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Ab Initio SCF Study of the $C_2H_4 + Cl_2$ Reaction

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Abstract: An ab initio SCF study of the $C_2H_4 + Cl_2$ reaction has been carried out, assuming an intermediate state. When only two molecules are involved in the reaction, the energy of this ionic state (bridged or open) is much too high for a chemically acceptable intermediate state. The stabilization of this intermediate state by a solvent can make the reaction possible through such a path. The nature of the transition state involved in the first step of the reaction is discussed. Our calculations confirm the possibility of a $C_2H_4\cdots Cl_2$ complex, due to a charge transfer from the π orbital of C_2H_4 toward the Cl_2 molecule.

1. Introduction

Since the early work of Roberts and Kimball,[1] an intermediate cyclic ion is often used to explain the trans addition of halogen molecules to olefins.[2-4] Several mechanisms have been discussed, involving, for instance, a nonsymmetric intermediate,[3] an open ion intermediate,[5,6] a radical path,[7] or a termolecular reaction.[4,5,8] However, the hypothesis of a cyclic halogenium intermediate ion is the most widely accepted one for an interpretation of experimental data. It is generally assumed that the first (slow) step of the reaction corresponds to the formation of the halogenium and halide ions, while the second (fast) step leads to the final product.[4] In fact, the first step might involve the formation of a complex olefin···halogen molecule. Analogously to the stable charge-transfer complexes (CTC) described by Mulliken,[9] Dubois et al.[10b-d] called such complexes "CTCE" (evolutive charge-transfer complexes[11]), meaning that they have a short lifetime and dissociate into the ions. Other authors[12,13] describe them as "Dewar's π complexes",[14] assuming a three-center covalent bond; the theoretical status of these complexes will be discussed below. The nature of the σ halogenium ion is not well defined and may have varying degree of carbonium character.[10d] It has also been suggested that the gas-phase reaction could proceed through not fully dissociated ions, while in solutions the separation can arise due to solvation.[15] This solvent effect and, related to it, the nature of the transition state of highest energy in the first step of the reaction are perhaps the most puzzling aspect of this problem. Olah et al.[13] studying the bromination of alkenes in low polar solvents suggest that, in this case, the transition states of highest energy should be early transition states,[13] while in polar solvents[10] they would occur later along the reaction coordinate.

With the hope that quantum chemical calculation can help to elucidate the mechanism of this reaction, we have undertaken an ab initio SCF study of the $C_2H_4 + Cl_2$ reaction.

2. Details of the Calculations

SCF-LCGO-MO calculations have been performed.[16] Thus the molecular orbitals are expanded over a set of Gaussian functions. A double ζ basis set, called basis I, is used in most cases. The exponents are taken from ref 17 for C and H, and from ref 18 for Cl. In the (9,5) [4,2] set used for C the s functions are contracted according to the scheme[19] 5-2-1-1 and the p functions according to 4-1. For H, the (4) [2] set is contracted to 3-1. In the (11,7) [6,4] set used for Cl, the s functions are contracted to 5-2-1-1-1-1 and the p functions to 4-1-1-1. As shown in ref 20 and 21, small basis sets can give misleading results. The basis set used in this work is a double ζ basis set. Thus the results obtained with such a basis are expected to be qualitatively correct. However, when a great accuracy is needed (for instance in the calculation of the long-range complex) a d function is added on each chlorine, optimized on Cl_2 or on the bridged ion. We shall discuss in detail the special problem of the determination of the π complex.

The geometries used are discussed in the text. In all cases we fixed the distance CH = 2.05 bohrs (1.086 Å) and the angle $\angle HCH = 115.6°$ to the values given in ref 22, while the parameters a, b, c, and α (see Figure 1) are varied.

3. Energy Data for the Initial, Intermediate, and the Final States

Initial States. Table I collects the computed energies. With basis I, the energy of the chlorine molecule is -918.8253 hartrees for an optimized distance $b = 4.140$ bohrs (2.190 Å). The addition of a d function with exponent 0.518142 gives -918.8664 hartrees for $b = 3.834$ bohrs (2.029 Å). The experimental distance is 1.988 Å.[23]

The energy of C_2H_4 is -78.0047 hartrees (basis I) for an optimized parameter $c = R_{CC} = 2.523$ bohrs (1.335 Å) (as mentioned above R_{CH} and $\angle HCH$ have not been varied). This distance is within the range of the experimental values ranging from 1.332 to 1.339.[22,23] Our energy is very close to that obtained by Basch et al. (-78.0054 hartrees[22]) and by Whitten et al. (-78.0048 hartrees[24]). Other results may be found in ref 25.

