Dications

DOI: 10.1002/anie.200704286

Bond Formation with Maintenance of Twofold Charge: Generation of $C_2O_3^{2+}$ in the Reaction of CO_2^{2+} with CO_2**

Jana Roithová, Claire L. Ricketts, Detlef Schröder, and Stephen D. Price*

One hundred years ago, Berthelot suggested the existence of the carbon oxide C_2O_3, the cyclic anhydride of oxalic acid, oxirandione.[1,2] However, C_2O_3 has not been isolated as a bulk compound, and thermodynamic considerations of Perk and Liebman suggest that oxirandione is approximately 230 kJ mol^{-1} less stable than the separated fragments CO and CO_2.[3] This prediction is in good agreement with a computed exothermicity of 222 kJ mol^{-1} for the dissociation of cyclic C_2O_3 into CO and CO_2, as reported by Peppe et al.[4] in their attempts to generate neutral C_2O_3 from appropriate ionic species using neutralization–reionization mass spectrometry.[5] In addition to the weakly bound van der Waals complex [CO·CO_2], the trioxapropellane structure of C_2O_3 has received attention in a number of theoretical studies.[6–8] Furthermore, the singly charged species $C_2O_3^-$ and $C_2O_3^+$ have been studied by experiment and theory;[4,9,10] for the $C_2O_3^+$ cation, a possible role in atmospheric isotope-exchange processes has been proposed.[10] Only a single report[11] has addressed the dicationic species $C_2O_3^{2+}$ by means of ab initio calculations, which predicted a cumulene-type structure $OCOCO^{2+}$. Herein, we report on the generation of the $C_2O_3^{2+}$ dication in a reaction of mass-selected CO_2^{2+} with neutral CO_2.

In 2002, Witasse et al. suggested the formation of CO_2^{2+} in the upper layers of the Martian atmosphere.[12] As carbon dioxide is the major constituent of the Martian atmosphere, the reaction of CO_2^{2+} with CO_2 was examined shortly afterwards,[13] and a predominance of electron transfer to yield singly charged ions was found.[14] Furthermore, the reaction of CO_2^{2+} with CO_2 may be regarded as a test case to probe the energy partitioning in electron-transfer reactions of gaseous dications.[15] Herein, we employ double isotopic labeling to determine the origin of the various products in the quasi-degenerate reaction of CO_2^{2+} with CO_2 using carbon dioxides enriched in ^{13}C and ^{18}O. While the electron-transfer pathways will form the subject of a full paper,[16] we restrict ourselves herein to the observation of a new bond-forming reaction that leads to the $C_2O_3^{2+}$ dication.

Figure 1 shows a mass spectrum of the reaction of mass-selected $^{13}C^{16}O_2^{2+}$ (m/z 22.5) with neutral $^{12}C^{18}O_2$.[17,18] Almost all of the products can be ascribed to electron transfer from the neutral to the doubly charged carbon dioxide: $^{16}O^+$, $^{13}C^{16}O^+$, and $^{13}C^{16}O_2^+$ from $^{13}C^{16}O_2^{2+}$ and $^{18}O^+$, $^{12}C^{18}O^+$, and $^{12}C^{18}O_2^+$ formed by ionization of $^{12}C^{18}O_2$; products arising from traces of water are also observed. Herein, we focus on the small signals at about m/z 37.5 and 38.5 (see lower inset in Figure 1). The mere fact that these signals appear at non-integer masses demonstrates that they are due to dicationic reaction products formed according to Equation (1).

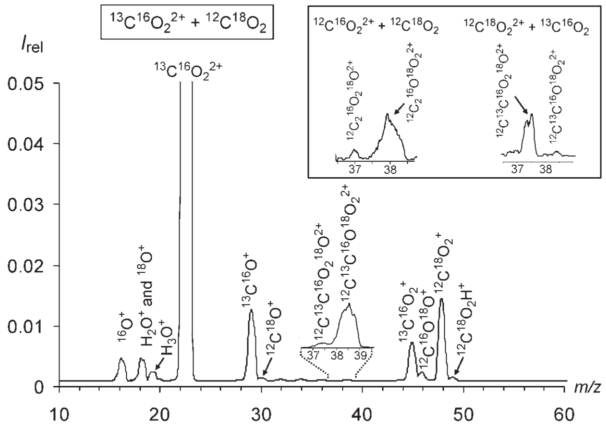

Figure 1. Reaction of mass-selected $^{13}C^{16}O_2^{2+}$ with neutral $^{12}C^{18}O_2$ at quasi-thermal energy. The vertical scale refers to the precursor dication $^{13}C^{16}O_2^{2+}$ with an intensity of 1.00. In the lower part of the figure, the mass region of the bond-forming product $C_2O_3^{2+}$ (m/z 36.5–39.5) is also shown amplified by a factor of 50. The upper right inset shows the expanded regions of the bond-forming products in the reactions $^{12}C^{16}O_2^{2+} + {}^{12}C^{18}O_2$ and $^{12}C^{18}O_2^{2+} + {}^{13}C^{16}O_2$. The ions H_2O^+, H_3O^+, and CO_2H^+ are due to traces of water present in the background.

