FORMATION MECHANISM OF 1,3-bis(2-OXOPROPYL)-3H-1,2,3-BENZOTRIAZOLIUM TRIIODIDE 
IN THE ALKYLATION REACTION OF 1,2,3-BENZOTRIAZOLE 
WITH 1-IODOPROPAN-2-ONE

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Within DFT (B3LYP) methods the potential surface of the interaction between 1-iodopropan-2-one and 1,2,3-benzotriazole resulting in the formation of 1,3-bis(2-oxopropyl)-3H-1,2,3-benzotriazolium triiodide is studied. A mechanism consisting of four steps (N1-alkylation of 1,2,3-benzotriazole, elimination of molecular iodine during partial reduction of 1-iodopropan-2-one with hydrogen iodide, formation of the triiodide structure, and formation of 1,3-bis(2-oxopropyl)-3H-1,2,3-benzotriazolium) is proposed. Thermodynamic and kinetic parameters of these steps are obtained.

DOI: 10.1134/S0022476613050041

Keywords: quantum chemical calculation, ionic liquid, reaction mechanism, alkylation, 1,2,3-benzotriazole, 1-iodopropan-2-one.

Ionic liquids are the systems with high conductivity and electrochemical stability, which provides their use as highly polar solvents and catalysts in preparative chemistry, materials for the production of solid state batteries and capacitors, liquid mirrors, special telescopes, and so on [1, 2].

Main methods of obtaining ionic liquids are based on direct alkylation of amines with alkyl halides [3-5]. A systematic study conducted by A. Katrizky with colleagues of the alkylation reaction of 1,2,3-benzotriazole with α-chloro-, bromoketones of aliphatic and aromatic series has shown the tendency of benzotriazole to form exclusively N1-alkylation products of one isomeric form [6]. In [7], performed with the participation of some authors of this work, it was found for the first time that 1-iodopropan-2-one II has a higher alkylating ability than its chloro and bromo derivative analogs because in the interaction with 1,2,3-benzotriazole I without a catalyst and solvent the alkylation and quaternization of organic base I proceeds in one preparation step and gives 1,3-bis(2-oxopropyl)-3H-1,2,3-benzotriazolium triiodide III with a 67% yield of a
new conductive ionic liquid (viscous dark red oil, the conductivity of 0.1 N solution in THF of $1.5 \times 10^{-3}$ Sm/cm).

In order to reveal the main regularities of the reaction course and the possible prediction of the synthesis of new types of ionic liquids based on azole alkylation with α iodoketones we carried out a quantum chemical analysis of gradient channels of the formation of 1,3-bis(2-oxopropyl)-3$^+$H-1,2,3-benzotriazolium triiodide.

**CALCULATION DETAILS**

The study of the interaction potential surface of 1,2,3-benzotriazole with 1-iodopropan-2-one is carried out using the DFT (B3LYP) method [8]. Taking into account a heavy element in the studied molecular systems, in the calculations we employed the SDD pseudopotential. All calculations were performed using the GAUSSIAN-09 program package [9]. Stationary points were identified by the analysis of the Hessian matrix. A search for and location of transition states (TSs) was performed by the QST method [10]. The analysis of vibrational frequencies at the saddle point and the correspondence of the critical points on the gradient line connecting them is carried out using the IRC method. All calculations were made for the gas phase.

**RESULTS AND DISCUSSION**

The NMR monitoring of the alkylation process [7] indicates that the starting intermediate of the reaction is the N1 substituted benzotriazole. Released hydrogen iodide partially reduces initial iodoketone (II) with the release of elemental iodine. The latter promotes the formation of the triiodide anion initiating the formation of the ketone carbocation. According to the NMR monitoring results we studied the potential surfaces of four possible steps of the formation of 1,3-bis(2-oxopropyl)-3$^+$H-1,2,3-benzotriazolium triiodide: the formation of N1 substituted benzotriazole (IV) as a result of the bimolecular interaction of 1-iodopropan-2-one with 1,2,3-benzotriazole; the reduction of 1-iodopropan-2-one by hydrogen iodide with the formation of molecular iodine; the formation of the triiodide structure in the interaction of molecular iodine with iodoketone; the formation of 1,3-bis(2-oxopropyl)-3$^+$H-1,2,3-benzotriazolium triiodide.

The formation of the pre-reactive bimolecular state of the first reaction step (the interaction of compounds I and II) leads to the stabilization of the molecular system by 3.1 kcal/mol (stabilization energy was estimated as a difference between the total energy of the molecular system and total energies of molecules forming it in the optimal state). The formation of N1 substituted benzotriazole (in molecular system I–II) proceeds through the four-center transition state TS1 (Fig. 1). The total thermal effect of this reaction step is $-3.1$ kcal/mol and the activation barrier is 45.1 kcal/mol (Fig. 2).

The second step involves the partial reduction of initial iodoketone II to acetone V released during the N1-alkylation with hydrogen iodide and is accompanied by the elimination of elemental iodine. The gradient channels of the second step were analyzed in two variants: iodoketone reduction as a result of a direct interaction of compound II with hydrogen iodide (Scheme 1, channel 2') and with regard to the high thermodynamic stability of the IV–HI adduct (≈8 kcal/mol, Table 1), the iodoketone reduction process due to the interaction of II with the IV–HI adduct (Scheme 1, channel 2''). Furthermore, we considered an alternative reaction channel with a potentially probable formation of the (III–HI)$^+$T ionic pair (Scheme 1, channel 2'''').