JOURNAL OF CHEMICAL PHYSICS VOLUME 112, NUMBER 10 8 MARCH 2000

# Bond-forming reactions of molecular dications with rare gas atoms: Production of $ArC^{2+}$ in the reaction $CO^{2+}+Ar$

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(Received 3 November 1999; accepted 16 December 1999)

Integral cross sections for the bond-forming reaction $CO^{2+}+Ar\rightarrow ArC^{2+}+O$ have been measured as a function of collision energy in a guided-ion beam mass spectrometer. The energy dependence is consistent with an endoergic reaction. Since the title reaction is in competition with several charge-transfer processes, the cross section at the maximum is only 0.023 Å$^2$ at a collision energy of about 3 eV. Simple kinematics considerations suggest that the falloff of the cross section at higher energies might be due to the vibrational predissociation of $ArC^{2+}$. State correlation diagrams are used for discussing the reaction mechanism. © *2000 American Institute of Physics.* [S0021-9606(00)01510-5]

## I. INTRODUCTION

In recent years the structure and the gas-phase reactivity of small doubly charged molecules have attracted increasing interest.[1–4] These species are usually unstable because of the Coulomb repulsion $XY^{2+}\rightarrow X^{+}+Y^{+}$; however, in some cases they can be either thermodynamically stable or long lived.[5] Such molecules exhibit high reactivity and their exoergic reactions with other molecules may release several electron volts in kinetic energy of the products. As an example, $He_2^{2+}$ has been proposed as a source of propulsive energy with performances which far exceed those of all known propellants.[6]

In the collision of $CO^{2+}$ dications with Ar atoms, several reactions were observed[7,8]

$$CO^{2+}+Ar\rightarrow CO^{+}+Ar^{+}, \tag{1}$$

$$CO^{2+}+Ar\rightarrow C^{+}+O+Ar^{+}, \tag{2}$$

$$CO^{2+}+Ar\rightarrow C+O^{+}+Ar^{+}, \tag{3}$$

$$CO^{+}+Ar\rightarrow C^{+}+O^{+}+Ar. \tag{4}$$

However, no bond-forming reactions were reported. As a result of our continuous effort in the study of doubly charged molecular ions containing rare gases, in the present paper we report the cross section as a function of collision energy for the production of $ArC^{2+}$ in the reaction

$$CO^{2+}+Ar\rightarrow ArC^{2+}+O. \tag{5}$$

The remarkable feature of this reaction is the formation of a new bond in a process which involves doubly charged ions both as reactants and products. In fact, bond-forming reactions usually produce singly charged ionic products,[9–12] such as $CF_2D^{+}$ from $CF_2^{2+}+D_2$. Only a few papers report the production of doubly charged ions from doubly charged reactants; however, these investigations involve either $C_{60}^{2+}$,[13] or transition metal dications,[14–17] or $Ar^{2+}$.[18,19] Apart from the special case of $C_{60}^{2+}$, to our knowledge the present work is the first observation of doubly charged molecular products in the gas-phase reactions of molecular dications.

## II. EXPERIMENT

The experiments were performed in a modified version of a guided-ion beam tandem mass spectrometer which has been described before.[20–22] The $CO^{2+}$ reactant ions are produced by electron impact of CO using an electron beam at 85 eV. Ions are extracted from the differentially pumped ion source, mass selected by a magnet mass spectrometer, and finally injected into a radio-frequency octopole ion guide[23] which is surrounded by the reaction cell. The axial energy distribution of the $CO^{2+}$ beam is determined by using the octopole guide as a retarding field energy analyzer. The typical $CO^{2+}$ energy distribution has a full width at half maximum (FWHM) of about 1.2 eV in the laboratory reference frame. The collision energy in the laboratory frame ($E_{lab}$) is varied by changing the dc potential of the octopole with respect to the ion source. The collision energy in the center-of-mass frame ($E_{cm}$) is obtained from $E_{lab}$ by the expression $E_{cm}=E_{lab}m/(M+m)$, where $m$ and $M$ represent the mass of the neutral and ionic reactants, respectively. Argon is introduced in the reaction cell at pressures below $10^{-4}$ mbar to avoid multiple collisions. Reactant and product ions are extracted, mass analyzed by a quadrupole mass spectrometer, and finally counted by standard technique.

Absolute integral cross sections $\sigma$ are obtained by $\sigma=aI_p/I_s$, where $a$ is a constant, $I_p$ is the intensity of the product ions, and $I_s$ is the intensity of the reactant ions. The constant $a$ is determined by normalizing our data on those obtained by Ehbrecht *et al.*,[8] who measured the cross section for the formation of $Ar^{+}$ — reaction (1) — at 18 eV (C. M.) to be 1.90 Å$^2$. For the absolute cross sections presented here, we estimate the errors within ±30%.