Thus the energy of the whole system at infinite separation is -996.8300 hartrees with basis I and -996.8711 hartrees when a d function is added on each chlorine (Table I).

The $C_2H_4\cdots Cl_2$ Complex (π Complex or CTCE). As stated above, the first step of the reaction probably involves a formation of a $C_2H_4\cdots Cl_2$ complex, described as a π complex (three-center covalent bond[12-14]) or as a CTCE,[10] the nature of this complex being somewhat ambiguous. In the present work, only the perpendicular and central approach of Cl_2 is

Table I. Energy Data (Basis I)[a]

		E_{SCF}, hartree		ΔE, kcal/mol[g]
Isolated molecule	Cl_2	−918.8253	(−918.8664)[b]	
	C_2H_4	−78.0047		
	Total	−996.8300[d]	(−996.8711)[b]	
π complex: $C_2H_4\cdots Cl_2$		−996.8308[d]	(−996.8721)[b]	−0.5 (−0.63)[b]
Intermediate ions	Cyclic ion	−537.1162[d]	(−537.1482)[c]	
	Cl^-	−459.4838	(−459.4846)[b]	
	Total	−996.6000	(−996.6328)	144.4 (149.6)
	Open ion	−537.1011[e]		
	Cl^-	−459.4838		
	Total	−996.5849		153.85
Final state	$C_2H_4Cl_2$	−996.8957[f]		−41.24

[a] Basis I is described in the text. [b] One d function with exponent 0.518 142 is added to basis I; the combination $x^2 + y^2 + z^2$ is kept in the calculations. [c] One d function with exponent 0.4 is added to basis I; the combination $x^2 + y^2 + z^2$ is kept in the calculations. [d] The optimization of the geometry is commented in the text. [e] The geometry is taken from ref 20 and not optimized with our basis set. [f] The geometry (not optimized) is described in the text. [g] With respect to the isolated molecules.

Table II. $C_2H_4 + Cl_2$ Population Analysis (Basis I)[a]

	1 isolated molecules	2 π complex	3	4	5	6	7 intermediate ionic pair
Geometry[b]							
a, bohrs	∞	7.066 (7.000)	5	4.5	4	3.65	3.624
b, bohrs	4.1401 (3.8336)	4.1401 3.8336)	4.1568	4.2476	5.3	12	∞
Atomic charge							
Cl(2)	0.0	−0.018 (−0.013)	−0.096	−0.182	−0.486	−0.905	−1.000
Cl(1)	0.0	0.015 (0.011)	0.011	0.008	0.066	0.096	0.078
H	0.144	0.147 (0.148)	0.165	0.185	0.236	0.294	0.310
C	−0.287	−0.293 (−0.296)	−0.288	−0.283	−0.262	−0.183	−0.160
C(π)	1	0.993 (0.995)	0.841	0.681			
Molecule							
Cl_2	0.0	−0.004 (−0.002)	−0.085	−0.174	−0.421	−0.809	
Molecule							
C_2H_4	0.0	0.004 (0.002)	0.085	0.174	0.421	0.809	
Overlap population							
Cl_1-Cl_2	0.217	0.211 (0.227)	0.146	0.108	0.153	0.000	0.000
Cl_1-C	0.0	0.001 (0.000)	−0.056	−0.101	−0.048	0.166	0.233
C_1-C_2	1.399	1.392 (1.391)	1.343	1.278	1.027	0.612	0.541
C-H	0.761	0.762 (0.762)	0.765	0.765	0.756	0.725	0.724
ΔE, kcal/mol	0.0	−0.5 (−0.6)	3.892	11.236	40.362	103.760	144.373

[a] For the values given in parentheses, a d function with exponent 0.518 142 has been added to basis I. [b] The geometry parameters other than *a* and *b* are discussed in the text.

