Solubility and Solvation of Carbon Dioxide in the Molten Li_2CO_3/Na_2CO_3/K_2CO_3 (43.5:31.5:25.0 mol-%) Eutectic Mixture at 973 K

II. Theoretical Part[+]

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Keywords: Ab initio calculations / Dicarbonate anion $C_2O_5^{2-}$ / Dicarbonate structure / Dicarbonate stability

A theoretical study of the structure and stability of the dicarbonate ion has been performed at the Hartree–Fock, MP2, and QCI/SD levels. A flexible 6-31+G(d) basis set was used to allow for the diffuse electron density appearing in the anions. A stable anion corresponding to two CO_2 entities covalently bound to a central oxygen has been found. The formation reaction starting from the carbonate anion and carbon dioxide has also been studied. Its thermodynamic features favour the formation of the dicarbonate anion, which in turn may account for the impressive solubility of carbon dioxide in carbonate melts.

Introduction

In the first part of this work[1] we described the measurement of the solubility of carbon dioxide in the ternary Li_2CO_3/Na_2CO_3/K_2CO_3 molten eutectic mixture under a pressure of 1 atm of CO_2. The experimentally determined value amounted to 0.995×10^{-1} mol L^{-1}, which is much higher than the values reported in the literature for the same melt at the same temperature. This solubility value is also 50 times higher than that deduced from the voltammetric peak current density measured for the electrochemical reduction of CO_2 dissolved in the melt under a pressure of 1 atm. In order to rationalize these data, it was suggested that CO_2 might combine with the carbonate ions to yield a strongly stabilized solvated species. The formation of dicarbonate ions has been proposed (Equation 1).

$$CO_2 + CO_3^{2-} \rightleftharpoons C_2O_5^{2-} \qquad (1)$$

The free energy change for this reaction was assumed to be sufficiently large to shift the cathodic reaction at potentials where the reduction of carbonate ions yet occurs. Unfortunately, however, the previous investigation did not provide any direct experimental evidence for the occurrence of dicarbonate ions.

The main goal of this study is to analyse by theoretical means the structure, stability and properties, especially thermodynamic properties, of the relevant species. A quantum chemical approach to such a problem remains difficult, even though current computer technology permits access to an explicit and extensive treatment of such systems.

These experiments are carried out by considering a condensed, globally neutral, liquid medium. In such a model approach, the carbonate ions are assumed to be able to move freely through the medium of the molten salt phase while interacting with their neighbours. With this assumption, the study may be reduced to that of a particular molecular event; a single carbonate ion and a single carbon dioxide molecule may be considered in isolation and their mutual interaction can be studied as if they were isolated in the gas phase. We thus explicitly neglect the bulk behaviour as well as the nature of the counterion at this level. These should, of course, be introduced in condensed-phase simulations, but we shall concentrate our study on the most elementary chemical process accessible by quantum chemical means.

At the level used, the main difficulty involved lies in obtaining an adequate description of the behaviour of electrons in anions, especially when multiple excess charges are present. To treat this problem with a suitable degree of accuracy, two criteria need to be fulfilled:

1. As the excess electrons may be delocalized over large domains in space, the basis sets needed to simulate their distribution must offer sufficient flexibility to allow for such a large extension. Theoretical calculations must therefore be based on large basis sets, including polarization functions as well as extra diffuse functions.
2. As the correlation between electrons within the molecular domain is more important than in the case of neutral molecules, theoretical calculations must go beyond the Hartree−Fock level and explicitly include electron correlation.

In the next section, we shall briefly describe the methodology used in this work. The results of our simulation will then be presented. Finally, we shall discuss the chemical properties obtained and their relation to the macroscopic problem of interest.