## III. RESULTS AND DISCUSSION

The electronic ground state of $CO^{2+}$ is $^3\Pi$. However, another $^1\Sigma^{+}$ state lies about 0.2 eV higher and might affect

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the beam composition. In our apparatus, the distance from the ion source to the entrance of the collision cell is about 10 cm. At collision energies of 0.2, 1, and 10 eV (center of mass), the time of flight of the $CO^{2+}$ ions from the ion source to the collision cell is about 65, 29, and 9 $\mu$s, respectively. The lifetimes of the $^3\Pi$ and $^1\Sigma^+$ electronic states have been calculated by Larsson *et al.*[24] These calculations suggest that only the $v=0$ vibrational levels are stable on the $\mu$s scale. Experimental determinations vary among literature. Some measurements give lifetimes on the scale of $\mu$s,[25–27] while others suggest the existence of components having a much longer lifetime ($>10^{-4}$ s).[28,29] The most recent experiments[30,31] confirm the latter conclusion and it was found that the lifetime of the $v=0$ level of the $^1\Sigma^+$ state is about 9 $\mu$s, while that of the $v=0$ level of the ground state $^3\Pi$ is longer than 3.8 s.[30] All other higher vibrational levels decay faster. Thus, it appears reasonable to assume that up to 10 eV collision energy, $CO^{2+}$ ions in the reaction region are in the $v=0$ $^3\Pi$ ground state, while at high collision energies the beam might contain a small percentage of the first excited state $^1\Sigma^+$.

The reaction energetics can be calculated using the known thermochemistry of reactants and products. In recent years, the appearance energy of $CO^{2+}$ from neutral CO has been the subject of a number of investigations.[25,32–34] The most recent measurements, performed by using the threshold photoelectron coincidence technique, gave an appearance potential of 41.24 eV for the $v=0$ level of the ground state $^3\Pi$.[34] From this result, and given the heat of formation of neutral CO, $\Delta_f H°(\mathrm{CO}) = -1.18$ eV, the heat of formation of $CO^{2+}(X\,^3\Pi)$ is found to be 40.06 eV. Regarding the products, several theoretical investigations concern the $ArC^{2+}$ molecular dication.[35–41] *Ab initio* calculations at different levels yield values for the dissociation energy $D_0(\mathrm{ArC}^{2+})$ of $-3.37$ eV,[36] $-2.86$ eV,[38] and $-3.41$ eV.[41] These values can be used to estimate the heat of formation $\Delta_f H°(\mathrm{ArC}^{2+}) = \Delta_f H°(\mathrm{Ar}^+) + \Delta_f H°(\mathrm{C}^+) - D_0(\mathrm{ArC}^{2+})$. By using $\Delta_f H°(\mathrm{Ar}^+) = 15.76$ eV, and $\Delta_f H°(\mathrm{C}^+) = 18.63$ eV,[36] we get $\Delta_f H°(\mathrm{ArC}^{2+}) = 37.76$, 37.25, and 37.80 eV, depending on the value assumed for the dissociation energy $D_0(\mathrm{ArC}^{2+})$. Finally, by using the auxiliary quantity $\Delta_f H°(\mathrm{O}) = 2.556$ eV, one can calculate the reaction energetics to be $\Delta H_0° = 0.26$, $-0.25$, or 0.30 eV, respectively. Here, a positive value indicates an endoergic reaction while a negative value indicates an exoergic reaction.

In Fig. 1 we plot the cross section of reaction (5) as a function of collision energy from 0.2 eV to about 25 eV. The cross section at the maximum is only 0.023 Å$^2$, and declines to values in the range of $10^{-3}$ Å$^2$ at about 25 eV. These values are much smaller than those observed for the other reaction channels, such as the charge-transfer reaction producing $CO^+ + Ar^+$. As a consequence, reaction (5) certainly has a minor impact on the overall chemistry of real systems. However, a detailed study of reaction (5) may be important to get a better picture of chemical bonding in such unusual species as molecular dications containing rare gases.

The overall profile of the cross section is consistent with an endothermic reaction, and this suggests that calculations reported in Ref. 38 underestimate the dissociation energy of $ArC^{2+}$. From the calculations of Vincent *et al.*[36] and Frenking *et al.*,[41] we get a reaction threshold of 0.26 and 0.30 eV, respectively. The experimental results are consistent with these theoretical evaluations. However, due to the energy broadening of the reactants and the consequent limited energy resolution in the threshold region, the exact reaction onset could not be quantitatively determined.

