Studying the possibility of substitution of different functional groups for exopolyhedral hydrogen atoms in the decahydro-closo-decaborate anion and developing appropriate synthetic methods is one of the practically important issues for the chemistry of boron cluster anions. Functionalized derivatives are treated as synthons (i.e., fragments for synthesis of more complex molecules) for synthesis of pharmaceuticals for boron neutron capture therapy [1]. The \([\text{B}_{10}\text{H}_{10}]^{2-}\) anion is a dicapped Archimedean antiprism. The boron atoms have CN 5 and 6; thus, they are classified as two groups of chemically equivalent vertices of the polyhedron: the apical B(1) and B(10) atoms are apices (“poles”), and the B(2)–B(9) atoms form the equatorial “belt” of the polyhedron. In the present work, we report the theoretical consideration of the elementary reaction of molecular hydrogen elimination from the \([\text{B}_{10}\text{H}_{11}]^{-}\) anion, which is presumably the rate-limiting stage of acid-catalyzed reactions of substitution of exopolyhedral H atoms in the \([\text{B}_{10}\text{H}_{10}]^{2-}\) decahydro-closo-decaborate anion, has been calculated by the density functional theory method (in the B3LYP/6-311++G*** approximation). Specific transition states of \(\text{H}_2\) elimination in which vacancies form near the boron atoms have been localized. It has been demonstrated that regioselectivity of substitution reactions can be related to the significant difference between the activation barriers for the pathways of \(\text{H}_2\) elimination from boron atoms with different coordination numbers (CN 6 and 5). The electron density of the \([\text{B}_{10}\text{H}_{9}]^{-}\) anion that forms after hydrogen molecule elimination has a characteristic shape of the lowest unoccupied molecular orbital for the interaction with nucleophilic reagents; in acid-catalyzed reactions, different anions, for example, a carboxylic acid residue, can act as such. The direct reaction of the \([\text{B}_{10}\text{H}_{9}]^{-}\) intermediate with nucleophilic anions is hindered by the Coulomb charge repulsion. To overcome this hindrance, the possibility of \([\text{B}_{10}\text{H}_{9}]^{-}\) protonation to form the neutral \([\text{B}_{10}\text{H}_{10}]\) system has been considered. It has been shown that the proton affinity of the \([\text{B}_{10}\text{H}_{9}]^{-}\) anion is ~280–290 kcal/mol. For the \([\text{B}_{10}\text{H}_{10}]\) cluster, the lowest-lying and low-lying isomers have been considered. For all the systems under consideration, the electronic chemical potential and Pearson hardness have been evaluated.

Theoretical Study of Molecular Hydrogen Elimination from the Undecahehydrodecaborate Monoanion \([\text{B}_{10}\text{H}_{11}]^{-}\). Exopolyhedral Substitution Intermediates: \([\text{B}_{10}\text{H}_{9}]^{-}\) Monoanion and Neutral \([\text{B}_{10}\text{H}_{10}]\) Cluster

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Abstract—The elementary reaction of molecular hydrogen elimination from the \([\text{B}_{10}\text{H}_{11}]^{-}\) anion, which is presumably the rate-limiting stage of acid-catalyzed reactions of substitution of exopolyhedral H atoms in the \([\text{B}_{10}\text{H}_{10}]^{2-}\) decahydro-closo-decaborate anion, has been calculated by the density functional theory method (in the B3LYP/6-311++G*** approximation). Specific transition states of \(\text{H}_2\) elimination in which vacancies form near the boron atoms have been localized. It has been demonstrated that regioselectivity of substitution reactions can be related to the significant difference between the activation barriers for the pathways of \(\text{H}_2\) elimination from boron atoms with different coordination numbers (CN 6 and 5). The electron density of the \([\text{B}_{10}\text{H}_{9}]^{-}\) anion that forms after hydrogen molecule elimination has a characteristic shape of the lowest unoccupied molecular orbital for the interaction with nucleophilic reagents; in acid-catalyzed reactions, different anions, for example, a carboxylic acid residue, can act as such. The direct reaction of the \([\text{B}_{10}\text{H}_{9}]^{-}\) intermediate with nucleophilic anions is hindered by the Coulomb charge repulsion. To overcome this hindrance, the possibility of \([\text{B}_{10}\text{H}_{9}]^{-}\) protonation to form the neutral \([\text{B}_{10}\text{H}_{10}]\) system has been considered. It has been shown that the proton affinity of the \([\text{B}_{10}\text{H}_{9}]^{-}\) anion is ~280–290 kcal/mol. For the \([\text{B}_{10}\text{H}_{10}]\) cluster, the lowest-lying and low-lying isomers have been considered. For all the systems under consideration, the electronic chemical potential and Pearson hardness have been evaluated.

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culated proton affinity value. Possible intramolecular rearrangements of the \([B_{10}H_{11}]^-\) anion caused by proton migration over the boron cage have been described [5]. Later, the \([B_{10}H_2]\) anion and proton migration in it have been studied by \(^{11}\)B NMR at different temperatures [6], and salts of this anion have been suggested for use as new starting reagents in exopolyhedral substitution and complexation reactions [7]. Elimination of a hydrogen molecule from \([B_{10}H_{11}]^-\) has not been considered.

