 mm thick and the entrance and exit apertures were 2 and 3 mm in diameter, respectively. The distance between the center of the collision chamber and the detection aperture, 4 mm in diameter, was 20.5 mm. Hence, the detection angle was $\pm 5.6°$ at the center of the collision chamber. A quadrupole mass filter was used. In the present experiment, the transmittance of the incident and the product ions in the mass filter is almost the same, since the difference between their masses is small ($\Delta M = 2$). Mass-analyzed ions were detected by a channel electron multiplier. A pulse counting system was used for detection, and the pulse height was such that the counting efficiency for all ionic species was about unity.

The pressure of the target gas in the collision chamber was measured with an ionization gauge which was mounted on the collision chamber. Since it was not suitable to keep the ionization gauge on during the collision experiment, the relationship between the reading of the ionization gauge and the revolution number of a variable leak valve was measured. During the experiment, the pressure of the target gas in the collison chamber was determined only by the revolution number of the variable leak valve. To realize the single collision condition and to obtain as many product ions as possible the pressure of D_2 was around 0.2 Pa throughout the present experiment. Under the single collision condition, σ was obtained by using the thin target formula, $\sigma = i/(INL)$

* Present address: The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106.

** Hereafter, the collision energy is in the center of mass system.

where N is the number density of the target molecules, L is the collision path length, and I and i are the intensities of the incident and the product ions respectively.

It is difficult to obtain the absolute value of N. Hence, we obtained experimentally the relative cross section of Reaction 4 with respect to Reaction 1, *i.e.*, the cross section was obtained from the equation $\sigma_4=\sigma_1 i_4 I_1/i_1 I_4$, where the subscripts 1 and 4 denote Reactions 1 and 4 respectively. The mixed ion beam of Ar^+ and CO_2^+ was employed, which was made by introducing the mixed gases of Ar and CO_2 into the ion source. The intensities, i_1/I_1 and i_4/I_4, were observed under the same scattering condition, *i.e.*, the same number density of D_2 and the same geometry.

Results and Discussion

The cross section σ_1 has been obtained in good agreement by three different groups over a wide range of collision energies.[3] Therefore, Reaction 1 was thought suitable as a reference reaction. The average value $\hat{\sigma}_1$ of σ_1's reported is shown by a solid line in Fig. 2 as a function of the collision energy. The cross section, σ_4, was obtained from the equation $\sigma_4=\hat{\sigma}_1(i_4/I_4)/(i_1/I_1)$ and was plotted as a function of the collision energy (Fig. 2). Differences, between the incident and product ions, in the transmittance of the mass filter and in the counting efficiency of the multiplier have been ignored in this experiment, as mentioned in the Experimental.

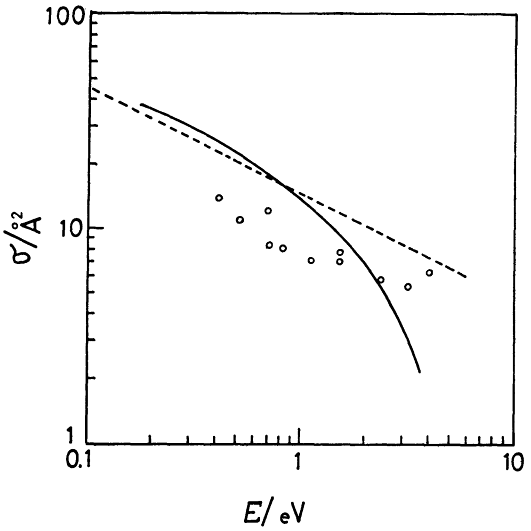

Fig. 2. Reaction cross section σ *vs.* collision energy E for Reaction 4. Open circles, observed cross sections; broken line, LGS cross section.[6] Solid line: average cross section for Reaction 1, $\hat{\sigma}_1$.[3]

In order to obtain an accurate value of σ_4, all of the product ions, DAr^+ or DCO_2^+, had to be collected in both reactions. The collection efficiency of DAr^+ for Reaction 1 in the present experiment was estimated by using data of the angular distribution observed by Herman *et al.*[15] The estimated values were about 70 and 90% at the collision energies 0.4 and 0.7 eV, respectively, and over 95% above 0.7 eV. In the estimation, the geometry mentioned above was used, and the collimated incident beam and the perfect alignment of the detection system were assumed.

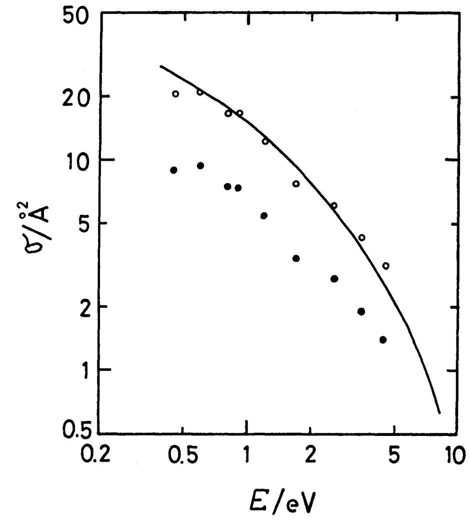

Fig. 3. Reaction cross section σ *vs.* collision energy E for Reaction 1. Solid line, average cross section, $\hat{\sigma}_1$[3]; closed circles, observed cross sections derived from the thin target formula; open circles, observed cross sections normalized to $\hat{\sigma}_1$ at 0.8 eV.

