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Theoretical investigation of carbon dioxide capture by aqueous boric acid solution: A termolecular reaction mechanism

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ABSTRACT

Hitherto, boric is suggested and used as a promoter or catalyst for carbon dioxide capture in various chemical absorption reactions, such as, absorption by aqueous potassium carbonate solution to increase mass transfer rate. But in this study, a single step termolecular reaction mechanism is suggested for the chemical absorption of carbon dioxide directly by boric acid and water. The reaction thermochemistry and reaction kinetics for termolecular mechanism are investigated by using density functional theory calculations at the B3LYP/6-31G(d) level of theory by taking into account of the implicit solvent effects of water through the polarizable continuum model and dispersion corrections. The findings obtained from theoretical calculations indicate that it is possible to capture carbon dioxide with boric acid in the form of $B(OH)_2OCOOH$.

1. Introduction

Due to the adverse effects of global warming especially on environment and human health, scientists spend a great effort to reduce the release of greenhouse gas emissions. Carbon dioxide is a major greenhouse gas which has a significant role on global warming and so, on human health. Its emissions have continuously been increasing since 1800s [1]. Therefore, decreasing of the carbon dioxide levels in the atmosphere by applying cost-effective and environmentally friendly capture and storage procedures is crucial. Mainly, carbon dioxide capture procedures can be categorized under three groups. The first technique is known as pre-combustion carbon dioxide capture, where carbon dioxide is captured before its combustion [2–4]. The other technique is called to be oxy-combustion capture where pure oxygen is generated using an air separation unit and this oxygen is used in combustion which results with almost nitrogen-free flue gas [5–7]. The last technique is the post-combustion capture where carbon dioxide is captured from the flue gas after the combustion of fossil fuels or other carbon containing materials. Post-combustion techniques has an advantage of flexibility and easy implementation to existing power plants without the need of massive change in the combustion process [8,9]. Absorption, adsorption, membrane separation and cryogenic distillation are some of the techniques used to separate post-combustion gases [10], and chemical absorption using solvents is probably the most convenient and cost-effective carbon dioxide capture technique among those [9,11–13]. Absorption of carbon dioxide by different solvents has been theoretically investigated in many different studies by utilizing quantum chemical calculations [14–17] and a single step termolecular reaction mechanism for the capture of carbon dioxide by 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and propanol mixture was suggested [17].

Recently, in our combined experimental and theoretical studies, we followed the single step termolecular reaction mechanism for the capture of carbon dioxide by 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN)/1-propanol and 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)/1-butanol mixtures [18], DBN/1-hexanol, TBD/1-hexanol and 2-tert-butyl-1,1,3,3-tetramethylguanidine (BTMG)/1-hexanol mixtures [19], and BTMG/1-propanol mixture [20]. Our findings in these combined experimental and theoretical studies [18,19,20] were in good agreement and our results suggested that the reaction among carbon dioxide, amine based organic solvent and alcohol takes place very likely according to the single step termolecular mechanism. Other than amine based solvent and alcohol mixtures, aqueous potassium carbonate and boric acid mixtures at

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*corresponding author: hakan.kayi@atilim.edu.tr different concentrations are also used in the carbon dioxide capture [21–25]. Solubility of carbon dioxide in aqueous potassium carbonate solution alone is high, but the reaction rate is slow, and therefore the mass transfer rate for the absorption of carbon dioxide into the liquid phase is low. Because of this, boric acid is considered as a promoter to increase the reaction rate. In a study of Ghosh et al. [23], it was shown that addition of 3% boric acid by weight to the potassium carbonate solution increased the reaction rate by a factor of two, but this rate was still below the one obtained for amine based solvents. In addition, the role of boric acid in the reaction mechanism of chemical absorption of carbon dioxide was not clear. In another study, Guo et al. [26] suggested a borate-catalyzed carbon dioxide hydration through the carbonic anhydrase mechanism. According to this study, boric acid is deprotonated to borate ion first, and then this anion reacts with carbon dioxide as the rate determining step, yielding boric acid bicarbonate intermediate and finally by the addition of water, bicarbonate is replaced with water, and boric acid is regenerated and bicarbonate is obtained as given below.

