Guided ion beam investigation of the reaction CO^+ + CO. C-O bond activation and C-C bond formation

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Abstract

We have investigated six different endothermic channels in the reaction of CO^+ ions with neutral CO. For each ionic product we have measured the kinetic energy dependence of the integral cross section and inferred the neutral products by the reaction energetics. The onset of the process producing C^+, O, and CO, has been identified by a feature of the integral cross-section located at about 8.5 eV. Measurements of the product isotopic ratio suggest that C^+ originates from both the CO^+ ion and the neutral CO molecule. For the reaction channels producing C_2^+ + O_2 and C_2O^+ + O respectively, measurements of the reaction thresholds allow us to estimate the heats of formation of these two ionic products, $\Delta_f H^0(C_2^+)$ = 19.8 ± 0.2 eV and $\Delta_f H^0(C_2O^+)$ = 14.7 ± 0.2 eV. These values are in good agreement with recent independent estimations. Finally, we re-evaluated the dissociation energy of $C_2^+(X\ ^4\Sigma_g^-)$, $D_0(C^+\text{-}C)$ = 6.2 ± 0.2 eV.

Introduction

In the past, the bimolecular reaction $CO^+ + CO$ has been studied by using mass spectrometry [1, 2] as well as ion cyclotron resonance (ICR) techniques [3]. Both C^+ and C_2O^+ ionic products were observed in these early studies, and it was concluded that they are produced in the reaction of electronically excited $(CO^+)^*$ ions since ground state CO^+ ions do not have enough internal energy to overcome the reaction endothermicity. In this work we have reinvestigated the title reaction with a precise control of the primary ion velocity, and measured the integral cross section for each product channel as a function of relative energy. One major difference between our work and previous ones is that while previous studies deal with the reaction of electronically excited $(CO^+)^*$ reactant ions, we have studied the reaction of CO^+ ions in the electronic ground state. Thus - in our case - the energy required to overcome the reaction endothermicity is largely provided by the collision energy.

The following endothermic [4] channels have been investigated:

$$CO^+ + CO \rightarrow C^+ + CO_2 \qquad\qquad \Delta H_0^0 = 2.90 \text{ eV} \qquad\qquad (1)$$
$$CO^+ + CO \rightarrow C^+ + O + CO \qquad\qquad \Delta H_0^0 = 8.36 \text{ eV} \qquad\qquad (2)$$
$$CO^+ + CO \rightarrow O^+ + C_2O \qquad\qquad \Delta H_0^0 \sim 7.5 \text{ eV} \qquad\qquad (3)$$
$$CO^+ + CO \rightarrow O^+ + C + CO \qquad\qquad \Delta H_0^0 = 10.72 \text{ eV} \qquad\qquad (4)$$
$$CO^+ + CO \rightarrow C_2^+ + O_2 \qquad\qquad \Delta H_0^0 \sim 8.2 \text{ eV} \qquad\qquad (5)$$
$$CO^+ + CO \rightarrow C_2O^+ + O \qquad\qquad \Delta H_0^0 \sim 5.6 \text{ eV} \qquad\qquad (6)$$

Other minor ionic products such as O_2^+, and CO_2^+ might be present. However, their signals are either too weak or are strongly affected by impurities, making their identification dubious.

Reaction (2), which produces the same ionic product as reaction (1), was not observed in previous studies. In the present work, this reaction channel is identified by a structure in the energy dependence of the cross section. Besides, we observed the additional reaction products O^+ and C_2^+. Finally, measurements of the appearance energies of C_2^+ and C_2O^+ allow us to evaluate the heat of formation $\Delta_f H^0$ and the dissociation energy D_0 for these two molecular ions.