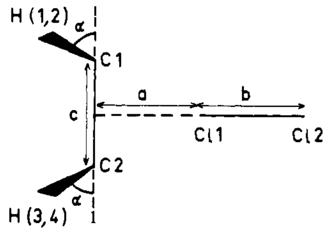

Figure 1. $C_2H_4 + Cl_2$ geometry parameters.

considered. At the SCF level, a stable complex is found for $a = 7.066$ bohrs (3.739 Å) with basis I. The parameters *b*, *c*, and α have been optimized and reproduce their initial values found in the isolated molecules. The stabilization energy (Table I) is −0.0008 hartree (−0.5 kcal/mol). When a d function is added on each chlorine, the stabilization energy is −0.0010 hartree (−0.63 kcal/mol) for $a = 7.000$ bohrs (3.704 Å). This distance is in good agreement with an estimate of Nelander[26] obtained from the benzene-chlorine complex. We must note that previous CNDO calculations[26,27] overestimate the stabilization energy and underestimate the intermolecular distance, as might be expected when using such methods to treat these kinds of complexes.

The computed dipole moment of the whole system is 0.24 D. A population analysis, given in Table II, shows that the nearer chlorine takes a small amount of positive charge, while the farther one becomes slightly negative as expected. This results in a very small polarization of both molecules. The π orbital is slightly depopulated, not only due to an electron transfer on Cl_2, but also due to a reorganization of the charge distribution in the ethylene molecule. From the overlap population between Cl(1) and C, it is clear that we cannot speak of a covalent tricenter bond. Actually both chlorines contribute very little to the π orbital. It thus appears that the hypothesis of a covalent three-center bond,[14] which initiated the first theoretical work in this direction[28] (based on the Hückel approximation), is not really appropriate for the description of this class of π complexes, which can be well described in terms of intermolecular interactions. It is well known that the methods used in the treatment of intermolecular interactions are generally based on one of these two approaches: the supermolecule treatment or the perturbation theory. In a perturbation treatment, we can expect that the π orbital of C_2H_4 and some empty orbitals of Cl_2 (in particular d orbitals) allow an important charge-transfer term. We can show that the role of such orbitals also appears in a SCF supermolecule treatment. In this case it is suitable to start the calculation from orthogonalized molecular vectors. Thus the difference between the SCF energy and the energy obtained at the first iteration represents the induction and charge-transfer energy. In the present case, the induction energy is small, since the isolated molecules have no dipole moment, so that this energy difference describes mainly the charge-transfer contribution. As expected, this contribution is large (-0.0007 hartree when the basis set includes a d function on each chlorine), the first-order energy being very much smaller (-0.0003 hartree).

This SCF treatment neglects the stabilization due to the dispersion energy. Calculations are in progress to evaluate this term, using a perturbation treatment which we exploited earlier for other cases.[29] Considering the polarizabilities of both molecules (4.61 and 4.26×10^{-24} cm^3 for Cl_2 and C_2H_4, respectively[30]) this dispersion energy could be an important element in the stabilization of such complexes.

Our calculations show that, even in the SCF determination, the molecules C_2H_4 and Cl_2 are able to form a long-range complex, the stability of such a compound being largely due to the charge transfer. In this work, only the perpendicular and linear approach of Cl_2 is considered. In semiempirical treatments,[26-28] this configuration is generally the most stable one. However, such treatments are very inaccurate.[27] We are presently studying this long range complex, using a very large basis set and including the dispersion energy, for several geometric configurations.

The Intermediate Ions. As mentioned above, an ionic intermediate state is assumed in the trans addition of halogen molecules to ethylene, a bridged halogenium ion being generally postulated to interpret an experimental work.

The energy of the cyclic ion $C_2H_4Cl^+$ is computed with basis I (Table I). We obtain $E = -537.1162$ hartrees for $a = 3.624$ bohrs (1.918 Å), $c = 2.746$ bohrs (1.453 Å), and $\alpha = 12.2°$. This energy is slightly lower than the value obtained by Hehre and Hiberty.[20] The energy of Cl^- being -459.4838 hartrees, the energy of the whole system is -996.6000 hartrees. Compared with the energy of the initial state (isolated molecules) the energy difference is 0.23 hartree (144.4 kcal/mol), which is much larger than one would expect for a possible intermediate state in the gas phase. The addition of a d function causes only minor changes of this value. With exponent 0.518 142, the energy of the chloronium cation is -537.1460 hartrees for $a = 3.400$ bohrs (1.799 Å), $c = 2.770$ bohrs (1.466 Å), and $\alpha = 14.7°$. The energy of Cl^- (including the combination s of the d components) is -459.4846 hartrees. The energy of the cation is slightly lowered by the use of an optimized exponent 0.4 which gives $E = -537.1482$ hartrees, the energy of the whole system being -996.6328 hartrees. Compared with the initial state, the energy difference is about 150 kcal/mol. Such a high energy was also found in semiempirical work[27] and in ab initio studies of the reaction $C_2H_4 + F_2$.[15]

