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Dynamics of $\text{CO}_2^+ - \text{D}_2$ Collisions. II.

Steven G. Hansen and Bruce H. Mahan

The reaction of CO_2^+ with H_2 and its isotopes has been extensively studied at thermal collision energies. Rate constants for the reaction $\text{CO}_2^+ (\text{H}_2, \text{H}) \text{HCO}_2^+$ have been measured¹ ranging up to the theoretical Langevin collision rate constant² ($1.4 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$), but the reaction $\text{CO}_2^+ (\text{H}_2, \text{OH}) \text{HCO}^+$ has never been observed at thermal energies. This is somewhat surprising as the energetics of HCO^+ formation are similar to HCO_2^+ formation, the reactions being exothermic by 0.8 eV and 0.9 eV respectively. The HCO^+ reaction channel was studied by Mahan and Schubart³ (hereafter referred to as I) using the ion beam technique in the initial relative energy range of 1-20 eV. Velocity vector distributions indicated that at relative energies below 4 eV the HCO^+ resulted from the decay of a long lived H_2CO_2^+ complex. In an effort to determine the threshold energy for HCO^+ formation, we have reinvestigated this reaction using a new ion-molecular beam apparatus designed to operate at lower ion energies. This apparatus will be described in detail in a future publication.⁴

CO_2^+ was produced by the impact of 160 eV electrons on CO_2 . Beam attenuation experiments showed that the electronic state distribution of these ions was identical to that of CO_2^+ extracted from a microwave discharge. Thus, as discussed in I, these ions are predominantly in their ground electronic and lowest vibrational states. Data were obtained by sending CO_2^+ beams of various energies through a rudimentary scattering

cell containing H_2 and measuring HCO^+ velocity spectra in the direction of the ion beam. Using the result given in I that at these energies the HCO^+ product velocity vectors are distributed symmetrically about the center of mass velocity, 3-dimensional maps were synthesized by rotating the velocity spectra about the center of mass velocity. The total volume under these surfaces was measured and is plotted vs relative collision energy in Figure 1. No attempt was made to calculate the actual relative total cross section for HCO^+ formation because of the limited resolution of the velocity spectra.

The threshold for HCO^+ formation as seen in Figure 1 is about 1.0 eV. We also obtained data for the reaction $\text{CO}_2^+ (\text{D}_2, \text{OD}) \text{DCO}^+$. DCO^+ was detected at a CO_2^+ laboratory energy of 14 eV (1.17 eV relative energy) but was not found at a CO_2^+ energy of 11 eV (0.92 eV relative). These results are consistent with the measured HCO^+ threshold. In spite of this agreement, we believe a cautionary note is in order. The apparatus used was designed to measure differential cross sections, not total cross sections. Also, variations in detector transmission efficiency as a function of product energy can lead to systematic errors. Therefore we report the measured threshold to be 1.0 ± 0.3 eV.

The reaction $\text{CO}_2^+ (\text{D}_2, \text{D}) \text{DCO}_2^+$ which was studied in the 2-10 eV relative energy range in I, was also reexamined at lower energies. In this study a beam of CO_2^+ produced either by electron impact or in a microwave discharge was crossed at

90° by a beam of supersonically expanded D₂. A typical DCO₂⁺ final velocity vector distribution is shown in Figure 2.

The contour map is asymmetric about the ±90° axis, which indicates that at an initial relative energy of 0.69 eV, DCO₂⁺ is formed mainly by a direct interaction mechanism. The asymmetry of the distribution persists down to 0.27 eV which was the lowest energy studied. Evidently, even at this low collision energy, most CO₂⁺-D₂ collisions do not sample the deep potential energy well (1.7 eV below D + DCO₂⁺) associated with the D₂CO₂⁺ intermediate.

One other point concerning the CO₂⁺(D₂,D)DCO₂⁺ reaction merits discussion. In order to rationalize a large spread in measured thermal rate constants for this reaction, it has been suggested⁵ that different internal states of CO₂⁺ are populated depending on the method of formation. In particular, it was theorized that CO₂⁺ ions which become thermalized in a microwave discharge react much faster than ions produced by electron impact. As stated earlier, we were unable to detect any difference between CO₂⁺ ions, or the reaction of these ions, regardless of how they were formed. Thus, our results tend to negate the hypothesis of Reference 5.

This work was done with support from the U. S. Department of Energy under Contract No. W-7405-Eng-48.

References:

1. F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys. 46, 2802 (1967).
2. G. Gioumousis and D. P. Stevenson, J. Chem. Phys. 29, 294 (1958).
3. B. H. Mahan and P. J. Schubart, J. Chem. Phys. 66, 3155 (1977).
4. J. M. Farrar, S. G. Hansen, and B. H. Mahan, to be published.
5. K. R. Ryan, J. Chem. Phys. 61, 1559 (1974).

Figure Captions

Figure 1. Plot of the integrated intensity of HCO^+ as a function of initial relative energy for the reaction $\text{CO}_2^+ (\text{H}_2, \text{OH}) \text{HCO}^+$. Different symbols denote data taken on different runs. A smooth line is drawn through the data points.

Figure 2. A contour map of the specific intensity of DCO_2^+ from $\text{CO}_2^+ - \text{D}_2$ collisions at an initial relative energy of 0.69 eV. The intensity maximum occurs near the spectator stripping velocity which is marked by a small cross.

Figure 1

Figure 2

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