Experimental

The experimental apparatus is a modified version of a previously used ion-molecule reaction mass spectrometer [5 - 7]. A schematic view of the apparatus is shown in figure 1. It consists of two differentially-pumped vacuum chambers. The first chamber - pumped by means of a 1000 l/s turbomolecular pump - contains the ion source which is followed by a 90° magnetic-sector mass spectrometer. The CO^+ ion beam is produced by electron-impact of CO. This ionization method may produce a large fraction of electronically excited ions. By varying the electron energy we indeed observe a shift of the product appearance energies. For the data presented here, we used electrons at 16 eV to ionize CO. Since the appearance energy of the first excited state $CO^+ (A\ ^2\Pi)$ is 16.58 eV [8], we expect that most of the CO^+ ions are in their ground electronic states $(X\ ^2\Sigma^+)$. However, the population of excited vibrational and rotational states cannot be excluded.

At the exit of the magnetic-sector mass spectrometer, the ion beam is focussed by means of a lens system and enters the second chamber. Here the ion beam is injected into a

radio-frequency octopole ion guide [9] which is surrounded by the reaction cell. Changing the octopole dc potential varies the collision energy. The axial energy distribution of the ion beam is measured by using the octopole as a retarding field energy analyzer. Typical ion energy distributions have a full width at half-maximum of about 0.5 eV in the laboratory reference frame. The collision energy in the laboratory frame (E_{lab}) is converted to that in the center-of-mass frame (E_{cm}) by using the expression $E_{cm} = E_{lab} \, m \, (M+m)^{-1}$, where m and M represent the mass of the neutral and ionic reactants, respectively.
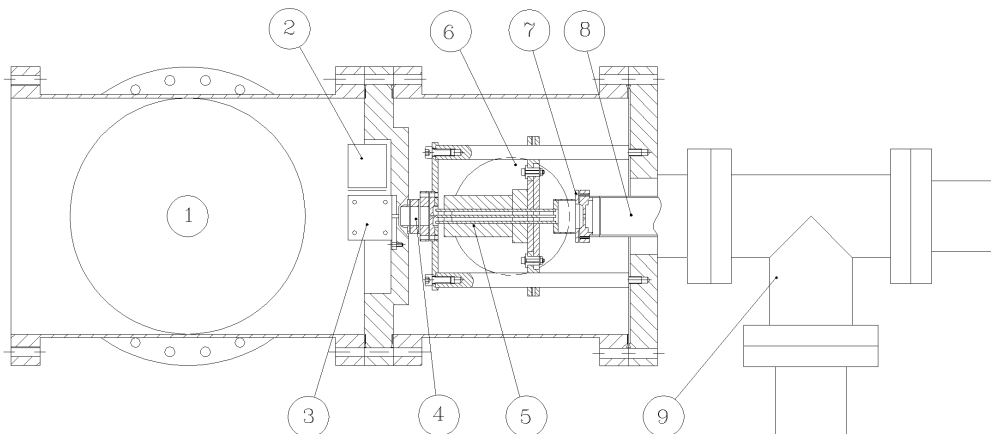

Fig. 1: Schematic view of the apparatus: 1) 1000 l/s turbomolecular pump, 2) ion source, 3) magnetic-sector mass spectrometer, 4) ion optics, 5) octopole ion guide and scattering cell, 6) 250 l/s turbomolecular pump, 7) ion optics, 8) quadrupole mass spectrometer, 9) ion detector.

The CO reactant gas is introduced in the reaction cell at pressures below 10^{-4} mbar to avoid multiple collisions. The second vacuum chamber is evacuated by a 250 l/s turbomolecular pump which keeps the background pressure below 10^{-6} mbar under operating conditions.

Reactant and product ions are collected, guided to a quadruple mass spectrometer and finally counted by means of a channeltron electron multiplier. Absolute integral cross sections $\boldsymbol{s}$ are estimated by using the expression $\boldsymbol{s} = a \, I_p / I_s$, where a is a constant, I_p is the intensity of product ions and I_s is the intensity of the primary ion beam. The constant a has been determined by normalizing our data on well known cross sections, such as $Ar^+ + CO$ [10]. Absolute cross sections thus determined may be affected by large errors. We conservatively estimated that the errors are within $\pm$ 30%. However, relative cross sections are much more accurate, uncertainties being estimated at $\pm$ 5%.