The energy of the open 2-chloroethyl cation is computed with our basis I. The most probable conformation of this cation is described in ref 31. Using the geometry determined by Hehre and Hiberty,[20] the energy obtained is -537.1011 hartrees. Thus the open 2-chloroethyl cation is less stable than the bridged cation by about 9.5 kcal/mol (9.2 kcal/mol in ref 20). An optimization of the distances in our calculation of the 2-chloroethyl cation could slightly lower this energy difference, but we do not expect that it could reverse the relative stabilities of the cations.

Though the 1-chloroethyl cation could be more stable than the bridged and the open 2-chloroethyl cation,[20,32] it is of little interest in the trans addition and we have not studied it.

Clearly the energies of the bridged and of the 2-chloroethyl cation differ very little (by <10 kcal/mol). In both cases, the energy of the ionic pair is too high to be acceptable as an intermediate state in the gas-phase reaction. Consequently other interactions and perhaps even other mechanisms should be considered. This will be discussed in more detail in section 4.

The Final State. The energy of $C_2H_4Cl_2$ is computed using the following geometry: when available, the experimental parameters are used (see ref 23 for d_{CCl}, d_{CC}, and β(ClCC)); for the CH_2 groups we have taken the same geometry as in ethane. Basis I gives $E = -996.8957$ hartrees. The energy of halogenation is -41.24 kcal/mol. This value can be compared with the experimental values of -43.653 kcal/mol obtained by Conn et al.[33] at 355 K. An optimization of the geometry of $C_2H_4Cl_2$ could slightly lower our result. However, such an optimization requires a considerable amount of work. Since it would involve only a minor change in the energy value, we have not performed such calculations.

4. Possible Reaction Mechanisms

Gas Phase. As noted in section 3, the energy of the ionic pair is too high for an intermediate state. In the gas phase Cl^- can be stabilized by another Cl_2 molecule. Our SCF calculations indicate that the best geometry of Cl_3^- is linear and symmetric. The stabilization energy is $\Delta E = -30.69$ kcal/mol (basis I) for the distance $d = 4.597$ bohrs (2.432 Å) between the two chlorine atoms (d is 10% larger than in Cl_2). However, this stabilization is not large enough to allow the reaction. It would be interesting to study if another Cl_2 molecule approaching the molecular complex from the back side could help the dissociation of the ions and make the reaction possible. We can also imagine that, though not completely dissociated, the more distant chlorine atom moves out of the CCCl(1) plane and approaches the complex from the back side. This possibility is discussed in section 5.

It would be also of great interest to study the radical path. Unfortunately an SCF treatment of such a path could lead to misleading results because of the probable variation of the correlation energy along the reaction path. In the ionic states, involving only closed-shell systems, we assume that the variation of the correlation contribution is negligible.

Solvent Effect. Experimental work is generally done in solutions. It is sometimes suggested that only the anionic part is solvated.[6,34] The solvation of Cl^- was rather extensively studied both experimentally[35] and theoretically.[36] The hydration energy of Cl^- lies around 90 kcal/mol.[35] However, since the bridged ionic state is about 150 kcal/mol above the initial state, the solvation of Cl^- alone would not allow the reaction. For the sake of simplicity we have chosen H_2O as a model in order to study the solvation of the chloronium cation. In addition to basis I, a set (9,5) [4,2] has been used for O, taken from ref 17, with a contraction[19] 5-2-1-1 and 4-1 for the s and p functions, respectively. The geometry parameters[23] $r_{OH} = 0.957$ Å and $\alpha = 104.5°$, providing E_{SCF} (H_2O) $= -76.000$ 16 hartrees, were used in all the calculations. One H_2O molecule has been placed perpendicularly to the plane defined by one of the CH_2 groups, the two hydrogen atoms of the water molecule being symmetrically placed with respect to this plane and O being located along one CH bond axis. For $d_{CO} = 5.626$ bohrs (2.977 Å), corresponding to $d_{HO} = 3.574$ bohrs (1.891 Å), the stabilization energy is -16.13 kcal/mol (a similar bonding with ethylene provides <1 kcal/mol for $d_{HO} = 2.338$ Å). Four such hydrogen bonds can be formed, providing a stabilization energy of -54.86 kcal/mol for $d_{HO} = 1.995$ Å. If we choose for Cl^- the hydration energy proposed by Morris[35a] (-87.5 kcal/mol),