Method

Owing to the size of the system, we chose to start our calculations at the valence split 6-31G basis set of Pople

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[+] Part I: Ref.[1]

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and co-workers, which was augmented by a set of 6 Cartesian "d" polarization functions.[2] An additional set of diffuse sp functions[3] completed the basis. This led to the 6-31+G(D) basis set, containing some 133 atomic orbitals for the $C_2O_5^{2-}$ system. The ab initio molecular orbital calculations were then performed at restricted Hartree−Fock (RHF) level using the GAUSSIAN series of programs.[4] Post-SCF level computations were subsequently performed to introduce the electron correlation. In these, the inner cores were frozen, but all single and double excitations of the valence orbitals were considered using one of two different approaches: In the first, second-order Moller−Plesset perturbation theory computations (MP2) were performed. Such calculations remain affordable for carrying out a full optimization of the geometry. The second approach involved quadratic configuration interaction (QCI/SD). This latter method was in fact adopted, since it provides, within the variation principle, size-consistent results. This is a prerequisite for obtaining reliable reaction energies.

The geometric structures were derived from a full geometry optimization of all $3N - 6$ internal coordinates, thereby relaxing any a priori symmetry constraints. A conventional gradient technique was used to perform the optimization process.

Analytical computation of the first and second derivatives of the energy hypersurface was completed at the SCF level in order to verify the good behaviour of the minima and maxima found and to obtain a vibrational analysis within the harmonic approximation. This provided some information regarding the ways in which the molecules may be distorted. Knowledge of the geometrical structure and of the related rotational and vibrational frequencies allows further thermodynamic insight into the problem by applying the relationships of conventional statistical thermodynamics. From such an analysis, a simulation of the IR spectrum may even be obtained. At this point, we should mention that the theoretical vibrational frequencies needed to evaluate the zero-point energy and thermal corrections were scaled to adjust theoretical frequencies to experimental ones (Equation 2).[5]

$$\nu(\mathrm{sc}) = 0.9\ \nu(\mathrm{th}) \qquad (2)$$

At post-SCF MP2 level, the analytical gradient was used in conjunction with the analytical SCF Hessian matrix. The same approach was used at the QCI level, although this was not possible for the dicarbonate ion as in this case computation of the analytical gradient remains beyond our computational facilities. For the latter, a single-point energy was obtained at QCI/SD level using the MP2-optimized geometry.

Considering the results obtained for some other systems, we suspect that a correctly optimized structure would induce a further modification of some 0.003 Å in the bond lengths while the energy might be lower by about 2−3 kcal mol^{-1}.

Results

The reactants and product of the reaction were fully optimized as described in the preceding section. The resulting structures and energies for CO_2 and CO_3^{2-} are given in Table 1. Corresponding results for $C_2O_5^{2-}$ are given in Table 2 and its structure is depicted in Figure 1. It is noteworthy that for the latter the potential energy surface around the minimum is very flat and allows a considerable degree of freedom with regard to the position of the central oxygen atom. The absolute minimum has a C_2-symmetric structure at both the RHF and MP2 levels, but an asymmetric adjustment of the central C−O bonds by 0.005 Å leaves the energy almost unchanged.

Table 1. Structures of the reactants at 6-31+G(d) level

Molecule	Method	C−O [Å]	Energy [a.u.]
CO_2	RHF	1.143	−187.6387868
($D_{\infty h}$)	MP2	1.181	−188.1179592
	QCI/SD	1.174	−188.1158356
CO_3^{2-}	RHF	1.286	−262.3193483
(D_{3h})	MP2	1.318	−263.0171893
	QCI/SD	1.313	−263.0184152

Table 2. Structure of the product at 6-31+G(d) level (labels according to Figure 1)

$C_2O_5^{2-}$ (C_2)	C−O [Å]	Angles [°]		Energy [a.u.]
RHF	(1,2) 1.388	C2−O1−C5	138.8	−450.0495857
	(2,3) 1.238	O1−C2−O3	113.6	
	(2,4) 1.230	O1−C2−O4	117.5	
MP2	(1,2) 1.437	C2−O1−C5	134.4	−451.220177
	(2,3) 1.268	O1−C2−O3	112.6	
	(2,4) 1.258	O1−C2−O4	117.4	
QCI/SD[a]				−451.223711

[a] Energy of MP2-optimized structure.