$$B(OH)_3 \cdot H_2O \rightleftarrows \mathrm{B(OH)}_4^- + H^+ \tag{1}$$

$$\mathrm{B(OH)}_4^- + CO_2 \rightarrow B(OH)_4CO_2^- \tag{2}$$

$$\underline{B(OH)_4CO_2^- + H_2O \rightarrow B(OH)_3 \cdot H_2O + HCO_3^-} \tag{3}$$

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \tag{4}$$

They concluded that a considerable increase in the reaction rate was observed by the addition of boron compounds at high temperature and pH values, and boric acid/borate system actually acted like a catalyst for the hydration of carbon dioxide [26]. Most of the current studies on carbon dioxide capture by boric acid are based on the mechanism suggested above where the role of boric acid is limited to produce borate ion.

As a continuation to our studies on the CO_2 capture [18–20,27], in which CO_2 was captured by different amine-alcohol mixtures through a single step termolecular mechanism as explained above [18-20] and also CO_2 was trapped between the amorphous form or crystalline ice slab of the water and methylamine [27], an alternative single step termolecular reaction mechanism among carbon dioxide, boric acid and water is suggested in the current study, and the methodology used and results obtained are given in the following sections.

2. Computational method

The interaction of boric acid with carbon dioxide in the presence of water is theoretically investigated by using quantum mechanical tools. First, the isolated most stable structures of the boric acid, carbon dioxide and water molecules are obtained through the geometry optimizations followed by vibrational frequency analyses by using density functional theory calculations at the B3LYP/6-31G(d) level of theory [28–32]. This level calculations yielded well results in our previously performed similar reaction mechanism studies [18–20]. After obtaining the most stable isolated structures of the boric acid, CO_2 and water molecules, reactant and product systems for the interaction of these molecules according to the termolecular reaction mechanism are prepared. Reactant and product systems are fully optimized at the B3LYP/6-31G(d) level of theory, but this time taking into account of the implicit solvent effects of water through the polarizable continuum model (PCM) [33–35] and applying density functional dispersion corrections [36]. Following the geometry optimizations of reactant and product systems, vibrational frequency calculations are performed using the same method on these systems to verify that both systems are corresponded to a proper local minimum and have no imaginary vibrational frequency values. After the reactant and product systems are located on the potential energy surface, transition state calculations are carried out to find the saddle point and hence the transition state structure. Transition state structure is then verified by intrinsic reaction coordinates and vibrational frequency calculations at the same level of theory. Structural, energetic, thermochemical and kinetic properties are obtained and presented in the next sections by the help of the data extracted from these calculations.

The Gaussian 09 Rev.D.0.1 [37] quantum chemistry software package is used for all density functional theory calculations and the GaussView 5.0.9 [38] is utilized for molecular visualizations.

3. Results and discussion

A similar termolecular reaction mechanism which was previously suggested in our studies for similar carbon dioxide capturing systems [18–20] can be adapted to current reaction system which contains boric acid, carbon dioxide and water.

$$CO_2 + B(OH)_3 + H_2O \rightleftarrows B(OH)_2OCOOH + H_2O \tag{5}$$

Observed reaction rate, r_{obs}, with the reaction rate constant, k_o, is assumed as below, under pseudo-first-order conditions since quantum chemical calculations restrict to that order.

$$r_{obs} = k_o [CO_2] \tag{6}$$

The value of k_o in s^{-1} for this single step termolecular reaction mechanism is then obtained by utilizing Eyring's methodology [39] and the quantum chemical calculations at the B3LYP/6-31G(d) level.

