

Ab Initio Molecular Orbital Calculations on the Water-Carbon Dioxide System. The Reaction $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$

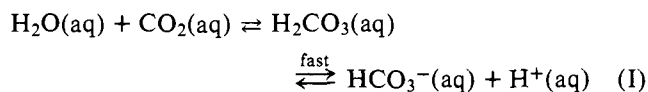
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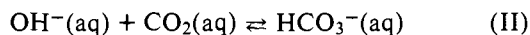
Abstract: The reaction of $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$ has been studied by ab initio MO-LCAO-SCF methods employing a basis set of double ζ quality augmented by diffuse s and p functions on carbon and oxygen. For the product HCO_3^- an unusually long C-OH distance of 1.43 Å emerges. The reaction was found to proceed without any energy barrier in contrast to experimental results in aqueous solution showing that this barrier is due to solvation effects. The calculations are used for a discussion of a possible mechanism for the enzyme carbonic anhydrase.

Introduction

The equilibrium between carbon dioxide and its aqueous ions HCO_3^- and CO_3^{2-} can be established through two different reaction mechanisms. At neutral pH the kinetics are consistent with the scheme

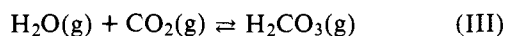


while in basic solutions the appropriate scheme is¹



Both reactions proceed with moderate rates and have Arrhenius activation energies of 74 and 55 kJ/mol, respectively.^{2,3} In fact, under physiological conditions the rate is so small that it is necessary for living systems to catalyze the hydration and dehydration reaction by the enzyme carbonic anhydrase (CA).

In order to obtain a better understanding of these important reactions we have performed a series of ab initio molecular orbital calculations determining molecular interactions in the water-carbon dioxide system.⁴⁻⁶ In ref 6 the energy barrier was determined for the reaction



The calculated barrier, 219 kJ/mol, is considerably higher than the experimental activation energy for the first step of scheme I, and this was interpreted as due to a specific solvent effect.

For reaction II solvation effects are expected to be even more important since ionic species are involved. One approach to the study of solvation effects is to investigate the reaction for the free species either through experiments in the gas phase⁷ or through quantum mechanical calculations. In the present paper we thus present an ab initio MO-LCAO-SCF calculation determining relevant parts of the $\text{CO}_2\text{-OH}^-$ energy surface. By comparing the enthalpies and the energies of activation for the reactions II and IV



the effect of the medium is revealed.

Computational Details

The ab initio computations were performed in the LCAO-MO-SCF scheme using Gaussian atomic orbitals as basis functions. Two different basis sets were used. Basis set A, which was used in all geometry optimizations, consisted of 7 s and 3 p primitive functions on oxygen and carbon and 4 s and

1 p on hydrogen.^{8,9} The functions were contracted to 4 s, 2 p and 2 s, 1 p, respectively. For the final energy comparisons a larger double ζ basis set, B, augmented by diffuse s and p functions on carbon and oxygen was used in order to obtain a better description of the negative ions. This basis set consisted of 9 s and 5 p functions⁹ contracted to 4 s and 2 p according to Dunning.¹⁰ The exponents of the diffuse s and p functions on carbon were 0.05 and 0.04 and on oxygen 0.09 and 0.06, respectively. These exponents were obtained through extrapolation so that the three smallest exponents formed a geometric series. All calculations were performed with the program system MOLECULE¹¹ and within the Hartree-Fock approximation.

Results

As a first step in the calculations the geometries of HCO_3^- and OH^- were optimized with basis set A. The results of the optimizations are shown in Figure 1. The bicarbonate ion was assumed planar, which was supported by crystallographic data¹² as well as previous calculations on H_2CO_3 .⁵

Total energies for different molecules and ions in the $\text{H}_2\text{O-CO}_2$ system calculated with basis set B are collected in Table I. From these total energies it is possible to estimate the heats of reaction for a number of reactions, which are shown in Table II together with the ΔH values for the corresponding reactions in aqueous solution.