In the present work, we theoretically study an elementary step of \(H_2\) molecule elimination in the course of the acid-catalyzed substitution reaction by scheme (1) put forward in [3]:

\[
[B_{10}H_{10}]^{2-} + CH_3COOH 
\rightarrow [B_{10}H_9(OOCOCH_3)]^{2-} + H_2. \tag{1}
\]

The elimination of an \(H_2\) molecule from \([B_{10}H_{11}]^-\) leads to the \([B_{10}H_9]^-\) anion with a “naked” boron atom vacant for substituents. The in situ existence of the \([B_{10}H_9]^-\) species was previously assumed on the basis of mass spectrometric studies [8]. The reaction of \([B_{10}H_9]^-\) with substituents presumably yields to ultimate products:

\[
[B_{10}H_{10}]^{2-} + H^+ \rightarrow [B_{10}H_9]^- \rightarrow [B_{10}H_9^- + H_2 \uparrow \rightarrow +CH_3COO^- \rightarrow [B_{10}H_9(OOCOCH_3)]^{2-}. \tag{1a}
\]

Formation of the \([B_{10}H_9]^-\) intermediated by scheme (1a) implies (to meet the charge balance) that the \([B_{10}H_9]^-\) anion reacts with the acetate anion \(CH_3COO^-\); however, this reaction is hindered by the repulsive character of the potential curve for the interaction of two anions. To remove this contradiction, it has been suggested, as one of the ways, to react the \([B_{10}H_9]^-\) anion with undissociated \(CH_3COOH\) molecule [3]. At the same time, the ability of boron–hydrogen anions to dimerize makes us to believe that other ways are also possible. The dimer obtained in a series of redox reactions can be reduced [9] to the anion stable in acid solutions and its protonated forms in which two \(B_{10}H_9^-\) moieties are linked through the bridging hydrogen atom (proton). With increasing pH of the solution, the bridging proton is removed to give the B–B bond, which is evidence of the instability of the dimer with a bridging proton so that there is equilibrium in solution:

\[
[B_{10}H_{10}]^{2-} + H^+ \leftrightarrow [B_{10}H_9]^- \rightarrow [B_{10}H_9^- + H_2 \uparrow \rightarrow +CH_3COO^- \rightarrow [B_{10}H_9(OOCOCH_3)]^{2-}. \tag{2}
\]

Since \([B_{10}H_{11}]^-\) dominates in the solution of \([B_{10}H_{10}]^{2-}\), equilibria (3) and (4) with protonated species should be added to scheme (2):

\[
B_{20}H_2^{2-} \leftrightarrow B_{10}H_9^\gamma + B_{10}H_{11}^\gamma. \tag{3}
\]

\[
B_{20}H_2^{2-} \leftrightarrow B_{10}H_9^\gamma + B_{10}H_{11}^\gamma + H^+. \tag{4}
\]

Thus, for equilibrium to persist in an acidic solution of the dimer [9], it would be accepted that the \([B_{10}H_9]^-\) anion reacted with the \([B_{10}H_{10}]^{2-}\) and \([B_{10}H_{11}]^-\) anions, which is hindered by the Coulomb repulsion. To compensate for the repulsion, it should be suggested that one of the reagents is protonated to form a neutral system. Protonation of the undeacydrodecaborate anion \([B_{10}H_{11}]^-\) to form neutral \([B_{10}H_{12}]\) was considered in detail in [10] where it was shown that the proton affinity of \([B_{10}H_{11}]^-\) is ~280–290 kcal/mol. However, according to calculated estimates in the present work, the proton affinity of the \([B_{10}H_9]^-\) system is also ~280–290 kcal/mol. Thus, from the energy standpoint, the protonations of \([B_{10}H_9]^-\) and \([B_{10}H_{11}]^-\) are almost equivalent and can be considered as alternative pathways for the dimerization reaction. Analogously, it can be suggested that the intermediate \([B_{10}H_9]^-\) anion is protonated to form the neutral \([B_{10}H_{10}]\) cluster, and the latter is involved in exopolyhedral substitution reactions. Thus, two alternative reactions can be suggested:

\[
[B_{10}H_9]^- + CH_3COOH \rightarrow [B_{10}H_{10}(OOCOCH_3)]^-, \tag{5}
\]
\[
[B_{10}H_{10}] + CH_3COO^- \rightarrow [B_{10}H_{10}(OOCOCH_3)]^- \tag{6}
\]

In the present study, we have demonstrated that reactions (5) and (6) occur without a barrier; i.e., the reactions of the reagents are not hindered, and the \([B_{10}H_9]^-\) and \([B_{10}H_{10}]\) species can be treated only as short-lived highly active intermediates, which cannot be isolated as compounds. The structure of neutral decahydro-closo-decaborane \([B_{10}H_{10}]\) is theoretically considered in detail in this work. The assumption of formation of protonated species means in some cases that the boron atom has CN = 7. Experimentally, CN = 7 has been identified in the \(B_{10}H_{11}^\gamma\) anion [11].

**COMPUTATIONAL DETAILS**

All calculations were performed by the density functional theory method in the B3LYP approximation [12, 13] with the 6-311++G** basis set. The systems to be studied do not contain transition metal atoms, and the error of B3LYP/6-311++G** calculation of electronic energy upon geometry optimization is, on average, 10–15 kcal/mol [14]. At the same time, the energy differences (i.e., relative energies), interesting in the context of studying elementary reactions, should be better reproduced owing to compensation of systematic calculation errors. After finding stationary points of the potential energy surface, normal mode frequencies were calculated in all cases with the use of the same 6-311++G** basis set. To consider elementary events of molecular hydrogen elimination from \([B_{10}H_{11}]^-\), transition states (TS) were localized, and then the paths of descend from the transition state to the nearest (primary) reaction products and to the initial reagents were studied by means of the IRC procedure (intrinsic reaction coordination). In the localized transition states, the directions of hydrogen atom displacements are shown by arrows (Fig. 1).