Chemical structures obtained from the full geometry optimizations of the reactant, transition state and product systems for the boric acid, carbon dioxide and water interaction in a single step are presented in Figure 1. Calculations are performed by including explicit water molecule in the reaction medium but also by implicitly addition of the solvent effect of water through the polarizable continuum model, and taking into account of the dispersion corrections at the B3LYP/6-31G(d) level of theory. Geometrical variables, such as bond lengths, bond angles and dihedral angles, are defined by an atom labeling scheme as shown in Figure 1, and the values obtained for these variables are given in Table 1. The 0.1807 nm distance between the H4 and O8 atoms in the reactant structure is an indication of the hydrogen bond formation between the boric acid and water moieties. In the transition state structure, this distance reduces to 0.1154 nm and then in the product it is found to be 0.0972 nm indicating the formation of the covalent bond. On the other hand, the 0.0988 nm O2-H4 distance in reactant reaches 0.1284 nm in the transition state structure. These findings show that the O2 atom takes part as a hydrogen donor during the termolecular interaction where H4 is transferred from O2 to O8. On the other hand, the O8 atom of the water molecule which accepts H4 atom from boric acid donates H9 atom to carbon dioxide. In the reactant structure O8-H9 bond length is calculated to be 0.0971 nm whereas it is found to be 0.1012 nm and 0.1692 nm, respectively, in the transition state and product structures. The H9-O12 distance of 0.2243 nm in reactant structure reduces to 0.1716 nm in transition state, and then H9 atom is covalently bound to O12 atom with a bond length of 0.1005 nm in the product. At the same time O8-H9 distance is obtained as 0.1692 nm indicating the hydrogen bond established between carboxylic acid moiety of the $B(OH)_2OCOOH$ (boric carbonic anhydrate) and the water molecule in the product system.

The C11-O2 distance and O12-C11-O13 bond angle in reactant system is calculated to be 0.3230 nm and 179.05°, respectively. It is known that the isolated carbon dioxide molecule in the gas phase is linear, and apart from termolecular system calculations, our geometry optimization calculations on the isolated carbon dioxide molecule yield the same results. Therefore, the very slight deviation (0.95°) from linearity in the carbon dioxide molecule indicates the very weak interaction between C11 atom of the carbon dioxide and the O2 atom of the boric acid in the reactant system. Moreover, C11-O2 distance significantly reduces to 0.1525 nm in the transition state system and finally by the formation of the covalent bond this distance is obtained to be 0.1344 nm in the product system.

By taking in the account of the structural changes in the termolecular reaction mechanism, it can be proposed that the water molecule behaves like a hydrogen bridge between the boric acid and carbon dioxide. It accepts one hydrogen (H4) from the boric acid and donates its another hydrogen (H9) to carbon dioxide causing the formation of the carboxylic acid moiety of the $B(OH)_2OCOOH$.