The main part of our investigation was to find out whether there was a barrier for the reaction IV or not. It is at present impossible to calculate a complete energy hypersurface for a system as large as $\text{OH}^- + \text{CO}_2$ even within the Hartree-Fock approximation. Therefore we were forced to introduce some approximations. The principal approximation is that the reaction coordinate is well described by the single parameter, the C-OH distance. The procedure is then to minimize all other bond parameters for a given C-OH distance. The pitfalls with such an approach when the energy hypersurface contains several minima have been discussed elsewhere.^{6,13}

The approximation seems acceptable for such a simple reaction as $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$ where only one bond is broken or formed. A test of this approximation is the behavior of the dependent parameters along the reaction coordinate. It is seen from Table III that there are no discontinuities in these parameters. Two further approximations were introduced, namely, the system was kept planar and the O-H distance was not varied. The calculations showed that there was no barrier to reaction (Figure 2). In Figure 2 it is also shown how the potential energy changes when CO_2 and OH^- are brought together under C_{2v} symmetry with no relaxation of the other parameters. Figure 3 gives an illustrative picture of how the

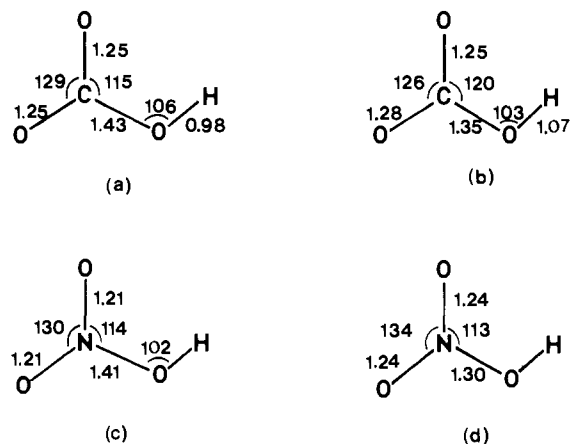


Figure 1. (a) Calculated structure of HCO_3^- . The optimized O-H distance in OH^- was found to be 0.98 Å and the C-O distance in CO_2 was calculated to be 1.16 Å (ref 4). (b) Crystal structure of the HCO_3^- moiety in NaHCO_3 (ref 12). (c) Gas-phase structure of HNO_3 from the microwave study of D. J. Millen and J. R. Morton, *J. Chem. Soc.*, 1523 (1960). (d) Crystal structure of HNO_3 : P. V. Luzzati, *Acta Crystallogr.*, 4, 120 (1951).

Table I. Total SCF Energies for Different Species in the $\text{H}_2\text{O}-\text{CO}_2$ System Calculated with Basis Set B

Molecule	Total energy, au
OH^-	-75.3975
H_2O	-76.0393
CO_2	-187.5583
HCO_3^-	-263.0448
H_2CO_3	-263.5963

Table II. Heats of Reaction for Some Possible Transformations in the $\text{H}_2\text{O}-\text{CO}_2$ System Calculated with Basis Set B

Reaction	$\Delta E_{\text{calcd.}}$, kJ/mol	$\Delta H_{\text{exp}}(\text{aq})$, kJ/mol
$\text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}$	-1686 ^a	-56 ^b
$\text{OH}^- + \text{CO}_2 \rightleftharpoons \text{HCO}_3^-$	-234	-47
$\text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3$	-1449	-1 ^c
$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$	3	8 ^c

^a The estimated Hartree-Fock limit is -1708 kJ/mol (H. Lischka, *Theor. Chim. Acta*, 31, 39 (1973)) and the experimental value calculated from Table V in A. C. Hopkinson, N. K. Holbrock, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, 49, 3596 (1968), is -1720 kJ/mol. ^b V. P. Vasilev and G. A. Lobanov, *Russ. J. Phys. Chem. (Engl. Transl.)*, 41, 434 (1967). ^c K. F. Wissbum, D. M. French, and A. Patterson, *J. Phys. Chem.*, 58, 693 (1954); F. J. W. Roughton, *J. Am. Chem. Soc.*, 63, 2930 (1941).

molecular arrangement changes under the course of the reaction. The Mulliken population analysis in Table IV shows how the electron distribution changes along the reaction coordinate.