$$CO_2^{2+} + CO_2 \rightarrow C_2O_3^{2+} + O \quad (1)$$

The formation of a $C_2O_3^{2+}$ dication according to Equation (1) is further confirmed by two other labeling combinations ($^{12}C^{16}O_2^{2+} + {}^{12}C^{18}O_2$ and $^{13}C^{16}O_2^{2+} + {}^{12}C^{18}O_2$), which lead

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[*] Dr. J. Roithová, Dr. C. L. Ricketts, Dr. D. Schröder
Institute of Organic Chemistry and Biochemistry
Academy of Sciences of the Czech Republic
Flemingovo nám. 2, 16610 Prague 6 (Czech Republic)
Fax: (+42) 220-183-583
E-mail: detlef.schroeder@uochb.cas.cz
Dr. J. Roithová
Department of Organic Chemistry
Faculty of Sciences
Charles University in Prague
Hlavova 8, 12083 Prague 2 (Czech Republic)
Prof. S. D. Price
Department of Chemistry
University College London
20 Gordon Street, London WC1H 0AJ (UK)

[**] This work was supported by a collaboration grant of the Royal Society London. Additional support for the labeled gases was provided by the Academy of Sciences of the Czech Republic and the Deutsche Forschungsgemeinschaft. On the Czech side, this work was performed in the context of a sociological EU project (Knowledge, Institutions and Gender, 07167, FP6).

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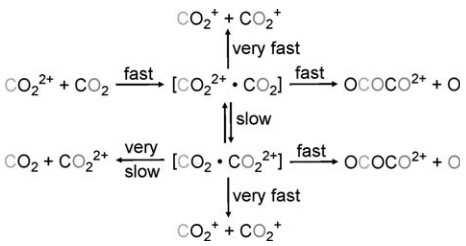
to the corresponding $C_2O_3^{2+}$ isotopes (upper inset in Figure 1). Furthermore, the oxygen isotopes are not distributed equally. Rather, the oxygen atom from the incident dication is lost with high preference, that is, ^{16}O from $^{12}C^{16}O_2^{2+}$ and $^{13}C^{16}O_2^{2+}$, but ^{18}O from $^{12}C^{18}O_2^{2+}$. This observation can be rationalized in terms of Scheme 1. Upon formation of the collision complex $[CO_2^{2+}{\cdot}CO_2]$,[19] either electron transfer (ET) to form monocations or O-atom loss to afford $C_2O_3^{2+}$ can occur rapidly. A process leading to the scrambling of the oxygen atoms, for example, a skeletal rearrangement of the encounter complex, is much slower and can hardly compete with the two other processes. Double electron transfer followed by the backward dissociation to the reactants cannot compete at all, because no signal from $^{12}C^{18}O_2^{2+}$ (*m*/*z* 24.0) is found in Figure 1.



Scheme 1. Kinetic scheme implied by the experimentally observed $^{12}C/^{13}C$ and $^{16}O/^{18}O$ isotope patterns observed in the reaction of mass-selected CO_2^{2+} with neutral CO_2.[19]

In a more general context, the generation of $C_2O_3^{2+}$ according to Equation (1) is remarkable, because the twofold charge of the precursor dication is maintained in the product, although ET affording two CO_2^+ monocations is exothermic by as much as 10.8 eV.[20,21] The energy behavior of these competing reactions clearly demonstrates that the formation of $C_2O_3^{2+}$ occurs as a quasi-thermal process, as the signal intensity of the dicationic coupling product has a sharp maximum at low collision energies, whereas the yields of the monocations formed by ET are almost energy-independent (Figure 2).[22]

For $C_2O_3^{2+}$, Pyykkö and Runeberg[11] suggested the cumulene structure $OCOCO^{2+}$ with a singlet ground state formally arising from double ionization (and cleavage) of the C−C bond in oxirandione. To gain further insight into the isomers involved and to rationalize the observed isotope patterns in the reactions of labeled reagents, we performed exploratory computational studies.[23] Three possible encounter complexes for the reaction of CO_2^{2+} with CO_2 were found (Figure 3). The most stable isomer corresponds to the symmetrical structure ^{1}**1**$^{2+}$, which bears a peroxidic bond between the oxygen atoms of the dicationic and the neutral reactants; this isomer is stable only as a singlet. Interaction between the carbon atom of one of the reactants and the oxygen atom of the second leads to structure **2**$^{2+}$ with singlet and triplet states that are close in energy. Attempts to locate a minimum for an interaction between the carbon atoms of CO_2^{2+} and CO_2 did not lead to any stable arrangement.

