Calculation of solvent effect on the reaction $OH^- + CO_2 \rightleftharpoons HCO_3^-$

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The solvent effect on energetic course of the reaction $OH^- + CO_2$ has been studied by semiempirical quantum chemical methods. A continuum solvaton model has been used for simulation of the solvent effect. The activation barrier has been shown to be exclusively caused by solvent effect, *i.e.* desolvation of the OH^- and CO_2 components during their mutual approach.

Полуэмпирическими квантовохимическими методами было изучено влияние растворителя на энергию реакции $OH^- + CO_2$. Для моделирования влияния растворителя была использована континуальная сольватонная модель. Было показано, что барьер реакции обусловлен исключительно сольватационным эффектом – десольватацией компонентов OH^- и CO_2 при взаимном приближении.

In recent years, the reaction of OH^- and H_2O with CO_2 has been studied theoretically [1, 2]. These processes are important mainly from the biological point of view because they play a significant role in the transportation of CO_2 in living systems. However, the rate of these reactions is strongly affected by the medium in which they proceed. The reaction of $OH^- + CO_2$

$$OH^- + CO_2 \rightleftharpoons HCO_3^- \qquad (A)$$

has activation energy of 55 kJ mol⁻¹ in aqueous medium [3]; in living organisms the reaction proceeds with low activation energy because of the effect of the enzyme carbonic anhydrase [4]. *Jönsson et al.* [2] used in their detailed *ab initio* computations of the reaction a relatively flexible basis of atomic orbitals. The reaction of the reactants themselves (without any solvent effect) proceeds according to calculations [2] without any activation barrier, the calculated value of the interaction energy (ΔE) being -234 kJ mol⁻¹ and its experimental value (heat of reaction ΔH) -47 kJ mol⁻¹. The energy barrier for the reaction (A) in aqueous solution should be thus caused only by solvent effect. Our aim was to investigate the solvent effect on the reaction using the continuum solvaton model. At the same time we compared the values of the solvation energies calculated on the basis of electron distribution by the MINDO/2 and *ab initio* methods and two different modifications of the method for calculating solvation energy.

Calculations

Since the system studied is charged, we can expect the electrostatic part to represent the greatest contribution of the solvation energy. The electrostatic (coulombic) part of the solvation energy can be expressed on the basis of perturbation theory as follows [5]

$$E_{solv}^{coul} = -\frac{1}{2}\left(1 - \frac{1}{\varepsilon}\right) \sum_{\mu} \sum_{\nu} \frac{Q_{\mu}Q_{\nu}}{4\pi\varepsilon_0 r_{\mu\nu}} \tag{1}$$

where ε is the dielectric constant for solvent (in our case $\varepsilon_{H_2O} = 80$, Q_{μ} and Q_{ν} are the calculated charges on the atoms of the solute system). If $r_{\mu\mu}$ ($\mu \in A$) is approximated by the van der Waals radius of the atom A and $r_{\mu\nu}$ ($\mu \in A$, $\nu \in B$) is approximated by the interatomic distance r_{AB}, it is obvious that the destabilizing part of the electrostatic interaction between solvent and solute [6] is overestimated. It is better to introduce approximation of $r'_{\mu\nu}$ by a sum of the interatomic distance r_{AB} and the van der Waals radius r^{vdW}, i.e.

$$r_{\mu\nu} = r_{AB} + r_A^{vdW} (\mu \in A, \nu \in B)\,; \; r_{\mu\mu} = r_A^{vdW}$$

For alternative computation of the solvation energy we used the solvaton model [7, 8] and applied it in the interpretation of the solvent effect on various properties (conformations, reaction enthalpies, electron distribution) of ion radicals [8]. The model also considers response solute to polarized dielectric, i.e. it takes account of the reverse polarization of a solute molecule. In this approach the interaction between solute and solvent is incorporated into the Hamiltonian of the solute molecule

$$\mathbf{H}_s = \mathbf{H}_0 - \frac{\varepsilon - 1}{2\varepsilon}\left[\sum_{s'=1}^{N} \sum_{i=1}^{M} \frac{Q_{s'}}{4\pi\varepsilon_0 r_{s'i}} - \sum_{s'=1}^{N} \sum_{n=1}^{N} \frac{Q_{s'} Z_n}{4\pi\varepsilon_0 r_{s'n}}\right] \tag{2}$$