Results and discussion

1. Production of $C^+ + CO_2$ and $C^+ + CO + O$

Our measurements, as well as previous work [1-3], indicate that C^+ is the major ionic product in the reaction $CO^+ + CO$. Figure 2 shows the total cross section for the production of C^+ as a function of center of mass energy (E_{cm}), in the range 2 ~ 30 eV. C^+ ions appear between 2 and 3 eV. The cross section rises up to 8 ~ 9 eV where a change of slope is
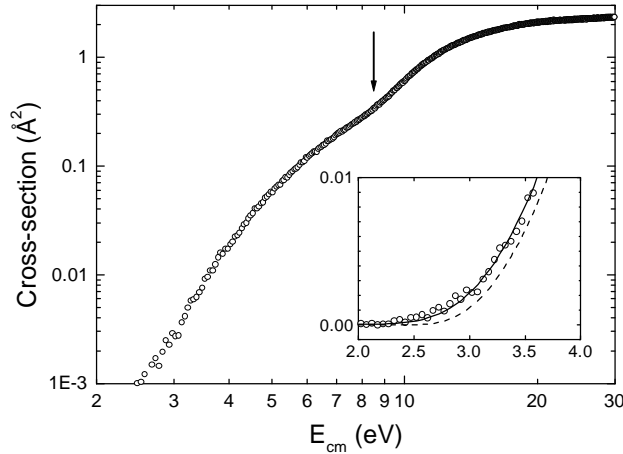
observed.

Fig. 2: Total cross section for the production of C^+ in the reactions (1) and (2), as a function of center of mass energy (E_{cm}). The arrow indicates the position of the change of slope attributed to the onset of reaction (2). The inset shows data in the threshold region. The dashed line represents the model cross section, whereas the full line represents its convolution over the reactant energy distribution.

One interesting thing here is the determination of the reaction threshold - E_0 - for the appearance of C^+. As in our previous work [7], we assume that the energy dependence in the threshold region can be analyzed by a model cross section of the form $s(E) = s_0 (E-E_0)^n E^{-1}$ where E_0, s_0 and n are adjustable parameters [11]. After the appropriate convolution over the reactant energy distribution, calculated cross sections are compared with experimental data and E_0, s_0, and n are optimized by an iterative fitting procedure, that yields $E_0 = 2.5$, $s_0 = 0.0225$, and $n = 2.7$. The experimental threshold value of 2.5 ± 0.1 eV for the production of C^+ appears to be smaller by 0.4 eV with respect to the thermodynamic endothermicity of reaction (1), 2.9 eV. This discrepancy can be rationalized by considering that primary CO^+ ions may be ro-vibrationally excited. It is well known that the ro-vibrational excitation of the reactants can promote endothermic reactions [12], therefore shifting the reaction onset to lower collision energies.

An interesting feature shown in figure 2 is the change of slope which occurs at about 8.5 eV. Similar structures have been observed by Teloy and co-workers who studied the reaction $N^+ + CO$ [13], and by Sievers and Armentrout who studied the reaction $NbO^+ + CO$ [14]. These structure have been attributed to the opening of new reaction channels. In our case, it appears reasonable to assume that the feature observed at about 8.5 eV marks the onset of reaction (2), since its thermodynamic value is 8.36 eV.

