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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Excited Biradical States in Thermal Dimerization of Bicyclo[2.2.0]hex-1(4)-ene

K. K. Kalnin'sh[a] and S. G. Semenov[b]

[a]*Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia*
[b]*St. Petersburg State University, St. Petersburg, Russia*

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Abstract—The mechanism of thermal dimerization and polymerization of bicyclo[2.2.0]hex-1(4)-ene **I** was studied by ab initio RHF/DH, ROHF/DH, and GVB/DH quantum-chemical calculations. The structure and electronic characteristics of the monomer **I**, hypothetical intermediate, and two observed dimerizatoin products in the ground and excited states of various multiplicities were calculated.

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Bicyclo[2.2.0]hex-1(4)-ene was prepared by electrochemical reduction of 1-bromo-4-chlorobicyclo[2.2.0]-hexane and was studied by NMR, IR, and Raman spectroscopy at low temperatures [1]. This compound can be stored at –200°C, and at –23°C polymerizes ($\tau_{1/2} < 10$ s [1]) to form a colorless polymer insoluble in the majority of solvents. In dilute solutions (0.002 M), monomer **I** rapidly dimerizes [2]. The structural parameters of one of the dimers were determined by single crystal X-ray diffraction [3].

In the Raman spectrum of the monomer, the C=C stretching vibrations are observed at 1610 cm^{-1} in the solid phase and at 1664 cm^{-1} in a CD_2Cl_2 solution at –50°C. The presence of strong low-frequency bands in the IR spectrum and their complete absence in the Raman spectrum suggest high symmetry (D_{2h}) of the molecule of **I**. Extremely high reactivity of the monomer is due to strained steric structure with the bond angles in the range from 85.5° to 95.5° and short H···H contacts (2.5 Å, according to ab initio calculations).

Relationship between the intramolecular chemical strain and reactivity of molecules follows from the general concept of electronic excitation in an elementary chemical process [4]. Lower electronically excited states of molecules are often biradical and therefore are chemically active. A decrease in the energy of these states under the action of internal chemical strain or external mechanical field within the framework of this concept [4] is equivalent to a decrease in the activation energy, which leads to acceleration of the chemical reaction.

Participation of biradical electronically excited states in thermochemical reactions was studied previously with dimerization/polymerization of bicyclobutanes [5] and perfluoroolefins [6] as example. The key step of these reactions is thermal excitation of the monomer molecule into a low-lying (<1 eV) electronic state, accompanied by cleavage of a carbon–carbon single bond or degradation of a double bond. The primary biradicals arising in the process exhibit high reactivity and undergo recombination and addition to neutral monomer molecules to form stable products or biradical intermediates undergoing subsequent oligomerization and polymerization.

In this study we consider the mechanism of dimerization of bicyclo[2.2.0]hex-1(4)-ene from the standpoint of the concept of biradical excited states. We performed ab initio quantum-chemical calculations of the structure and electronic characteristics of monomer and dimer molecules in the ground and excited electronic states and constructed the energy diagrams of the reactions on the basis of these data.

EXPERIMENTAL

Quantum-chemical calculations were performed by ab initio RHF/DH, ROHF/DH, and GVB/DH methods using GAMESS program [7, 8]. The calculation procedure for

