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14. ABSTRACT

The overall rate constant of the dissociative recombination of CO_2^+ was first measured in 1967. Since then, the room-temperature rate was measured several times and the values obtained varied in the narrow range of $(3.1\text{-}4.0) \times 10^{-7}$ cm^3 s^{-1}. Recently, the rate was measured at the Aarhus storage ring in Denmark (ASTRID) and found to be larger, 6.5×10^{-7} cm^3 s^{-1} at 300 K. with an electron temperature dependence of $T^{-0.8}$. Experiments carried out at the ion storage ring CRYRING, operated by the Manne Siegbahn Laboratory of Stockholm University, yield data that are in excellent agreement from 0.008 to 0.2 eV. Below 0.008 eV, the CRYRING data are higher, and are believed more reliable at lower energies because of the narrower energy distribution in the CRYRING experiment. A small difference at higher energies may be caused by smaller accumulation times and therefore poorer statistics in the CRYRING experiment.

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Rate constants and branching ratios for the dissociative recombination of CO_2^+

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INTRODUCTION

Dissociative recombination (DR) of CO_2^+ has been the subject of numerous studies. The overall rate constant of this reaction was measured for the first time in 1967.[1] Since that time the room-temperature rate was measured several times using swarm techniques[2–4] and the obtained values were found to vary in the narrow range of $(3.1–4.0) \times 10^{-7}$ cm^3 s^{-1}. Recently, the rate constant was measured in the Aarhus storage ring in Denmark[5] (ASTRID) and found to be larger, 6.5×10^{-7} cm^3 s^{-1} at 300 K with an electron temperature dependence of $T^{-0.8}$.

There are three exothermic channels,

$$\begin{aligned}
CO_2^+ + e \quad &\rightarrow CO_2 + 13.8 \text{ eV}, \\
&\rightarrow C + O_2 + 2.3 \text{eV}, \\
&\rightarrow CO + O + 8.3 \text{ eV}.
\end{aligned} \quad (1)$$
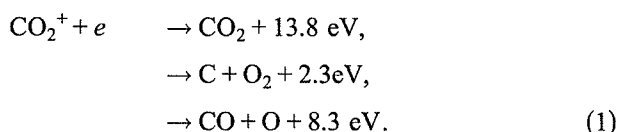
The three-body channel producing $C+2O$ is endothermic by 2.8 eV. Until recently, it was assumed that the reaction proceeded exclusively through the $CO+O$ channel. However, the ASTRID storage ring results showed that the $C+O_2$ channel occurred in $9\pm3\%$ of the reactions and that possibly some CO_2 did not dissociate ($4\pm3\%$), although that was described as unlikely. In addition to this work on rates and overall products, much recent work has also gone into elucidating which states of CO were produced.[2,6–8]

The recombination of CO_2^+ is important in the atmospheres of Venus and Mars.[9,10] When the ASTRID results showing a significant $C+O_2$ channel were incorporated into models of the ionospheres of these planets, it was shown that the predicted amount of C atom production increased significantly.[9,11] Due to the importance of this reaction and the surprise that the rearrangement channel was relatively prominent, we have remeasured the energy dependence of the rate constants and the product distribution in the cryogenic ion source ring (CRYRING) storage ring.

EXPERIMENT

The experiments were carried out at the ion storage ring CRYRING, operated by the Manne Siegbahn Laboratory of Stockholm University. The techniques used at CRYRING have been described in detail[12,13] and we give only a brief description here. CO_2^+ is made in a Nielsen plasma source, run in a mode where CO_2 and Ar are added to the source ($P \sim 10^{-1}$ Torr) and the high anode voltage is pulsed (1 kV). The pulsing helps extend the lifetime of the source before maintenance is needed. The CO_2^+ ions are injected into the ring and accelerated to 2.2 MeV. Electrons are merged with the CO_2^+ ions in an electron cooler. The ions are stored for 2.6 s before the data are taken. Fast neutral products from the DR reaction are detected with a surface-barrier detector (SBD) and preamplifier with an output signal amplitude that is given by the total energy deposited in the detector within the integration time of the electronics, i.e., all particles from one DR event arrive simultaneously and deposit an energy equal to that of the main CO_2^+ beam. Rate constants/cross sections are studied by ramping the electron beam around a center-of-mass energy of 0 eV. In the present study, the cross sections and rate constants were derived in the normal manner.[13] Corrections were made for the background and for the end effects due to the toroidal nature of the guiding magnetic fields at both ends of the electron cooler. Product branching information was derived at nominally zero energy by inserting a grid in front of the detector (Ref. 13). In this way, one or more of the neutral products from a specific recombination event may hit the grid rather than the detector. That event then is detected at the energy corresponding to the mass of the particle(s) that are transmitted through the grid. A probability matrix is created and diagonalized yielding the product information.