Table III. The Variation of the Dependent Parameters along the Reaction Coordinate $R_{\text{C-OH}}$ ^a

	$R_{\text{C-OH}}$					
	1.1	1.43	1.50	1.70	2.00	3.00
C-O ₁	1.28	1.25	1.24	1.22	1.20	1.18
$\angle \text{O}_1\text{CO}_3$	126	129	133	139	147	164
$\angle \text{O}_1\text{CO}_2$	116	115	115	111	105	104
$\angle \text{CO}_2\text{H}$	113	106	106	107	102	93

^a The two C-O distances were optimized separately but they were found to differ less than 0.01 Å. (Distances in Å and angles in degrees).

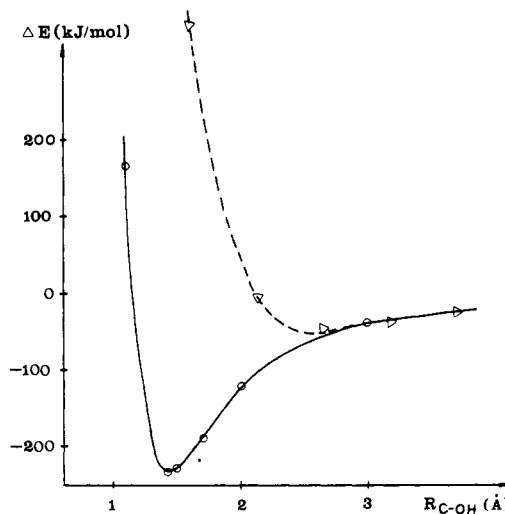


Figure 2. Variation of the interaction energy, ΔE , along the reaction coordinate, $R_{\text{C-OH}}$. The dashed line represents an approach of OH^- and CO_2 under C_{2v} symmetry without relaxation of the dependent parameters.

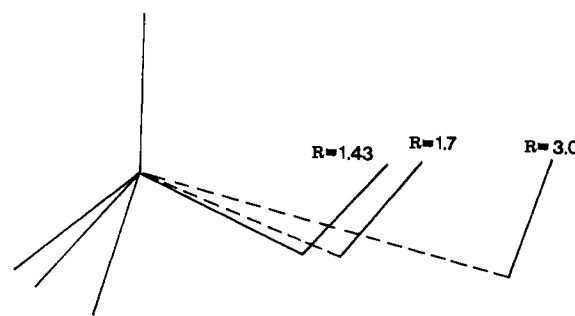


Figure 3. The reacting system at three positions along the reaction coordinate $R_{\text{C-OH}}$. The dashed line indicates the C-O bond formed.

Discussion

A. Geometry of HCO_3^- . A remarkable feature of the calculated equilibrium geometry of the free HCO_3^- ion is the long C-OH distance of 1.43 Å. This is significantly different from the value 1.345 Å found in crystalline NaHCO_3 ¹² and also different is the C-OH distance of 1.34 Å previously calculated for carbonic acid.⁵ Since negatively charged systems in general require a more flexible basis set we reoptimized the C-OH distance using basis set A augmented with a diffuse p function on oxygen. However, the bond distance changed less than 0.01 Å indicating that the value 1.43 Å is essentially correct. Further support for this conclusion is obtained from a comparison with the isoelectronic molecule HNO_3 , where, as seen in Figure 1, there is a lengthening of the N-OH distance amounting to 0.10 Å when changing from solid to gas phase.

It is likely that the substantial difference between the C-OH and N-OH distances in the crystal and in gas phase for

Table IV. Gross Atomic Populations Calculated with Basis Set B at Different Positions along the Reaction Coordinate^a

	<i>R_{C-OH}</i>						
	1.1	1.43	1.50	1.70	2.00	3.00	∞
C	5.605	5.477	5.477	5.467	5.435	5.383	5.440
O1	8.786	8.637	8.594	8.516	8.426	8.346	8.280
O2	8.167	8.513	8.558	8.675	8.834	9.065	9.093
O3	8.730	8.614	8.596	8.538	8.462	8.302	8.280
H	0.712	0.760	0.775	0.803	0.842	0.903	0.907
CO ₂	-1.12	-0.73	-0.67	-0.52	-0.32	-0.03	0
OH ⁻	+0.12	-0.27	-0.33	-0.48	-0.68	-0.97	-1.00

^a The two lowest rows show the net charge on the CO₂ and OH⁻ fragments (distances in Å). See Figure 4 for the numbering of the atoms.