Further data on the collection efficiency in Reaction 1 has been obtained by comparing the energy dependence of the observed cross sections, the closed circles in Fig. 3, with that of $\hat{\sigma}_1$, the solid line in Fig. 3. The observed cross sections were matched to $\hat{\sigma}_1$ at 0.8 eV by multiplying by a constant. The fitted values, the open circles in Fig. 3, are in good agreement with $\hat{\sigma}_1$. This agreement may indicate that the collection efficiency of DAr^+ in the present experiment was almost the same as that of other experiments,[2-4] and that the discrepancy between the observed cross section and $\hat{\sigma}_1$ was caused by an incorrect value of the observed pressure of D_2 in the collision chamber.

The angular distribution of DCO_2^+ reported by Mahan and Schubart[13] was similar to that of DAr^+ in the laboratory system at 2 and 5 eV. Hence, the cross sections, σ_4, obtained in the present experiment give accurate values.

The magnitude of the cross section σ_4 was about 50% of $\hat{\sigma}_1$ in the low energy region and almost the same or larger at energies higher than 2.5 eV. The cross section σ_4 was approximately proportional to $E^{-1/2}$ over the energy range studied in the present experiment, and the magnitude of σ_4 was about 50% of the LGS cross section.

Mahan and Schubart detected the DCO^+ ion in the collision of CO_2^+ with D_2 above the collision energy 1 eV.[13] The peak height corresponding to DCO^+ on the contour map at 4.36 eV, at which the scattering intensity of DCO^+ was strongest, was only 5% of that corresponding to DCO_2^+. Thus, the small cross section was not caused by other reactive collisions.

The magnitude of σ_4 was observed to be about 50% of the LGS cross section which is in good agreement with that obtained by other techniques. Harrison and Myher studied Reaction 4 by mass-spectrometry and observed the reaction rate constant to be 0.6×10^{-9} $cm^3\,s^{-1}$ at a collision energy 0.3 eV.[8] McAllister and

Pitman measured the rate constant by ion cyclotron resonance mass-spectrometry and reported it to be 0.5×10^{-9} cm^3 s^{-1} at thermal energy.[11] These values are about 50% of the rate constant value predicted by the polarization theory,[6] 1.1×10^{-9} cm^3 s^{-1}. That the small rate constant is not due to charge transfer or other reactive collision has been reported.[10]

The small value of σ for Reaction 4 will be discussed by the modified polarization theory, by which the magnitude of the cross section for Reaction 3 can be explained. This will be described and presented in detail in a later paper.[16] Under this theory the incident ion is regarded as a two- or three-centered charged particle.

In Reactions 1—3, σ decreases more steeply than $E^{-1/2}$ with increasing collision energy above 1 eV,[1-5] as is illustrated by the solid line in Fig. 2 for Reaction 1. σ_4 does not illustrate this behaviour. It appears that this steep decrease of σ at the high collision energy is due to the dissociation of the product ion. In Reaction 4, the collision energy may be transferred efficiently into the internal energy of DCO_2^+ and distributed to all vibrational modes. Moreover, the minimum collision energy, above which DCO_2^+ dissociates into $CO_2 + D^+$ or $CO_2^+ + D$, is about 8 eV, if the spectator-stripping reaction occurs. The experiments of Mahan and Schubart indicate that the spectator-stripping reaction is the dominant process of Reaction 4.[13]

Hiroshi Tochihara acknowledges thanks to the Itoh Science Foundation and Matsunaga Science Foundation for partial financial support.

References

1) R. B. Turner, M. A. Fineman, and R. F. Stebbings, *J. Chem. Phys.*, **42**, 4088 (1965).

2) J. B. Homer, R. S. Lehrle, J. C. Robb, and D. W. Thomas, *Nature*, **202**, 795 (1964).

3) M. Henchman, "Ion-Molecule Reactions," Vol. 1. ed by J. L. Franklin, Plenum Press, New York (1972), pp. 101, 259.

4) D. Hyatt and K. Lacmann, *Z. Naturforsch., Teil A*, **23**, 2080 (1968).

5) P. M. Hierl, L. W. Strattan, and J. R. Wyatt, *Int. J. Mass Spectrom. Ion Phys.*, **10**, 385 (1972/1973).

6) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

7) F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, *J. Chem. Phys.*, **46**, 2802 (1967).

8) A. G. Harrison and J. J. Myher, *J. Chem. Phys.*, **46**, 3276 (1967).

9) K. R. Ryan, *J. Chem. Phys.*, **61**, 1559 (1974).

10) D. L. Smith and J. T. Futrell, *Int. J. Mass Spectrom. Ion Phys.*, **10**, 405 (1972/1973).

11) T. McAllister and P. Pitman, *Int. J. Mass Spectrom. Ion Phys.*, **19**, 423 (1976).

12) A. Ding, *Z. Naturforsch., Teil A*, **24**, 856 (1969).

13) B. H. Mahan and P. J. Schubart, *J. Chem. Phys.*, **66**, 3155 (1977).

14) B. R. Turner, J. A. Rutherford, and D. M. J. Compton, *J. Chem. Phys.*, **48**, 1602 (1968).

15) Z. Herman, J. Kerstetter, T. Rose, and R. Wolfgang, *Discuss. Faraday Soc.*, **44**, 123 (1967).

16) H. Tochihara and Y. Murata, to be published.