C^+ ions can originate either from primary CO^+ ions (by simple collision induced dissociation (CID) or by reaction (1)), or from neutral CO molecules (by dissociative charge transfer reaction). Since these processes are in fact different reaction channels, we tried to identify each of them. The measurements presented here were performed by using the natural mixture of $^{13}CO/^{12}CO$, 1.1/98.9. We changed the ratio $^{13}CO^+/^{12}CO^+$ in the primary ion beam and measured the corresponding $^{13}C^+/^{12}C^+$ ratio in the product signal.
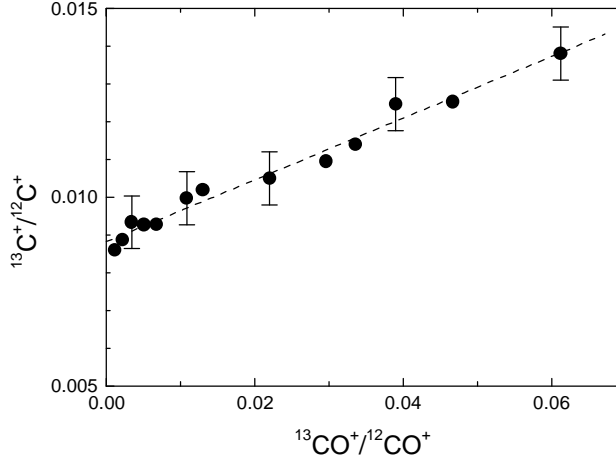
Fig. 3: Isotopic ratio of the C^+ product ions as a function of the isotopic ratio of the CO^+ reactant ions. See text for details.

Results at $E_{cm} = 40$ eV are plotted in figure 3. We found a linear relation between the $^{13}C^+/^{12}C^+$ product ratio and the $^{13}CO^+/^{12}CO^+$ reactant ratio, with a non-zero intercept of the linear regression. With $^{13}CO^+/^{12}CO^+ = 0$, that is with a pure $^{12}CO^+$ beam, the $^{13}C^+/^{12}C^+$ ratio is about 0.009. Clearly, the $^{13}C^+$ signal observed in this case results from the neutral CO. On the other hand, the value 0.009 is smaller than the natural abundance ratio of carbon isotopes (about 0.011), value that would be expected if all the C^+ products would result from neutral CO molecules. This finding, together with the observation that the $^{13}C^+/^{12}C^+$ ratio increases by increasing the $^{13}CO^+/^{12}CO^+$ ratio in the primary beam, suggests that there are additional contributions of $^{12}C^+$ originating from $^{12}CO^+$ reactant ions. Therefore, we conclude that C^+ ions originate from both the ionic and the neutral carbon monoxide reactants. It would be interesting to extend these measurements at low energies, where different reaction mechanisms are operative. Unfortunately in this energy range the cross section is very small and measurements very difficult. The use of isotopically labeled reactants could be of help, and such experiment is planned in the future.

2. Production of O^+ + C + CO

The O^+ signal was found to be much weaker than that of C^+. Essentially this is related to the fact that in the CO^+ ion the positive charge is mainly on the carbon atom [15]. We had problems to detect O^+ due to impurities present in the apparatus. Corresponding to mass 16, we found a large count rate (about 250 count s^{-1} (cps)), at collision energies well below the expected onset for the production of O^+. Since the typical noise of our machines is ≤ 1 cps, we concluded that this signal is due to some impurities, most probably hydrocarbons. The real count rate of O^+ ions - obtained after subtraction of the background signal - is about 150 cps at the maximum position. Of course, this procedure is not free from systematic errors and provides a signal-to-noise ratio that is much worse with respect to the other measurements.