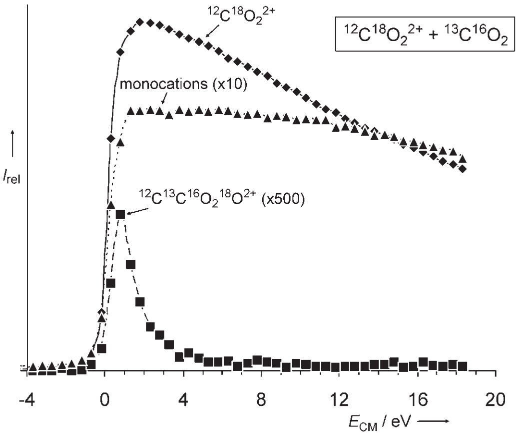


Figure 2. Ion abundances of the precursor dication (◆), the monocationic products due to ET (▲), and the dicationic bond-forming product (■) in the reaction of mass-selected $^{12}C^{18}O_2^{2+}$ with neutral $^{13}C^{16}O_2$ as a function of the collision energy (given in eV in the center-of-mass frame); the signals vanish below $E_{CM} = 0$ eV, because the ions can no longer pass through the octopole collision cell.

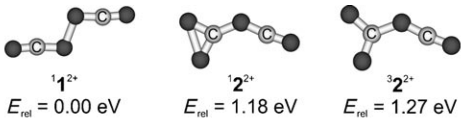


Figure 3. Optimized structures of possible $C_2O_4^{2+}$ intermediates in the reaction of mass-selected CO_2^{2+} with CO_2.

On the basis of two arguments, we propose ^{3}**2**$^{2+}$ as an intermediate in the formation of $C_2O_3^{2+}$ according to Equation (1). The CO_2^{2+} dication has a triplet ground state,[24] and a spin-conserving channel[25,26] is more likely to be able to kinetically compete with exothermic single-electron transfer. The $^{16}O/^{18}O$ patterns observed experimentally are not symmetrical with respect to the oxygen atoms of the doubly charged projectile and neutral CO_2, whereas the opposite behavior would be expected if the symmetrical species ^{1}**1**$^{2+}$ were formed. In a simple chemical scheme, the role of ^{3}**2**$^{2+}$ as an intermediate can also be rationalized as the interaction between the carbon atom of CO_2^{2+}, which represents the center with the largest positive charge, and one of the (electron-rich) oxygen atoms of neutral CO_2. From these considerations, a mechanistic scenario for the generation of $C_2O_3^{2+}$ can be derived. The ground state of CO_2^{2+} ($^3\Sigma_g^-$) has two unpaired electrons localized at the oxygen atoms, and the analysis of the spin density of ^{3}**2**$^{2+}$ suggests that the unpaired electrons stay at these oxygen atoms (Figure 4), whereas the positive charge is delocalized over the whole skeleton of $C_2O_4^{2+}$. It follows that the dominant route for the dissociation of ^{3}**2**$^{2+}$ into $C_2O_3^{2+} + O$ involves homolytic cleavage of the C−O bond to an oxygen atom that bears an unpaired electron (pathway a in Figure 4), thereby accounting for the preferential elimination of an oxygen atom stemming from the original CO_2^{2+} dication, as observed experimentally. Other scenarios are less probable (pathways b and c in Figure 4), because they lead to less stable isomers of $C_2O_3^{2+}$ (^{1}**4**$^{2+}$, ^{3}**4**$^{2+}$, ^{1}**5**$^{2+}$, and ^{3}**5**$^{2+}$). Moreover, with these routes, scrambling of the