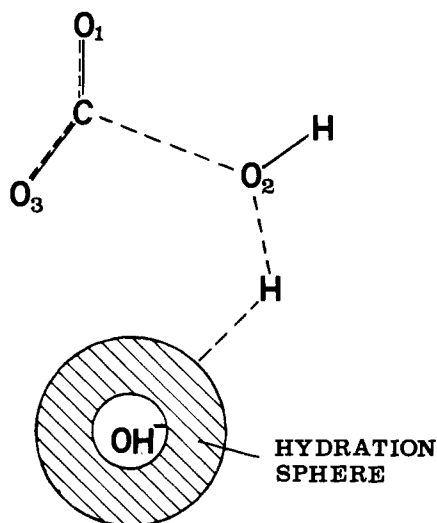


Figure 4. A possible transition state for the OH⁻ + CO₂ → HCO₃⁻ reaction in aqueous solution.

HCO₃⁻ and HNO₃, respectively, is due to the formation of strong hydrogen bonds in the solid. As a result the structure of the heavy atom skeleton approaches that of the symmetrical ions CO₃²⁻ and NO₃⁻, respectively. The shortening of the C-OH and N-OH bonds is thus accompanied by a lengthening of the other C-O and N-O bonds.

B. The Reaction between CO₂ and OH⁻. The calculations unequivocally show that there is no potential energy barrier for the formation of HCO₃⁻ from CO₂ and OH⁻ in the gas phase. Similar results were obtained by Scheiner et al.¹⁴ for a number of other negative ion-molecule reactions using *ab initio* and semiempirical quantum chemical methods.

That the attack by OH⁻ on CO₂ in aqueous solution (scheme II) is a relatively slow process with a sizable activation energy must thus be attributed to solvation effects. Along the reaction coordinate in Figure 2 the solvation energy will vary and since a substantial energy barrier is created the solvation energy must decrease more strongly than linearly with the reaction coordinate. For a barrier to result without invoking very dramatic solvation effects one expects that the transition state occurs at a comparatively long C-OH distance. On a molecular level this could be interpreted in several ways. An appealing possibility is that a water molecule of the carbon dioxide hydration sphere donates a proton to a (solvated) OH⁻ ion, while simultaneously the C-OH bond is formed as shown in Figure 4. The interesting aspect of this mechanism is that it can be generalized to apply to reaction I. In this case the donated proton is accepted by another water molecule. This means that the difference in activation energy between reactions I and II reflects the difference in proton affinity between a solvated OH⁻ ion and a water molecule.

C. The Enzymatic Hydration of Carbon Dioxide. In biological systems the hydration and dehydration of CO₂ could constitute the rate-limiting steps in the processing and transportation of CO₂. To avoid this the CO₂ reactions are catalyzed by the enzyme carbonic anhydrase. This enzyme has a molecular weight of ~30 000 and contains one zinc atom.¹⁵ The catalytic activity is intimately connected to the Zn atom, which is situated in a rather deep active cleft.¹⁶ The kinetics of CA have been investigated by several workers and its turnover number is one of the highest known.^{17,18} In spite of the large number of investigations the mechanism for the activity of CA is poorly understood. There has been some controversy as to whether HCO₃⁻ or H₂CO₃ is the substrate for the dehydration reaction. Arguments have been put forward against both alternatives by consideration of the diffusional motion.¹⁹⁻²¹ However, it has recently been shown both experimentally²² and theoretically²³ that the bicarbonate ion is the substrate for the enzymatic dehydration reaction. The necessary proton transfer reaction is facilitated by buffer molecules present both *in vitro* and *in vivo*.

The most advocated explanation of the CA activity is the Zn-bound hydroxide ion mechanism.^{24,25} In this model a Zn-bound OH⁻ ion is assumed to attack a CO₂ molecule giving HCO₃⁻. Basically two objections have been raised against this idea. Firstly, the mechanism requires an unusually low p*K*_a value for the equilibrium



as compared to other Zn complexes.²⁴ Secondly, it is far from obvious why the barrier for the reaction II should essentially disappear when the OH⁻ ion is bound to the positive Zn atom. The present calculation gives additional insight into the second of these objections.