In figure 4 we show the cross section of O^+ from 5 to 25 eV. At the maximum, the cross-section for O^+ production is about 100 times smaller than that for C^+. O^+ could be produced in either reactions (3) and (4).
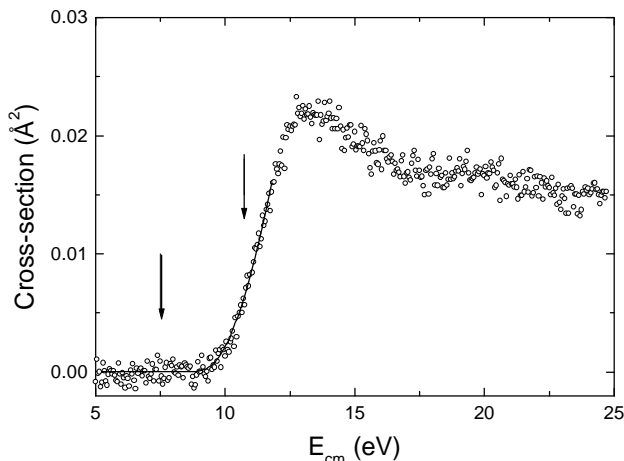
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Fig. 4: Total cross section for the production of O^+, as a function of center of mass energy (E_{cm}). The two arrows mark the thermodynamic thresholds of reactions (3) and (4).

The endothermicity of reaction (3) is not known exactly, due to the lack of knowledge about the heat of formation of the C_2O radical at 0 K. If one uses the value at 298 K, 2.97 eV [16], as a close approximation, together with the auxiliary quantities $\Delta_f H^0(CO^+) = 12.83$ eV, $\Delta_f H^0(CO) = -1.18$ eV, and $\Delta_f H^0(O^+) = 16.18$ eV, the threshold is expected to be at 7.5 eV. As it is shown in figure 4, the fitting of experimental data by means of a model cross section convoluted with the reactant energy distribution yields a threshold value of 9.3 eV ($E_0 = 9.3$, $s_0 = 0.029$, and $n = 1.96$). Again the problem here is the possible vibrational excitation of the CO^+ reactant. The previous analysis of the data concerning the production of C^+ indicates that this excitation shifts the threshold to a lower value by about 0.4 eV, and this must be taken into account when estimating the reaction onset for other products. If we assume that the excitation of CO^+ affects in the same way all the processes, then the threshold has a value of 9.7 eV. Thus the reaction onset is located at an energy value that is both higher than the thermodynamic threshold of reaction (3), and lower than the threshold, 10.72 eV, of reaction (4). At the present, it is not clear if this discrepancy is due either to an energy barrier or to a systematic error caused by the poor signal-to-noise ratio of this measurement.

3. Production of $C_2^+ + O_2$

In addition to C^+ and O^+, the reaction of CO^+ with CO produces also C_2^+. This ion is of considerable importance in combustion chemistry and astrophysics [17]. Though a number of theoretical [18-27] and experimental [28-37] studies address its thermodynamic properties, such as the heat of formation and the dissociation energy, these values are not yet known precisely.

Another reason of interest for this reaction is related to the simultaneous formation of C-C and O-O bonds. This process seems to be limited by severe geometrical constrains. On the contrary, its cross section is about 0.1 $Å^2$ at the maximum (see figure 5), and is therefore comparable with that of other reaction channels. Simple considerations about the electronic structure of the reactants may help to understand the reaction mechanism. The neutral CO is polar, with the negative charge largely located on the C atom. On the contrary, the positive charge in CO^+ is largely located on the C atom. Thus the resulting electrostatic interaction

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promotes the activation of the C-O bonds and the formation of C-C and O-O bonds. This mechanism reminds the formation of metal-carbonyl compounds M-(CO)$_n$, in which the M-C bond is promoted by the donation of σ electrons from C to M, and by the simultaneous retro-donation of π electrons from M to the non-occupied antibonding orbitals of C in the CO molecule.