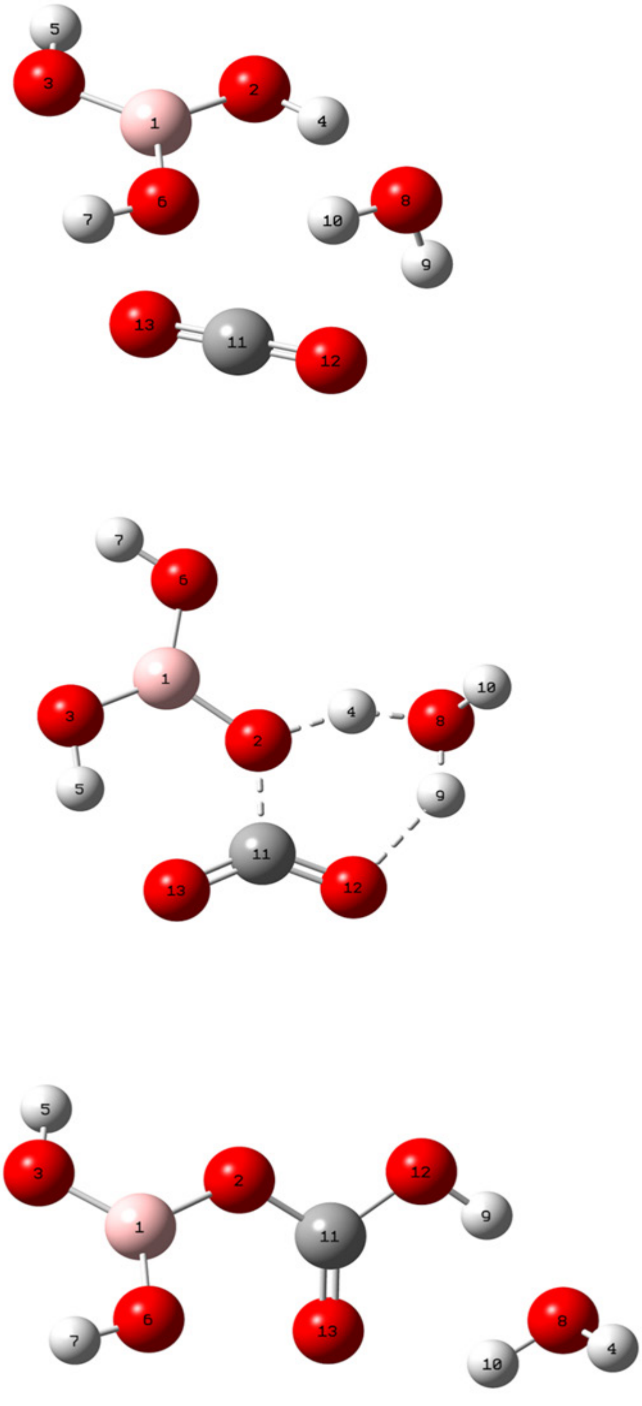

Figure 1. Chemical structures of the reactant (top), transition state (middle) and product (bottom) for termolecular reaction system.

Figure 2 represents the IR spectra of the reactant, transition state and product systems from top to bottom, respectively. The v_1 symmetric stretching, v_2 bending and v_3 asymmetric stretching vibrations of water appear at 3654, 1715 and 3790 cm^{-1}, respectively, in the reactant system, and they also appear at 3111, 1659, and 3718 cm^{-1}, respectively, in the transition state

Table 1. Geometrical variables obtained for the termolecular reaction system.

Bond Length (nm)	Reactant	Transition State	Product
B1-O2	0.1364	0.1413	0.1404
B1-O3	0.1371	0.1352	0.1362
B1-O6	0.1387	0.1362	0.1357
O2-H4	0.0988	0.1284	-
O3-H5	0.0969	0.0985	0.0969
O6-H7	0.0969	0.0969	0.0969
O8-H4	0.1807	0.1154	0.0972
O8-H9	0.0971	0.1012	0.1692
O8-H10	0.0977	0.0977	0.0979
O12-H9	0.2243	0.1716	0.1005
C11-O12	0.1170	0.1237	0.1325
C11-O13	0.1168	0.1226	0.1221
C11-O2	0.3230	0.1525	0.1344
Bond Angle (º)	**Reactant**	**Transition State**	**Product**
B1-O2-H4	110.19	125.90	-
B1-O3-H5	111.09	107.53	112.48
B1-O6-H7	112.42	111.35	111.36
H9-O8-H10	103.27	107.57	87.50
O12-C11-O13	179.05	134.81	125.68
O2-C11-O12	92.74	110.67	109.57
O2-C11-O13	88.09	114.52	124.72
B1-O2-C11	76.99	125.48	124.60
C11-O12-H9	125.65	112.09	107.04
Dihedral Angle (º)	**Reactant**	**Transition State**	**Product**
O6-B1-O2-H4	-7.40	-0.12	-
O6-B1-O2-C11	63.86	179.88	32.59
B1-O2-C11-O13	54.69	-0.15	21.88
B1-O2-C11-O12	-125.78	179.82	-160.16
O13-C11-O12-H9	174.03	179.95	-0.19