RESULTS AND DISCUSSION

Figure 1 shows the present results for rate constants as a function of the center-of-mass kinetic energy along with
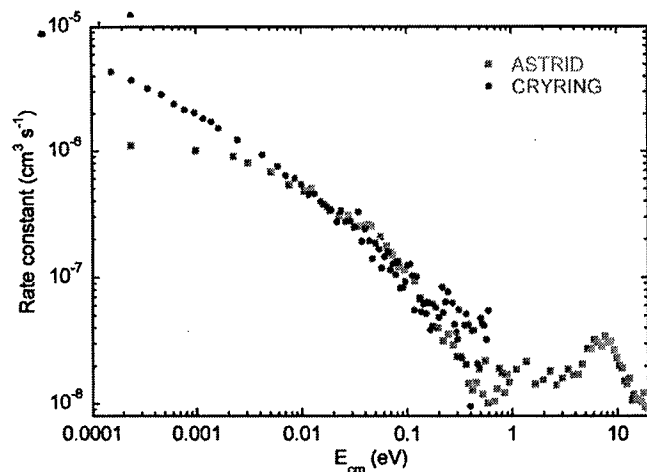
FIG. 1. Rate constant vs center-of-mass kinetic energy. Circles are the present data and the squares are data from the ASTRID storage ring (Ref. 5). The data have not been deconvoluted, i.e., do not represent thermal distributions of electrons.

FIG. 2. Raw signals used to determine the CO_2^+ dissociative recombination branching ratio. Red (upper curve), blue (lower curve, except for 12 amu), and green (middle curve, except for 12 amu) refer to the total signal, a background signal, and that due only to dissociative recombination (total background).

similar data from the ASTRID experiment.[5] These are the raw data not accounting for the electron-energy spread in the experiments. The data are in excellent agreement from 0.008 to 0.2 eV. Below 0.008 eV, the CRYRING data are higher. The difference is due to the fact that the energy distribution is narrower in the CRYRING experiment, which allows more reliable measurements to be made at lower energies. Just above 0.2 eV, the experiments diverge slightly and the present data stop at energies just above this. These low values are very hard to measure, requiring long integration times, and are at the limit of measurability. The small difference at higher energies may be caused by smaller accumulation times and therefore poorer statistics in the CRYRING experiment. The ASTRID data show a resonance at just below 10 eV.

Absolute cross sections are obtained by accounting for the energy spread in the experiment. The thermal rate constants are calculated by convoluting the resulting cross sections with a thermal electron distribution. The results can be expressed as $4.2 \times 10^{-7}(T_e/300)^{-0.75}$ cm^3 s^{-1}. The absolute systematic error is estimated to be ±20%. The truly thermal (300 K) rate constant has been measured previously in several swarm experiments.[1–4] The values range from 3.1 to 4.0×10^{-7} cm^3 s^{-1}, in good agreement with the present measurement. A similar deconvolution–reconvolution procedure was also undertaken in the ASTRID storage ring,[5] where the rate constants were found to be represented as $6.5(\pm 1.9) \times 10^{-7}(T_e/300)^{-0.8}$ cm^3 s^{-1}. The 300-K value from ASTRID agrees within error with the other measurements, and the energy dependence is in excellent agreement with the present results.