In section B it was concluded that the barrier for the reaction II was created by the strong solvation of the hydroxide ion in aqueous solution. The enzyme would thus be an efficient catalyst if it could strip the OH⁻ ion of its solvation sphere and at the same time keep it stable relative to protonation. It seems that this task has been effectively accomplished by binding the OH⁻ to a Zn²⁺ ion kept in the rather hydrophobic environment of the active cleft in the enzyme. In the active cleft there is little room for an effective solvation of the ZnOH⁺ moiety. The price that is paid is that instead of a hydrated OH⁻ one has a Zn-bound OH⁻. This binding decreases, of course, the nucleophilicity of the OH⁻ ion. However, the calculations show that this nucleophilicity can be substantially decreased before a barrier is created. If the formation of HCO₃⁻ can be carried out with continuous contact with the Zn atom it seems plausible that the barrier can be kept very low.

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Relative Stability of Planar and Perpendicular Olefins

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Abstract: The rotational barriers around carbon-carbon double bonds and the relative stability of the planar and perpendicular olefins were analyzed within the framework of the ab initio unrestricted Hartree-Fock theory in terms of electrostatic, exchange repulsion, polarization, charge transfer, and their coupling interactions. The olefins we have investigated are $CX_2=CH_2$ ($X = H, Li, F, CH_3, CN, BeH$ and Na), $CX_2=CY_2$ ($X = Li, CH_3$ and $Y = F, CN$), and polyolithioethylenes. The charge transfer and exchange repulsion interactions play an essential role in the stabilization of perpendicular olefins.

I. Introduction

A number of experimental investigations have been made on thermal rotational isomerizations about carbon-carbon double bonds as well as photochemical and catalytic isomerizations.²⁻⁴ The thermal rotation about a double bond is severely hindered and the planar olefin is more stable than the perpendicular form. There have been several ab initio calculations reported on the rotational barrier around a double bond in ethylene.⁵⁻⁷

The high rotational barrier of ethylene molecule should be lowered significantly by a proper selection of substituents. Their effects are thought to be both steric and electronic in origin.^{3,8} While bulky substituents can raise the energy of the planar form,⁹ electronic effects can stabilize the charge separation or biradicals in the perpendicular form.¹⁰ An effective combination of these two interactions could produce more stable perpendicular olefins.¹¹ A theoretical approach to this possibility was examined recently with an ab initio molecular orbital method.¹² It was found that the rotational barrier of 1,1-dilithioethylene not only is very low, but also the perpendicular form may actually be more stable than the planar form and that the carbon-carbon bond length does not change greatly during rotation.

Our purpose here is to analyze and find the origin, from the point of view of intermolecular interactions, of the rotational barrier around a double bond. Since in the supermolecule approach each molecule is treated as a whole, an interpretation of the spectrum of substituents tends to be obscured. Thus, we decided to view each molecule as an interacting system of two

fragments and decompose and interpret the rotational barrier in terms of five chemically meaningful interaction components—electrostatic (ES), exchange repulsion (EX), polarization (PL), charge transfer (CT), and their coupling (MIX) terms. Electron densities and Mulliken populations¹³ can also be divided into components. The molecules we have investigated systematically are $CX_2=CH_2$ ($X = H, Li, F, CH_3, CN, BeH$ and Na), $CX_2=CY_2$ ($X = Li$ or CH_3 and $Y = F$ or CN), and polyolithioethylenes.

II. Computational Aspects

All calculations reported here were performed within the framework of ab initio unrestricted Hartree-Fock (UHF) theory, employing a modified version of the GAUSSIAN 70 package.¹⁴ The split-valence 4-31G¹⁵ (5-21G for lithium atoms)¹⁶ and minimal STO-3G¹⁷ basis sets were used with the suggested standard parameters. As for the molecular geometries, standard bond lengths and angles proposed by Pople et al.¹⁸ were employed to systematically examine the substituent effects.

In our calculation a (substituted) ethylene molecule was considered to form as a result of interaction between two triplet (substituted) methylenes which have the geometry of the CH_2 part of ethylene. The partitioning is justifiable, for the two triplets can be coupled smoothly to form the ground state of ethylene.¹⁹⁻²¹ A restricted single-determinant representation of the ground state of ethylene becomes progressively less satisfactory as the rotation angle, θ , is increased from 0° (planar) to 90° (perpendicular). When the perpendicular form is