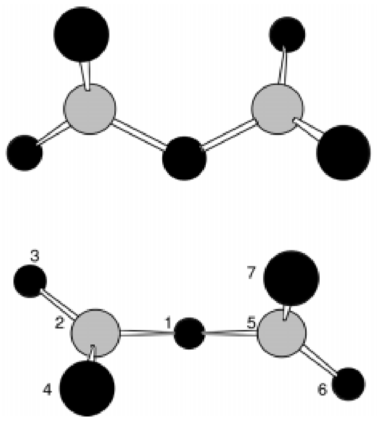


Figure 1. Structure of the $C_2O_5^{2-}$ anion; two views showing the C_2 symmetry of the system

With regard to the charge distribution, it is meaningless to use a conventional Mulliken population analysis with polarized and diffuse atomic basis sets, as their spatial extension and overlap is far too great. Mulliken charges obtained using a 6-31G basis set computation are listed in Table 3.

Table 3. Mulliken charges at 6-31G level for the various molecules

	CO_2	CO_3^{2-}	$C_2O_5^{2-}$
C	+0.86	+0.85	+0.95
O	−0.43	−0.95	(O1) −0.80 (O3) −0.79 (O4) −0.76

Discussion

The collected results offer an insight into the general behaviour of the studied system.

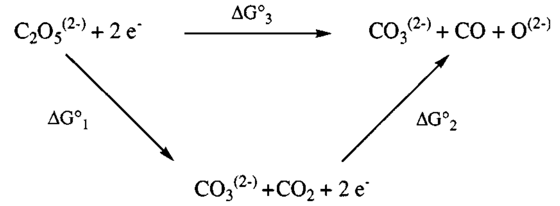
1. From a thermodynamic point of view, starting from the force constants obtained at Hartree−Fock level, one may compute the vibrational frequencies of the reactants and products. Furthermore, the computed energy, the moment of inertia, and scaled frequencies allow us to estimate, using statistical relationships, the reaction enthalpy, the entropy, and the Gibbs′ free energy at various temperatures. The results obtained at 298.15 K are presented in Table 4, along with those at the higher temperatures of 698.15 K and 973.15 K, which are closer to those of molten salts.

Table 4. Thermodynamic reaction properties derived from the theoretical results at 6-31+G(D) level

Method	$\Delta H(T)$ [kcal mol^{-1}]	$\Delta S(T)$ [cal K^{-1}mol^{-1}]	$\Delta G(T)$ [kcal mol^{-1}]
$T = 298.15$ K			
RHF	−56.09	−27.90	−47.77
MP2	−52.05	−	−43.73
QCI/SD	−54.83	−	−46.51
$T = 698.15$ K			
RHF	−55.382	−26.50	−36.87
MP2	−51.342	−	−32.83
QCI/SD	−54.123	−	−35.61
$T = 973.15$ K			
RHF	−54.62	−25.60	−29.71
MP2	−50.58	−	−25.67
QCI/SD	−53.36	−	−28.45

It can readily be seen that the product of this reaction has appreciable thermodynamic stability at any considered temperature. On the one hand, since the structure is not totally optimized at the QCI level, the reaction energies must still be more negative. On the other hand, the theoretical reaction energy of such systems may still be subject to some errors (basis set limitations, electronic correlation). However, we feel that with the presented methodology, especially at QCI level, further sophistication will not lead to a modification of the results by more than a few kcal mol^{-1}, which would be negligible compared to the −54 kcal mol^{-1} enthalpy variation. The reaction entropy is of course negative, but the overall Gibbs′ free energy remains negative, confirming the stability of the dicarbonate species. We may add to the argument that the reaction medium modifies the reaction entropy, generally leading to slightly less negative entropy contributions due to the bulk properties of condensed phase media.[6] This further confirms the thermodynamic stabilization of the dicarbonate ion in the molten medium.