The grid in raw data used to determine the branching ratio are shown in Fig. 2. In this figure, the energy deposited into the surface barrier detector is converted to mass in amu by normalizing to the full beam peak at a mass of 44 amu. Three spectra are shown: (1) the total signal at a center-of-mass energy of zero, (2) a background signal recorded at a center-of-mass energy of 1 eV, and (3) the difference between the two which is the signal due to dissociative recom-
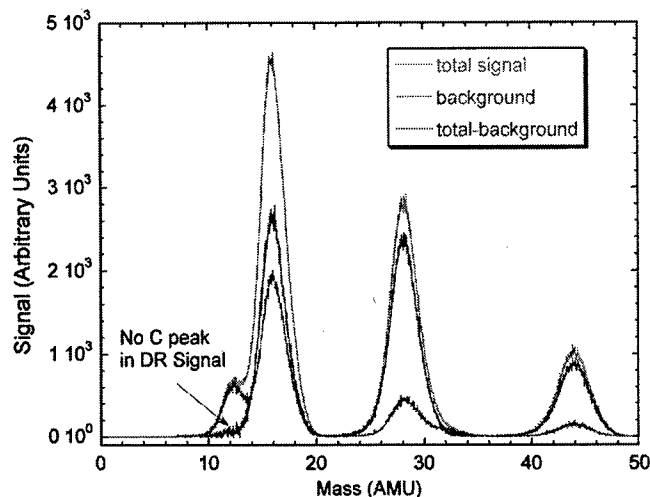
bination. Note that the spectra in Fig. 2 are normalized to the total number of counts hitting a residual gas analyzer (in a separate section of the ring) during the accumulations for both the total signal and the background signal. This procedure accounts for drifts in the total beam current. In the total and background spectra, four peaks are observed corresponding to the masses C, O, C+O, and C+2O hitting the detector. The latter peak represents all products from a single recombination event hitting the detector in a short-time window and therefore counted at the full beam mass/energy. The dissociative recombination spectrum has only three peaks within error, corresponding to O, CO, and all particles passing the grid. No definitive peak corresponding to only C or O_2 hitting the grid is observed after the background subtraction. Note that the area under the O and CO peaks is the same even though the peaks heights appear different.

After solving the probability matrix to derive the branching ratios, we find that all or most of the recombination proceeds through the CO+O channel; 100(−6)%. Note that the (−6) is the error which is unidirectional. The C+O_2 and CO_2 channels can be presented as 0(+4)% and 0(+2)%, respectively. Again unidirectional error bars apply. The absence, within our errors, of the C+O_2 and CO_2 channels is in contrast to the results from ASTRID where 9±3% and 4±3% were found for these two channels, respectively. Even though error limits given for the latter channel indicate that some CO_2 must have been detected in that experiment, they considered it unlikely since the parent neutral has never been observed in the recombination reactions of small ions.

The C+O_2 channel, while exothermic, requires an unlikely rearrangement. Two oxygen atoms on opposite ends of the linear CO_2^+ must form a bond on a very fast time scale since the reaction is quite exothermic and there are only a few degrees of freedom to absorb the energy needed to increase the lifetime of the excited parent. Such bond forming is observed in CH_2^+ (12%) (Ref. 14) but not in NH_2^+ DR.[15] However, that reaction involves H atoms, which are much

more mobile. The likely source of the disagreement is an incorrect background subtraction. The 4% CO_2 product in the ASTRID experiment may indicate that slightly more background should have been subtracted. Another possible explanation is that the CRYRING source operates at higher pressure than the ASTRID one. The CRYRING ions would probably be cooler due to quenching collisions in the source, and the $C+O_2$ channel would be related to the vibrationally excited ions at ASTRID. In any case, the present results indicate that at least for cooler ions this channel is absent.

The recent ASTRID results, which showed that there was a significant $C+O_2$ channel, were incorporated into models of the atmospheres of Venus and Mars.[9,11] The incorporation of this channel had a substantial effect on the models showing that this reaction was a major source of C in both planets. The present results show that this modification was, in fact, misleading.

In summary, the present results confirm that all the recombination of CO_2^+ results in a simple bond breaking to form CO plus O within our experimental error. This negates the need to reanalyze the ionospheric models of Mars and Venus. The present rate constants show good agreement with previous measurements at 300 K and the electron energy dependence is essentially identical to the previous storage ring results.

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