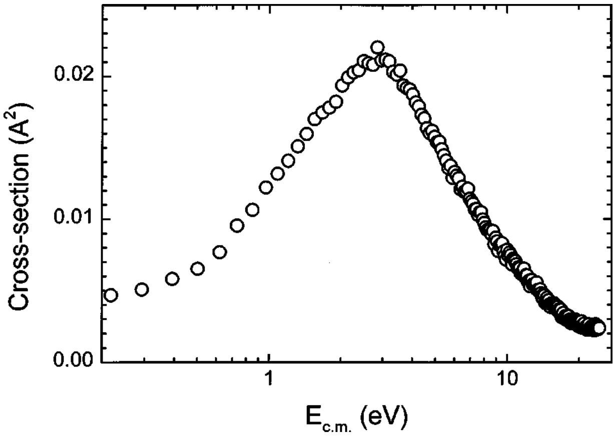

FIG. 1. Integral cross section as a function of collision energy for the reaction $CO^{2+} + Ar \rightarrow ArC^{2+} + Ar$.

The declines of the cross section at high energy might be related to the vibrational predissociation of the metastable $ArC^{2+}$ dications. Different theoretical calculations give a dissociation barrier of 1.38[36] and 1.1 eV,[38] respectively. If one assumes that the position ($E_{\max} \approx 3$ eV) of the maximum cross section is related to the threshold for the dissociation of $ArC^{2+}$, then, neglecting the small endothermicity, the fraction of collision energy disposed in vibration of the diatomic product is given by $D_0(\mathrm{ArC}^{2+})/E_{\max} = 0.37$ or 0.46, depending on the barrier value. The partitioning of the product energy between vibration along the molecular bond and translational motion of departure depends on the details of the interaction potential. However, the analysis of the coordinate transformation that is needed to go from a system suitable for describing the reactants to one suitable for the products in a collinear configuration, shows that the upper bound of the fraction of the collision energy disposed in vibration, $E_{\mathrm{vib}}$, is determined by a kinematic factor depending only on the mass of the colliding particles.[42] For the collinear reaction $A + BC \rightarrow AB + C$, we get $E_{\mathrm{vib}}/E_{\mathrm{cm}} = \sin^2\beta$, where

$$\beta = \arctan\left(\frac{m_B}{m_A} + \frac{m_B}{m_C} + \frac{m_B^2}{m_A m_C}\right)^{1/2}. \tag{6}$$

In the present case, we get $E_{\mathrm{vib}}/E_{\mathrm{cm}} = 0.56$. Considering that 0.56 is the upper bound to the fraction of energy disposed in vibration, the comparison with the experimental estimates (0.37, 0.46) suggests that the $T-V$ energy transfer is quite efficient.

In Fig. 2 we show a simplified electronic correlation diagram for the collinear configuration. It is immediately clear that ground-state reactants $CO^{2+}(X\,^3\Pi) + Ar(^1S_g)$ correlate directly with ground-state products $ArC^{2+}(X\,^1\Sigma^+)$

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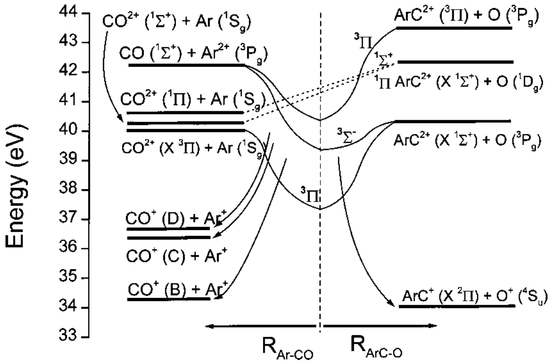

FIG. 2. State correlation diagram for $C_{\infty v}$ symmetry.

$+\mathrm{O}(^3P_g)$ via a $^3\Pi$ surface. The process can be considered a transfer of the $\mathrm{C}^{2+}$ dication, as indicated in the following scheme:

$$\mathrm{CO}^{2+}+\mathrm{Ar}\rightarrow[\mathrm{O}+\mathrm{C}^{2+}+\mathrm{Ar}]^{\ddagger}\rightarrow\mathrm{ArC}^{2+}+\mathrm{O}.$$

However, this reaction is in competition with many charge-transfer processes. In fact, along the $R_{\mathrm{Ar-CO}}$ coordinate there are several avoided crossings with the surfaces determined by the repulsive interaction between $\mathrm{CO}^+$ and $\mathrm{Ar}^+$. Dynamics at the crossings with the $A^+ + B^+$ surfaces is well understood by the simple ''reaction window'' concept based on the Landau–Zener model,[43–45] and has been the subject of detailed discussions in recent papers.[7,8] The key point of the reaction window approach is that the charge transfer is effective whenever the crossing occurs at internuclear distances between 2 and 6 Å.