As stated in the introduction, the free energy change for the production of dicarbonate ions from carbon dioxide and carbonate ions must be sufficient to shift the electrochemical reduction at potentials where the reaction of carbonate ions yet occurs. The reduction potential of dicarbonate ions may be calculated from the free energy change associated with reaction according to Equation 1. From the thermodynamic cycle shown in Scheme 1, Equation 3 may be derived.



Scheme 1. Thermodynamic cycle involving $C_2O_5^{2-}$

$$\Delta G°_3 = \Delta G°_1 + \Delta G°_2 \quad \text{or} \quad \Delta E°_3 = -\Delta G°_1/n\mathrm{F} + \Delta E°_2 \tag{3}$$

Here, $\Delta G°_1$ is the calculated free energy change associated with reaction according to Equation 1, which is given in Table 4 (−28.45 kcal.mol^{-1}); $\Delta E°_3$ and $\Delta E°_2$ are the standard potentials of the $C_2O_5^{2-}$/CO and CO_2/CO redox systems, respectively, and $-\Delta G°_1/n\mathrm{F}$ is the difference between these two standard potentials. The latter thus represents the difference between the reduction potentials of CO_2 and $C_2O_5^{2-}$.

The value calculated in this way amounts to 617 mV, which is close to the difference between the reaction potential of CO_2 and the cathodic limit of the accessible electrochemical window in the molten ternary eutectic mixture of carbonates, which is of the order of 600 mV. Although the result obtained by our theoretical approach must be treated with caution as no medium effects are taken into consideration, the trend indicated by this estimation is in reasonably good agreement with the assumption made in the first part of this work.

2. From a structural point of view, the association of a CO_2 molecule with a CO_3^{2-} anion does not lead to a molecule−ion complex, as might have been expected, but to a well-defined dicarbonate molecular species. The distances between the C and O atoms correspond to those of covalent bonds. The symmetry of the system indicates that the two CO_2 moieties are equivalent. The integrity of an incoming CO_2 molecule is lost in the formation of the product, in which the central oxygen atom is trapped between two CO_2 units. It is readily conceivable that at the surface of the condensed molten carbonate medium, CO_2 may be absorbed from the gaseous environment forming a $C_2O_5^{2-}$ species,

which will then be able to diffuse inside the molten salt. A possible mechanism for the diffusion could be described in terms of the interchange of oxygen atoms with neighbouring CO_3^{2-} ions (Equation 4).

$$O_2C^* + O'CO_2^{2-} \rightleftharpoons O_2C^*O'CO_2^{2-} \rightleftharpoons O_2C^*O'^{2-} + CO_2 \rightleftharpoons \text{etc.} \quad (4)$$

This description is further supported by the presence in the IR spectrum of a low-energy asymmetric stretch of the central C−O bonds and by the aforementioned observation that the potential energy surface remains almost constant under deformation of the C−O−C arrangement.

Of course, our description only relates to an ideal "gas phase" level, which may indeed be appropriate close to the interface between the gaseous and liquid phases, justifying the solubility of CO_2. However, one must be cautious in generalizing such a mechanism to the bulk, where the nature of the counterions and the existence of high electric fields will presumably modify this mechanism.

Indeed, it was concluded in the first part of this work that the regeneration of CO_2 from the dicarbonate ion should be a slow process, since the electrochemical reduction of CO_2 appears to be restricted to free CO_2. With regard to the proposed transport mechanism, this slowness is unexpected and may highlight an inconsistency.

General Conclusions

We have shown herein that CO_2 interacts with the carbonate anion to produce a stable dicarbonate ion. The latter exhibits C_2 symmetry, the central oxygen atom being covalently bonded by two equivalent CO_2 moieties. Analysis of the potential energy surface, completed by a vibrational analysis, shows that the central oxygen atom has sufficient freedom of motion to undergo ready exchange with the CO_2 species. This leads to the assumption that carbon dioxide should be highly soluble in the molten mixture of carbonates and consequently points to the existence of dicarbonate ions in this medium.

Acknowledgments

The authors are indebted to the Belgian National Fund for Scientific Research and the Fonds de Développement Scientifique of Louvain University for financial support of this research.

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