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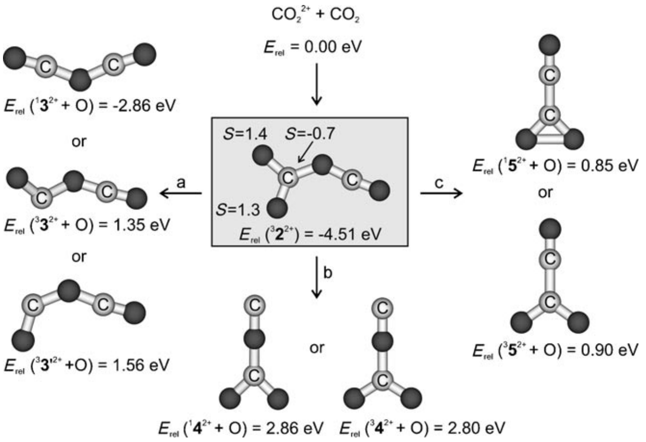

Figure 4. Mechanism suggested for the formation of $C_2O_3^{2+}$ according to Equation (1). The relative energies and computed spin densities (*S*) obtained by Mulliken population analysis are given.

oxygen atoms or even preferential O-atom loss from neutral CO_2 would be expected.

The overall energy balance with respect to CO_2^{2+} and CO_2 in their ground states ($E_{rel} = 0.00$ eV) predicts a considerable exothermicity of -4.51 eV associated with the formation of the intermediate $^3\mathbf{2}^{2+}$. Furthermore, product formation to yield the $C_2O_3^{2+}$ dication $^1\mathbf{3}^{2+}$, that is, the structure predicted in 1991 by Pyykkö and Runeberg,[11] concomitant with expulsion of O (^{3}P) is computed to be exothermic by -2.86 eV and to be an overall spin-allowed process. These theoretical results are in complete agreement with the experimental findings presented above (Figures 1 and 2).

In addition to the first experimental observation of $C_2O_3^{2+}$ one hundred years after Berthelot's first report about the neutral counterpart, the most notable result of this work is the observation of a bond-forming reaction under maintenance of the twofold charge [Eq. (1)], even for a system as small as $CO_2^{2+} + CO_2$. Investigations at quasi-thermal collision energies are crucial for the observation of such processes, and as the formation of $C_2O_3^{2+}$ has been overlooked before,[13] several other bond-forming reactions of multiply charged ions might have escaped detection in earlier studies of multiply charged ions conducted under hyperthermal conditions.

Received: September 17, 2007
Published online: October 31, 2007

Keywords: carbon oxides · computer chemistry · dications · mass spectrometry

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[17] The experiments were performed with a TSQ mass spectrometer which has an exchangeable ion source and a quadrupole–octopole–quadrupole configuration as described elsewhere.[15,18] The precursor ions generated by electron ionization (EI) and were characterized by investigations of their metastable components and their reactions with noble gases.[16] The first quadrupole (Q1) was used as a mass filter to select the parent ion of interest (CO_2^{2+} isotopologues) the octopole served as a collision cell to which neutral CO_2 isotopologues are introduced under single-collision conditions, and the second quadrupole (Q2) was scanned in the desired mass range. In all experiments, the mass resolution of Q1 was sufficiently high to select a single isotopologue of CO_2^{2+}. The mass resolution of Q2 was varied between intermediate values (ensuring a proper resolution of the singly and doubly charged ions) and deliberately lowered values in the kinetic-energy scans (to minimize possible discrimination effects in ion collection). Carbon dioxide (Linde, 99.995%), $^{13}C^{16}O_2$ (Cambridge Isotope Laboratories, greater than 99%, 99 atom% ^{13}C, less than 1 atom% ^{18}O), and $^{12}C^{18}O_2$ (Isotec, greater than 99%, 97 atom% ^{18}O) were used as purchased.
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[23] Initial calculations were performed using the B3LYP method with 6-311G* basis sets as implemented in Gaussian03 (Gaussian Inc., Pittsburgh, USA, 2002). All intermediates were characterized by frequency analysis, and the energies given refer to 0 K including corrections for zero-point energy. To briefly test the performance of this theoretical approach for the carbon oxides of interest, the ionization energies (IEs) of CO and CO_2 were computed and found to be in good agreement with experiment, for example, IE(CO) = 14.14 eV (exptl 14.01 eV), IE(CO_2) = 13.67 eV (exptl 13.78 eV), and IE(CO_2^+) = 23.70 eV (exptl 23.56 eV). The final energies given in the text refer to single-point calculations using the CCSD(T) method (CCSD(T) = coupled cluster with single and double excitations and perturbative inclusion of triple excitations) in conjunction with correlation-consistent valence triple zeta basis set, that is, CCSD(T)/cc-pVTZ//B3LYP/6-311G*. At this level of theory, the first and second IE of CO_2 are computed to be 13.65 and 23.44 eV, respectively.

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