QUANTUM CHEMICAL STUDY OF THE EFFECT OF HYDROGEN BROMIDE–WATER ASSOCIATES ON THE BROMINATION OF 1-HEPTENE

A. N. Miroshnichenko

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The MNDO method was used to study the extremal points on the potential energy surface of the reaction of bromine and 1-heptene. The formation of 1,2-dibromoheptane is energetically favored relative to formation of 1-bromo-2-heptene. \((H_2O)_nHBr\) associates reduce the activation energy of the transition state and act as a strong catalytic agent for the molecular reaction.

The competition of mechanisms is a frequent feature in the bromination of unsaturated compounds in the liquid phase. The relative contribution of a particular direction depends on the reaction conditions such as solvent polarity, temperature, reagent concentration, and presence of catalysts [1]. The low-temperature molecular bromination of olefins leads to the predominant formation of dibromides [2].

Since most organic reactions are carried out in solution, the analysis of their mechanism, kinetics, and thermodynamics must encompass the effect of the medium. Water in concentrations of about \(10^{-3}\) M and hydrogen bromide in concentrations of about \(10^{-4}\) M act as a strong catalytic agent for both the molecular and radical reactions [2]. Such a concentration of water remains in the system when standard drying procedures are used, while hydrogen bromide accumulates in the system since it is one of the products of the substitution reaction.

In the present work, we carried out a theoretical study of the mechanism of the molecular bromination of 1-heptene and studied the effect of associates of water and hydrogen bromide on the ratio of the yields of the products of the molecular reaction.

Data on the structure of the potential energy surface in the vicinity of the transition states (TS) are required to answer these questions.

CALCULATION PROCEDURE

The quantum chemical calculations for the reactions in systems containing bromine and 1-heptene were carried out using the MNDO method and the HYPER program package.

Rigorous quantum chemical analysis of the effect of solvation on reactivity with direct calculation of the unified system of reactant molecules and the catalyst in all stages of their transformation is laborious in light of the complexity of the calculations. Thus, the calculation of the energy of the reactant molecules in the field of water and hydrogen bromide molecules was carried out in the framework of the "supermolecular" approximation, in which the reagent and catalyst molecules are combined into a single supermolecule system [3, 4]. In this case, the solvation shells in the supermolecule method are constructed as follows: catalyst molecules are placed in the vicinity of greatest interaction of the bromine–heptene complex and complete optimization of the system geometry is carried out.
RESULTS AND DISCUSSION

Substitution products (3-bromo-1-heptene and 1-bromo-2-heptene) and an addition product (1,2-dibromoheptane) are formed in the bromination of 1-heptene. A side-product of a radical reaction, namely, 3-bromo-1-heptene, is formed when this reaction is carried out in dilute solution and the yield of this product does not exceed 3-4\% [5]. Thus, in studying the molecular reaction, we only analyzed the formation of 1,2-dibromoheptane and 1-bromo-2-heptene. The formation of the allylic and dibromide products in the low-temperature bromination is accompanied by formation of a bromomethyl group, which permits us to take the trajectory of approach of a bromine atom toward the methyl group as the reaction coordinate in the initial stage.

The calculated geometrical parameters of all the stationary states are given in Fig. 1. Table 1 gives the calculated energies of the stationary states given in Fig. 1. A profile of the potential energy surface taking account of the intermediate stages are shown in Fig. 2.

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The Br$_2$ molecule in TSI interacts with carbon atom Cl and a hydrogen atom of the methyl group H1. Br1 is also bound to another hydrogen atom of the methyl group H2 and with C2 but these bonds are weak. Br2 is weakly bound to H4. Transition species TSI has low charge separation.

The structure of the intermediate (Fig. 1, structure IN) is weakly polarized and mainly corresponds to formation of the bromomethyl group. The Cl--Br1 bond length is 2.02 Å, the Br1--Cl--C2 bond angle is 113°8', the Br2--Br1--Cl bond angle is 115°7', and H1 and H2 extrude from the plane of the double bond by 4°20'. The Br2--Br1--Cl--C2 torsion angle is 28°3'. The lengths of the Cl--C2 and C2--C3 bonds are not altered. The length of the Br1--Br2 bond is longer than in the free Br$_2$ molecule by 0.06 Å.

The quantum chemical study showed that the formation of the addition product P1 proceeds through TSII. The change in the Br2--Br1--Cl bond angle was taken as a new coordinate. Reaching TSII requires overcoming an activation barrier of 27.2 kcal/mol, which involves contraction of the Br2--Br1--Cl bond angle to 83.5°. The Cl--C2 and C2--C3 bonds have bond order 1.5 and their lengths are 1.47 and 1.49 Å, respectively. The Br2--Br1--Cl--C2 torsion angle contracts to 27°, while the length of the Br1--Br2 bond is extended relative to the free molecule by 0.12 Å. Formation of the bromomethyl group is completed in TSIL The Br1--Cl bond length is 1.90 Å, while the Br1--Cl--C2 bond angle is 117°. The structure of TSII is highly polarized.

Analysis of the geometrical parameters of the saddle points indicates that the existence of two TS on the coordinate for the addition of bromine results from two consecutive processes. The bromomethyl group is formed initially, followed by addition of another bromine atom to the heptene molecule. This process occurs in steps within the framework of a single molecular mechanism.

A modification of the search for a reaction coordinate with independent variation of not one but two geometrical parameters and optimization of all the other parameters of each fixed value of the reaction coordinate parameter was used to search for the transition state leading to formation of the molecular substitution reaction [5]. In our case, the H4--C3 distance and Br2--Br1--Cl--C2 torsion angle were varied.

The quantum chemical study showed that the formation of the substitution product is possible only through TSIII, which requires an additional energy expenditure to 82.6 kcal/mol. The greatest charge redistribution is achieved in TSIII. The substitution of a hydrogen atom proceeds at the most negatively charged carbon atom. The result obtained is in good accord with the assumption of Minkin et al. [6] that electrophilic substitution reactions will proceed predominantly at the site of greatest electron density and, thus, greatest negative charge. TSIII corresponds to the onset of formation of the hydrogen bromide molecule. The Br2--H4 distance decreases relative to TSII from 2.58 to 1.85 Å, possibly due to breakage of the bond between C3 and H4, which is removed. The H4--C3 distance in TSIII is 1.67 Å, while it is only 1.11 Å in TSII. The Br2--Br1--Cl angle reaches 83.5°, while the Br2--Br1--Cl--C2 torsion angle is 10°.

Such a substitution reaction mechanism suggests that the primary product (P2) is the molecular complex of HBr with 1-bromo-2-heptene.

Thus, the formation of the substitution products must proceed through a highly polarized structure. This correlates well with the experimental results of Buckles and Womer [7], who showed that substitution product