Though nearly all the $\mathrm{CO}^+$ electronic states ($X$, $A$, $B$, $C$, $D$, $G$) are accessible via one electron transfer, the $\mathrm{CO}^+$ product is formed predominantly in the $B\,^2\Sigma^+$, and higher states.[3,8,46] The crossing with $\mathrm{CO}^+(B\,^2\Sigma^+)+\mathrm{Ar}^+(^2P_u)$, $\mathrm{CO}^+(C\,^2\Delta)+\mathrm{Ar}^+(^2P_u)$, and $\mathrm{CO}^+(D\,2\Pi)+\mathrm{Ar}^+(^2P_u)$ occurs at an internuclear distance of 2.84 Å (2.48 Å in Ref. 8), 4.09 and 4.38 Å, respectively.[7] All these crossings occur at the right distance, well before the formation of an intermediate complex where new bonds can be formed. As a consequence, the charge-transfer process is very efficient, and only a small fraction of reactants survives on the $^3\Pi$ surface, eventually correlating with the final products $\mathrm{ArC}^{2+}+\mathrm{O}$. However, before they can further proceed to the final products, another crossing will occur with the repulsive surface $\mathrm{ArC}^+(X\,^2\Pi)+\mathrm{O}^+(^4S_u)$. The position at which this crossing occurs can be approximately calculated by using $R=14.4/\Delta E$,[8] where $\Delta E$ (in eV) is the energy difference between $\mathrm{ArC}^{2+}(X\,^1\Sigma^+)+\mathrm{O}(^3P_g)$ and $\mathrm{ArC}^+(X\,^2\Pi)+\mathrm{O}^+(^4S_u)$. For this purpose we need the heats of formation of the reagents and of the products. Following the previous discussion, here we assume $\Delta_f H°(\mathrm{ArC}^{2+})=37.76$ eV, $\Delta_f H°(\mathrm{O})=2.556$ eV, and $\Delta_f H°(\mathrm{O}^+)=16.18$ eV. Concerning $\mathrm{ArC}^+(X\,^2\Pi)$, its heat of formation can be calculated from its dissociation energy $D_0(\mathrm{C}^+-\mathrm{Ar})$. This is calculated to be either 0.92[38] or 0.88 eV.[37] Experiments give values such as 0.938[47] and 0.5 eV.[48] If one uses the calculated dissociation energy of 0.92 eV, the heat of formation of $\mathrm{ArC}^+$ is found to be 17.71 eV. $\Delta E$ is then easily calculated to be 6.43 eV, and eventually one finds that the crossing occurs at $R=2.24$ Å. We did not observe $\mathrm{ArC}^+$ ions in large amounts, most probably because the reaction is very exoergic (by 6.17 eV) and, since $\mathrm{ArC}^+$ has a small binding energy (about 0.9 eV), $\mathrm{ArC}^+$ products may quickly dissociate into $\mathrm{C}^+ + \mathrm{Ar}$.

Since all the charge-transfer channels are in competition with the bond-forming reaction,[49] only a small percent of the initial reagents can eventually be transformed into $\mathrm{ArC}^{2+}+\mathrm{O}$. As a consequence, the cross section is expected to be very low, in agreement with the present experimental observations.

## IV. CONCLUSION

In this work the cross section for the reaction $\mathrm{CO}^{2+}+\mathrm{Ar}\rightarrow\mathrm{ArC}^{2+}+\mathrm{O}$ has been measured as a function of relative energy. The important feature of this bond-forming process is the conversion of the reactant molecular dication in the product molecular dication. This is unusual as only singly charged products are generally observed. The energy dependence of the cross section suggests that the reaction is endoergic, in agreement with some theoretical predictions. The cross section rises to reach a maximum of about 0.02 Å$^2$ near 3 eV before declining at higher energies. A simple estimate of the fraction of energy disposed in product vibration suggests that the falloff might be due to vibrational predissociation of $\mathrm{ArC}^{2+}$. State correlation diagrams show that a $^3\Pi$ surface evolving from ground-state reactants correlates adiabatically with ground-state products. The competition between this pathway and several charge-transfer reactions explains the low efficiency observed for the title reaction.

## ACKNOWLEDGMENTS

We acknowledge the financial support by MURST, Grant No. 9802623099, and the European Commission, Grant No. RTN1-1999-00254.

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