system, and at 3622, 1697, and 3781 cm^{-1}, respectively, in the product system. For the isolated water molecule, the same v_1, v_2 and v_3 fundamental vibrations are calculated at the 3728, 1709, and 3832 cm^{-1}, respectively, by using the same theoretical level of calculations. It can be seen that vibrational frequency values for reactant, transition state and product systems shift from the ones obtained for isolated water due to the interactions take place in the termolecular reaction system. In addition, symmetric and asymmetric stretching vibrations are a bit distorted in the transition state due to the strong interactions with boric acid and carbon dioxide. The similar trends are also obtained for carbon dioxide molecule. Symmetric stretching, bending and asymmetric stretching vibrations are calculated to be 1373, 631, and 2410 cm^{-1}, respectively, for the reactant system, and to be 1274, 781, and 1951 cm^{-1}, respectively, for the transition state system. One needs to consider that in the product system, carbon dioxide is bound to boric acid in the form of carboxylic acid moiety, and hence it is not possible to observe pure carbon dioxide vibrations in the product system. Our calculations on pure carbon dioxide molecule yield these vibrations at 1372, 634 and 2408 cm^{-1}, respectively. When these values are compared with the ones in the reactant system, almost no shift is obtained, but when compared with transition state the shifts are considerable due to the strong interactions. The intense CO_2 asymmetric stretching peak at 2410 cm^{-1} in the reactant system redshifts to 1951 cm^{-1} in transition state and disappears at the product spectrum. The O-H stretching vibrations of boric acid appear at 3413 and 3788 cm^{-1} in reactant, at 3475 and 3781 cm^{-1} in transition state, and at 3778 and 3782 cm^{-1} in product system, while they are calculated at 3783, 3784 and 3785 cm^{-1} for the isolated boric acid molecule alone. For the reactant and transition state systems, one of O-H stretching vibrations redshifts about more than 300 cm^{-1} comparing with product system and isolated boric acid due to the interaction with surrounding molecules.