Concerning the thermochemistry of C_2^+, theoretical calculations suggest that the adiabatic ionization potential of C_2 is about 11.35 eV [22], while experimental work gives larger values such as 12.0 ± 0.6 eV [28], 12.15 ± 0.05 eV [29], and 11.92 ± 0.09 eV [33]. It seems likely that these disagreements are the consequence of unfavourable Franck-Condon factors, so that the ionization of ground state C_2 does not lead to ground state C_2^+ (X $^4\Sigma_g^-$) ions [17]. Rather it produces the first excited state $^2\Pi_u$, whose energy was calculated to be above the ground state by $0.6 - 0.8$ eV [22-25]. Very recently, C.J. Reid *et al.* [37] found that C_2^+ ions are formed in the X $^4\Sigma_g^-$ ground state when acetylene is ionized by electrons of 23 eV. Below this energy, C_2^+ ions are formed in the metastable $^2\Pi_u$ state. In contrast, ionization of cyanogen (C_2N_2) by electrons with energies ranging from 18 to 100 eV produces only C_2^+ ($^2\Pi_u$) ions. Ionization energies of ground state C_2 to produce the X $^4\Sigma_g^-$ and $^2\Pi_u$ states of C_2^+ were deduced to be 11.4 ± 0.3 and 12.3 ± 0.3 eV, respectively. Given the recently determined heat of formation of C_2, 8.47 ± 0.08 eV [38, 39], the heat of formation of ground state C_2^+ (X $^4\Sigma_g^-$) can be then calculated to be 19.9 ± 0.3 eV. The usual fitting procedure applied to the experimental data gives $E_0 = 7.75$, $s_0 = 2.8\cdot10^{-4}$, and $n = 3.3$. If we assume that the threshold has to be shifted by 0.4 eV due to the vibrational excitation of CO^+, then the value for reaction (5) is about 8.15 ± 0.2 eV. By using $\Delta H_0^0 = 8.15 = \Delta_f H^0 (C_2^+) - \Delta_f H^0 (CO^+) - \Delta_f H^0 (CO)$ we get $\Delta_f H^0(C_2^+) = 19.8 \pm 0.2$ eV. This value is in good agreement with the estimate of 19.9 ± 0.3 eV previously discussed. It also indicates that C_2^+ ions produced here are in the ground state. The above calculation is valid under the assumption that no barrier exists. A theoretical paper by Cao and Tian [40] indicates a barrier of 0.134 eV in the reaction path between $C_2^+ + O_2$ and $CO^+ + CO$. Should this be the case, then $\Delta_f H^0(C_2^+)$ would be correspondingly lower. It is interesting to note that the value recommended in literature refers to the $^2\Pi_u$ state and it is larger by almost 1 eV, $\Delta_f H^0(C_2^+) = 20.64$ eV [41]. The discrepancy on $\Delta_f H^0(C_2^+)$ reflects directly on the dissociation energy: given that the energies of $C^+(^2P_u)$ and $C(^3P_g)$ are 18.63 and 7.37 eV respectively [4], we estimate a value of $D_0(C^+-C)$ for ground state $C_2^+(X\ ^4\Sigma_g^-)$ of 6.2 ± 0.2 eV. Again this number differs by almost 1 eV from a recent literature value, $D_0(C^+-C) = 5.4$ eV [42]. We suspect that the discrepancy is due to the fact that - in the work described in ref. 42 - C_2^+ ions were produced in the excited $^2\Pi_u$ state.

4. Production of $C_2O^+ + O$

Cross sections for the production of C_2O^+ as a function of collision energy are depicted in figure 5. The maximum of about 0.017 Å^2 is located at about 9.6 eV. The successive decline with collision energy is likely related either to the competition with process (5) leading to the formation of C_2^+, or to the dissociation of C_2O^+. This latter process might contribute to the increased C^+ production seen above 8.5 eV .