Solvation energy is

$$\Delta E_{solv} = \langle \psi | \mathbf{H}_s | \psi \rangle - \langle \psi_0 | \mathbf{H}_0 | \psi_0 \rangle \tag{3}$$

$\mathbf{H}_0$ is the Hamiltonian of the isolated solute molecule, $Q_{s'}$ are the induced charges in a solvent, the so-called solvatons; it holds $Q_{s'} = -Q_s$. The second term of eqn (2) represents the interaction of solvatons (s') with electrons (i) of the solute molecule and the third term denotes the interaction of solvatons (s') with the core (n) of the solute molecule. The way of
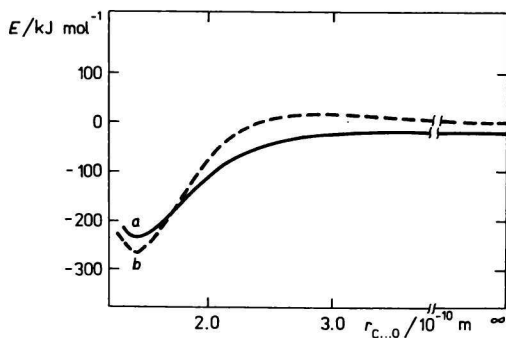

Fig. 1. Plot of interaction energy against $r_{C\cdots O}$ for the reaction $CO_2 + OH^-$ in gaseous phase

a) ab initio calculations; b) MINDO/2 calculations.

application of the method and details about the choice of $Q_{s'}$ and $r_{s'i}$ in semiempirical quantum chemical methods have been described earlier [8]. The optimized geometries of the reacting system along the reaction coordinate (Fig. 1, curve a) were taken from Ref. [2]. For the isolated CO_2 molecule we considered the C—O length of 1.16×10^{-10} m, the O—C—O angle of 180°, and the O—H distance in OH$^-$ of 0.98×10^{-10} m [2].

Results and discussion

At first we calculated ΔE_{solv} according to eqn (1) using charges calculated by the *ab initio* method with a double zeta basis set [2]. The obtained values are shown in Fig. 2 (curve a). The solvation energy shows maximum along the reaction coordinate, the separated reactants CO_2 and OH$^-$ being most solvated. If the values of E_{solv} are added to the energy of reactants without considering solvent effect (taken from Ref. [2]; Fig. 1, curve a), a dependence is obtained which in Fig. 3 (curve a) describes the course of the reaction (A) between CO_2 and OH$^-$ in aqueous solution. This simple electrostatic model describes qualitatively correctly

Fig. 2. Plot of solvation energy against $r_{C...O}$.
a) According to eqn (1) and using *ab initio* charge distribution; b) according to eqn (1) and using MINDO/2 charges; c) according to eqn (2) and using MINDO/2 charges.
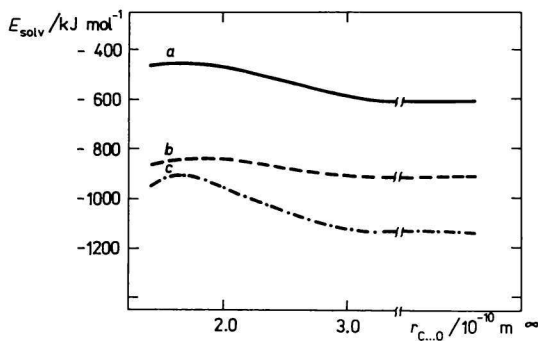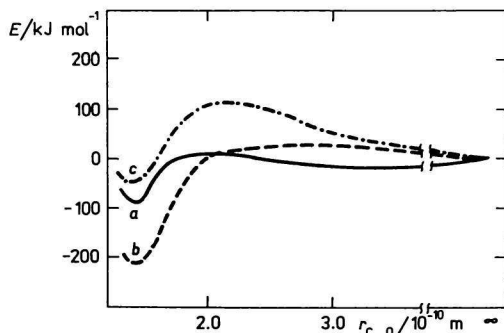