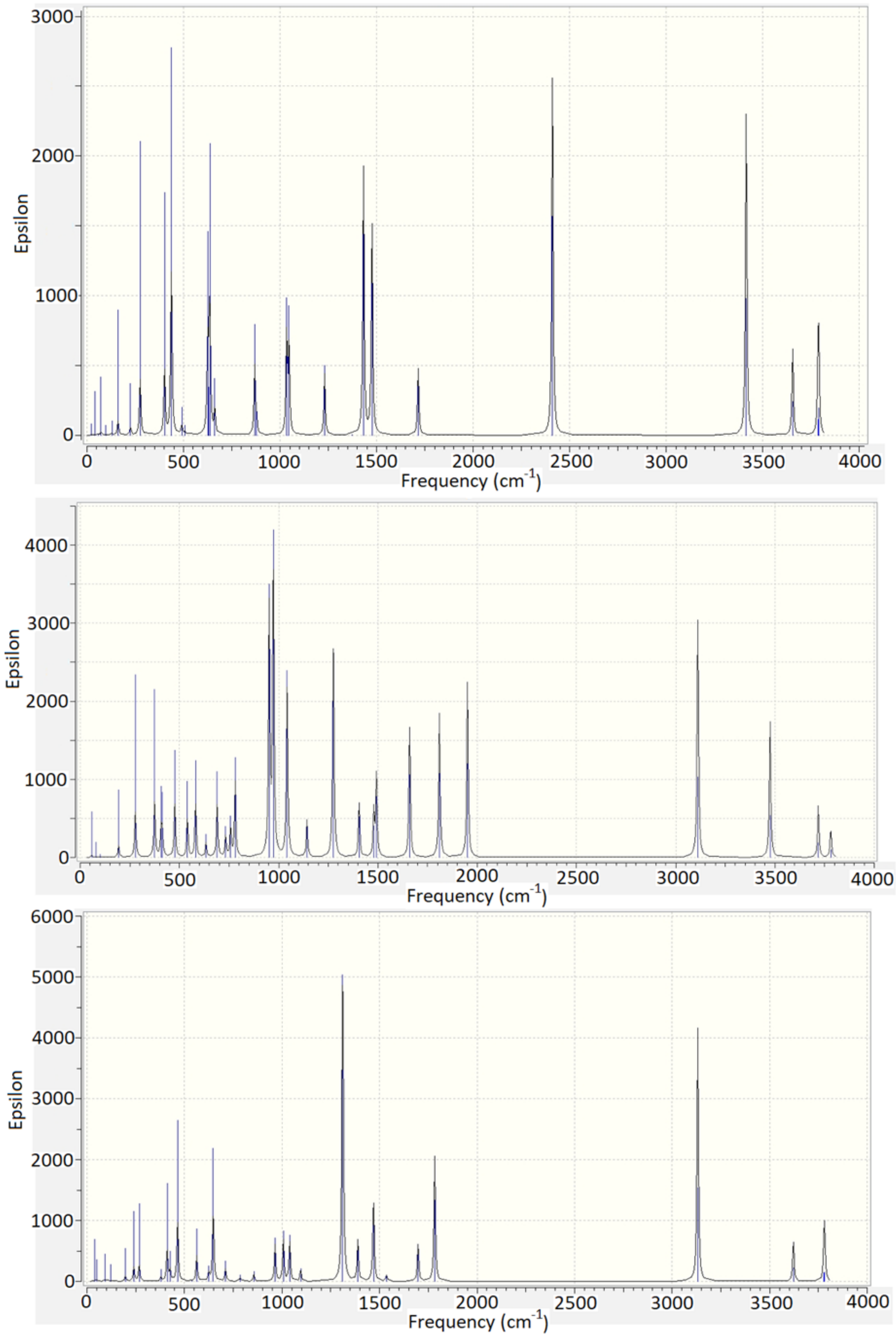

Figure 2. Theoretical IR spectra of the reactant (top), transition state (middle) and product (bottom) for termolecular reaction system.

The intense peak which appears at 1311 cm^{-1} in the IR spectrum of the product system belongs to the stretching vibration between the O2 atom of the boric acid and the C11 atom of the carbon dioxide because of the formation of the new O2-C11 bond. In the similar way, the other intense peak at the 3131 cm^{-1} belong to the newly formed O12-H9 bond stretching in the carboxylic acid moiety of the $B(OH)_2OCOOH$ molecule.

In the last part of the study, thermochemistry of the termolecular reaction mechanism suggested as an alternative for boric acid, carbon dioxide and water interaction is investigated and kinetic parameters are obtained. Quantum calculations at the B3LYP/6-31G(d) level of theory with implicitly inclusion of the solvent effect of water through the polarizable continuum model and also dispersion corrections yield an observed reaction rate constant value k_o of $2.7x10^{-5}$ s^{-1} under pseudo first order conditions at 25 ºC. Gibbs free energy of activation for this termolecular reaction mechanism is obtained to be 99.1 kJ/mol, and the Gibbs free energy change of the reaction is calculated to be 44.9 kJ/mol at the same temperature value. The positive Gibbs free energy change of the reaction indicates that the forward reaction is not spontaneous and also it is slow according to the calculations performed at 25 ºC and 1 atm pressure conditions, and by feeding 1 mole from each of boric acid, carbon dioxide and water, in this study. Unfortunately, investigation of the direct effect of the reaction medium pH to the reaction dynamics and thermochemistry is technically not possible through quantum chemical calculations, and could not be investigated. These findings actually explain why the other studies, in which aqueous boric acid is generally used as a promoter or catalyst, are performed at a temperature range of 50 to 120 ºC, at different molar or weight ratios and pH [22–24,26,40]. Because, boric acid promoted, especially potassium carbonate, solutions at high temperatures enhances the mass transfer rate of carbon dioxide. As a consequence, thermochemistry and kinetic of the suggested termolecular reaction mechanism may need to be investigated further at different experimental reaction conditions by experimentalists to evaluate its validity.

4. Conclusions

Interaction of carbon dioxide with boric acid and water is investigated by means of quantum chemical calculations. In contrary to previous studies available in the literature, boric acid is not considered here as a promoter or borate source to increase the reaction rate of chemical absorption of carbon dioxide. Instead, a single step termolecular reaction mechanism is suggested and the direct role of boric acid in carbon dioxide capture is examined. Our calculations indicated that, it is possible to capture carbon dioxide by boric acid in the form of $B(OH)_2OCOOH$ in the aqueous reaction environment where hydrogen transfer from boric acid to carbon dioxide take place through the water molecule. Therefore, water molecule acts like a hydrogen bridge. Nevertheless, reaction rate for the proposed single step termolecular mechanism is slow at the room temperature and atmospheric pressure. The forward reaction is not spontaneous under these conditions and needs to be further investigated at higher temperature values, experimentally.

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