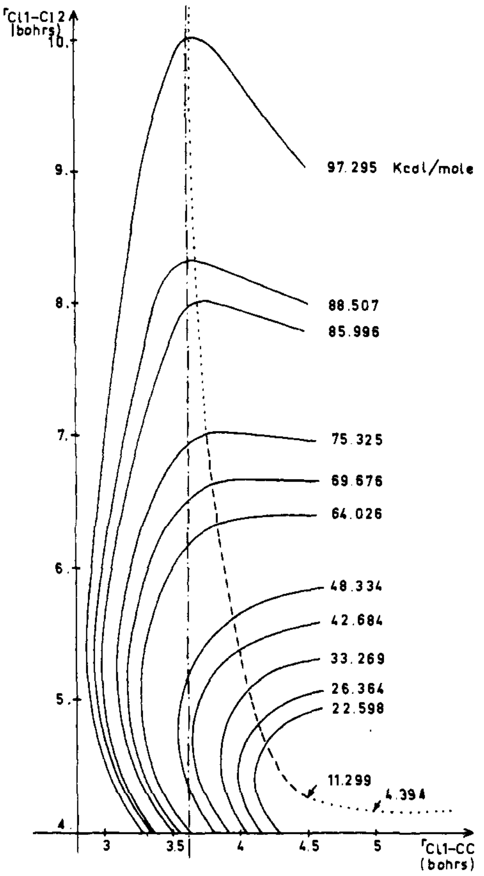

Figure 2. $C_2H_4 + Cl_2$ reaction path: ··· minimum energy path; - - - "guessed" path; - · - · - value of a in the bridged ion. The energy differences, given in kilocalories per mole, refer to the energy of the $C_2H_4 \cdots Cl_2$ complex. Distances are given in bohrs (1 bohr = 0.529 177 Å).

the stabilization of the ionic pair by the solvent is −142.36 kcal/mol (such a high value was also obtained from a semiempirical determination in acetic acid[27]). This stabilization energy almost completely compensates the energy necessary to form the ionic pair from the isolated molecules (Table I). Of course, these calculations are not an accurate determination of the solvation energy of the ionic pair, but they clearly show that a solvent can make the reaction possible through this path. In the case of ethylene, the solvation of the cation, though less important than that of the anion, is not negligible. The stabilization energy should be somewhat smaller with a low-polar solvent.

5. Nature of the Transition State of Highest Energy

One of the purposes of this work was to determine the nature of the transition state of highest energy in the first step of the reaction, assuming the formation of a bridged halogenium intermediate state. Starting from the π complex and choosing a as a reaction coordinate, we have optimized the parameters b, c and α. Up to $a = 5$ bohrs, we observe only a very small change in these parameters. The energy at this point ($a = 5$ bohrs) is about 4.4 kcal/mol higher than the energy of the π complex (Figure 2). Population analysis (Table II) shows that both molecules are slightly more polarized than in the π complex. This is mainly due to a small increase of the negative charge on Cl_2 and a small depopulation of the π orbital of C_2H_4. This tendency is more pronounced at $d = 4.5$ bohrs, but we can still recognize the orbitals of the isolated molecules, which only become more perturbed than in the π complex. This is no longer the case for shorter distance a, when it is difficult to determine the reaction path. We thus present the pertinent potential surface (Figure 2), choosing a and b as reaction coordinates, Since the changes in c and α cause only a relatively small variation in the energy of the system we have optimized these parameters only for some geometries and interpolated in other cases. All calculations have been done with basis I. The overlap population between Cl(1) and Cl(2) (Table II) describes the evolution of the Cl(1)–Cl(2) bond in this region: it remains mainly covalent until $a = 4.5$ bohrs, while its nature qualitatively changes near $a = 4$ bohrs; however, there is still no bond between Cl(1) and each C. Clearly, even though there is some uncertainty in the part of the reaction path represented by the dashed line, there is no possibility for an early π transition state to be formed (Figure 2). For short distance a, b becomes the main reaction coordinate. Figure 2 shows that the energy of the point defined by $b = 10$ bohrs and $a = 3.65$ bohrs is 97.29 kcal/mol higher than the energy of the π complex. Calculations performed for $a = 3.65$ bohrs and $b = 12, 14, 17, 20, 40, 60, 100$, and 500 bohrs show that the energy is monotonically increasing with b. For these points, a is nearly equal to the distance in the cyclic ion, the electronic charge on Cl(2) is close to one unit, and the overlap population between Cl(1) and each C becomes positive, corresponding to the formation of a bond (Table II). Within the accuracy of our calculations we cannot decide whether or not there is a σ transition state for very large b values when only two molecules are involved. In any case, its energy would be so high that it would be of little chemical interest. Moreover, Figure 2 shows no possibility for an incompletely dissociated intermediate state as suggested in ref 15, We can also see that for $a = 4$ bohrs (2.117 Å), the energy difference is already 40 kcal/mol when $b = 5.3$ bohrs (2.805 Å), this value of b being only 28% larger than the distance in the Cl_2 molecule. Thus it seems very unlikely that the more distant Cl atom (not completely dissociated) would be able to move to the back side of the complex as proposed in section 4. These mechanisms are probably not favorable for the reaction in the gas phase.