Fig. 3. Plot of the overall energy of the system $CO_2 + OH^-$ against $r_{C...O}$.
a) Solvation energy according to eqn (1) and interaction energy from *ab initio* calculations; b) solvation energy according to eqn (1) and MINDO/2 interaction energy; c) solvation energy according to eqn (2) and MINDO/2 interaction energy.

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solvent effect on the reaction studied. The reaction A was also investigated by the MINDO/2 method [9]. The geometry of CO_2 and OH^- along the reaction coordinate found by the *ab initio* computation [2] was used here. The change in interaction energy along the reaction coordinate for the reaction without considering solvent (Fig. 1, curve b) is similar to that in the *ab initio* calculation; the difference is in the energy minimum at 1.43×10^{-10} m which lies lower in the MINDO/2 method than in the *ab initio* method. Moreover, the shortcoming of the MINDO/2 method in calculating interaction energy is that between 2.4 and 3.4×10^{-10} m a shallow maximum occurs (18 kJ mol^{-1}). Expression of E_{solv} according to eqn (*1*) using the charges calculated by the MINDO/2 method gives a curve of similar shape as that obtained by the *ab initio* computations but because of the overestimated charge polarization in the MINDO/2 method the values of E_{solv} are appreciably greater (Fig. 2, curve b). By adding solvation energy to the interaction energy of the system $CO_2 + OH^-$ a course is obtained corresponding to the reaction (*A*) in aqueous medium.

Then we expressed the effect of hydration in the MINDO/2 method according to the solvaton model (eqns (*2*) and (*3*)). Fig. 2 (curve c) shows a plot of the solvation energy along the reaction coordinate. The course of the solvation energy is similar to that expressed in eqn (*1*). The difference between both curves is approximately assigned to the polarization component of solvation. The change is particularly evident at smaller distances between CO_2 and OH^- of the energy minimum of the CO_2OH^- complex. Analogously to the previous case, after adding E_{solv} to the interaction energy of the unsolvated system, we get the dependence of the interaction energy along the reaction coordinate for the reaction (*A*) proceeding in aqueous medium (Fig. 3, curve c).

A comparison of the three used methods (Fig. 3, Table 1) indicates that in all three methods the activation barrier caused by the solvent effect occurs and the energy difference between the HCO_3^- complex and isolated components decreases. The size of the effect is different. Inclusion of only coulombic component of the interaction (according to eqn (*1*)) becomes evident as a barrier formed on the

Table 1

Calculated and experimental values of activation energy E_a and the heat of reaction ΔE_r for the reaction $CO_2 + OH^- \rightleftarrows HCO_3^-$

	ab initio and eqn (*1*)	MINDO/2 and eqn (*1*)	MINDO/2 and eqns (*2*) and (*3*)	exp[a]
E_a/kJ mol^{-1}	27	28	111	55
ΔE_r/kJ mol^{-1}	− 94	− 210	− 46	− 47 (ΔH)

a) Experimental values are taken from [3].

reaction coordinate, which, however, is smaller than the experimental value (55 kJ mol^{-1}). The energy belonging to the heat of reaction is much higher mainly in the MINDO method. By incorporating the polarization part of the solvation energy (solvaton model) an activation barrier obtained is even greater than its experimental value and the value of the heat of reaction is very close to the experimental result. The occurrence of the second minimum between 3.0 and 3.5×10^{-10} m in the *ab initio* calculation (Fig. 3, curve *a*) is interesting.

In investigating this problem by considering the discrete structure of the solvent we can expect that the activation barrier is due to necessary desolvation of the CO_2 and OH^- components when they are brought together. It is noteworthy that the methods used by us have qualitatively correctly defined the solvent effect in all cases in spite of the fact that the protic solvent (H_2O) is characterized in the methods as a continuum.

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