C_2O^+ can be produced in other processes, such as electron impact ionization of C_3O_2 [43], ionization of C_2O [44], photodissociation of $Fe(CO)_5^{2+}$ [45] and oxidation of C_2^+ by O_2 [46], and a number of values for the heat of formation are available [1, 3, 43, 44]. We can estimate the enthalpy of formation of C_2O^+ from its appearance energy.
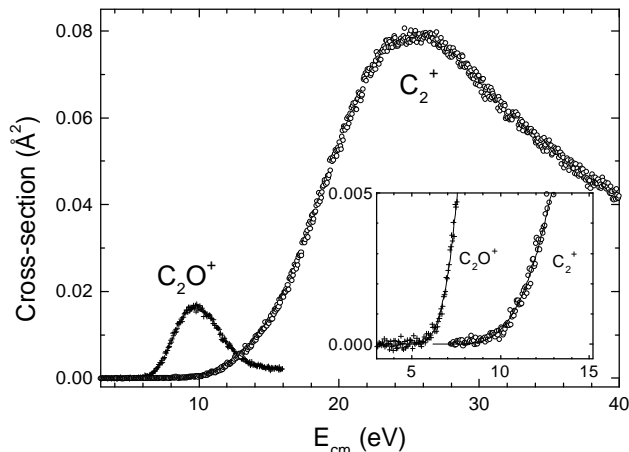
Fig. 5: Total cross sections for the production of C_2O^+ (crosses) and C_2^+ (open circles), as a function of center of mass energy (E_{cm}). The inset shows data in the threshold region. Full lines represents results of the fitting used to estimate the energy thresholds (see text for details).

By using the usual fitting procedure, we estimate the threshold for the formation of C_2O^+ to be 5.2 ± 0.2 eV ($E_0 = 5.2$, $s_0 = 1.7 \cdot 10^{-3}$, and $n = 3.5$). As for previous cases, the reaction threshold has to be shifted by 0.4 eV, due to the ro-vibrational excitation of CO^+. The corrected value is then 5.6 ± 0.2 eV. Given $\Delta_f H^0(O) = 2.56$ eV, and by using the expression $\Delta H_0^0 = \Delta_f H^0(C_2O^+) + \Delta_f H^0(O) - \Delta_f H^0(CO^+) - \Delta_f H^0(CO)$ one gets $\Delta_f H^0(C_2O^+) = 14.7 \pm 0.2$ eV. This value is in good agreement with the recent determination $\Delta_f H^0(C_2O^+) = 14.63 \pm 0.05$ eV [44].

Conclusions

We have investigated six different endothermic channels in the reaction of CO^+ ions with neutral CO molecules. For each ionic product we measured the kinetic energy dependence of the integral cross section and inferred the neutral product by the reaction energetics.

For reaction (1), producing C^+ and CO_2, the comparison between the thermodynamic threshold and the experimental one shows a discrepancy of about 0.4 eV, which is attributed to some degree of excitation of the primary ions. We have subsequently corrected for such value all the experimentally determined reaction thresholds.

The appearance of process (2), producing C^+, O, and CO, has been identified by a feature at about 8.5 eV. Measurements of the product isotopic ratio suggest that C^+ originates from both CO^+ ions and neutral CO molecules. However, another cause of the increased production of C^+ observed above 8.5 eV might be the dissociation of C_2O^+ ions produced in reaction (6).

Concerning the production of O^+, we estimate a threshold at 9.7 eV. This value is both higher than the energy, 7.5 eV, required by reaction (3) to proceed, and lower than the threshold, 10.72 eV, of reaction (4). At the present, it is not clear if this discrepancy is due either to an energy barrier or to a systematic error caused by the poor signal-to-noise ratio of this measurement.

For reactions (5) and (6) producing $C_2^+ + O_2$ and $C_2O^+ + O$ respectively, measurements of the reaction thresholds allow us to estimate the heats of formation of these two ionic products, $\Delta_f H^0 (C_2^+) = 19.8 \pm 0.2$ eV and $\Delta_f H^0 (C_2O^+) = 14.7 \pm 0.2$ eV. These values are in good agreement with recent independent evaluations. Finally, we re-evaluated the

dissociation energy of $C_2^+(X\ ^4\Sigma_g^-)$, $D_0(C^+-C) = 6.2 \pm 0.2$ eV.

Acknowledgements

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