As seen in section 4, the intermediate state can be strongly stabilized by the interaction with a solvent and we shall now discuss how a transition state could arise under such conditions. It is clear that the strongest stabilization occurs when the ions are fully dissociated, while it is negligible for large a values ($a > 4{,}5$ bohrs, for instance). For intermediate a values the interaction with the solvent will increase as the ions will dissociate. If the solvent effect is large enough to compensate the increase of energy along the reaction path, then chemically acceptable transition states may exist. An importance of the solvent effect discussed in section 4 makes us convinced that one or more transition states are possible. A semiempirical study of the solvent effect, though inaccurate, led to the same interpretation.[27] If the compensation occurs already for a very small degree of dissociation, an early transition state may exist. Clearly this compensation should be more important for a strong polar solvent than for a low polar solvent. Thus we can expect that, if a π transition state exists, it will be of lower energy in a strong polar solvent than in a low-polar solvent. This would be compatible with the hypothesis of a σ transition state of highest energy in polar solvents.[10,13,34]

Let us summarize our main results. Our calculations confirm the possibility of a $C_2H_4 \cdots Cl_2$ complex, the stabilization energy being due to a charge transfer from the π orbital of C_2H_4 toward the Cl_2 molecule. When only two molecules are considered the energy of the $C_2H_4Cl^+$ (bridged or open geometry) and Cl^- ions is much too high for a possible intermediate state in the halogenation of C_2H_4. A solvent can strongly stabilize this intermediate state, allowing the reaction through such a path.

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Ab Initio Molecular Orbital Calculations on the Water–Carbon Dioxide System. Reaction Pathway for $H_2O + CO_2 \rightarrow H_2CO_3$

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Abstract: The reaction pathway for $H_2O + CO_2 \rightarrow H_2CO_3$ has been calculated using ab initio methods. The energy barrier was found to be 234 kJ/mol in the Hartree–Fock approximation with a basis set of double ζ quality. Correlation was accounted for by means of a configuration interaction calculation including singly and doubly excited configurations from the ground state. The inclusion of correlation effects lowered the energy barrier to 219 kJ/mol. The reaction was found to proceed with an attack of the oxygen atom in water on the carbon atom in carbon dioxide simultaneous with the proton transfer from the water to the carbon dioxide skeleton.

(I) Introduction

The formation of carbonic acid, H_2CO_3, and its associated ions, HCO_3^- and CO_3^{2-}, occurs through two different reaction mechanisms in aqueous solution.[2a] At neutral pH carbon dioxide reacts with water to form carbonic acid

$$H_2O + CO_2 \xrightarrow{k_1} H_2CO_3 \tag{I}$$

which is in a fast equilibrium with the ionic species. In basic solution, pH >9.5, a hydroxide ion attacks carbon dioxide to form a bicarbonate ion directly

$$OH^- + CO_2 \xrightarrow{k_2} HCO_3^- \tag{II}$$

Both these reactions require the rearrangement of covalent bonds and it is therefore perhaps not surprising that these reactions proceed with moderate rates ($k_1 = 0.03\ s^{-1}$ and $k_2 = 8.5\ s^{-1}\ mol^{-1}\ m^3$)[2a] at room temperature. The ionizations of