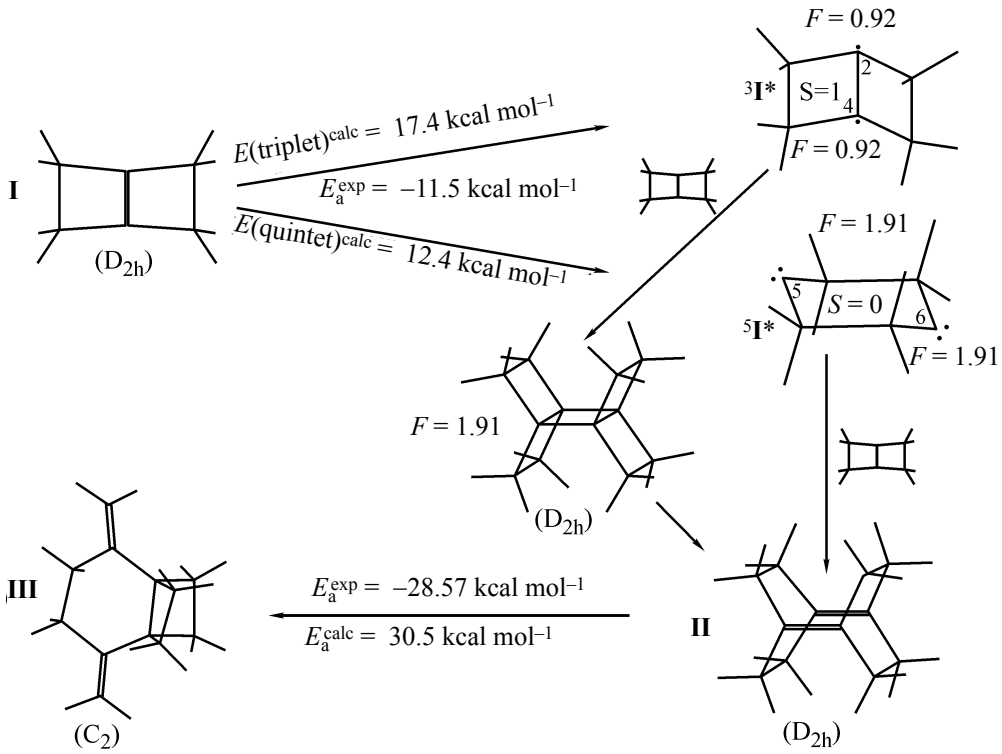

Fig. 1. Steric structure of strained bicyclo[2.2.0]hex-1(4)-ene and its dimers and pathways of thermochemical dimerization. (**I**) Monomer in the ground state S_0, (^{3}**I***) monomer in the triplet excited state T_1, (^{5}**I***) monomer in the quintet excited state Q_1, (**II**, **III**) experimentally observed dimers, and (**IV**) unobserved hypothetical dimerization product.

the ground (S_0) and excited (S_1, T_1) states of molecules is described in [9]. In all the cases, the correspondence of the optimized geometric parameters of molecules to the energy minimum was confirmed by the absence of imaginary frequencies in the calculated vibration spectra. The electronic excitation energies were calculated taking into account zero-point vibrations of nuclei in the ground and excited states.

Steric and electronic structure of bicyclohexene. For the ground electronic state, the calculation methods used give a planar structure of the monomer molecule of high symmetry (D_{2h}) (Fig. 1), with the following C=C bond length and C–C=C angle: 1.315 Å, 95.6° (RHF/DH) or 1.295 Å, 95.7° (RHF/6-311G**). In the vibration spectrum of **I**, intense low-frequency transition at 157 cm^{-1} (RHF/DH) or 136 cm^{-1} (RHF/6-311G**) corresponds to "flapping wing" vibrations of the C–C=C–C fragment. Such vibrations, owing to vibronic interactions, can populate the lowest equilibrium triplet state T_1 with an energy of 17.4 kcal mol^{-1} (Figs. 1, 2), characterized by an increase in the length of the degraded carbon–carbon double bond from 1.315 to 1.565 Å (ROHF/DH) and by deviation of the equilibrium structure of **I** from planarity (the C–C=C–C torsion angle changes from 180 to 120.6°). In this triplet biradical state, the π bond is broken, and two chemically active radical centers arise on the corresponding carbon atoms C^2 and C^4 with free valence indices $F = 0.92$ (Fig. 1). These centers participate in the subsequent events of recombination or addition to neutral molecules. The dipole moment of the molecule of **I** in the triplet state is 1.32 D.

In the lowest-energy singlet excited state S_1, the monomer molecule has an equilibrium structure that does not differ significantly from that in the T_1 state. The free valence indices on the C^2 and C^4 atoms in the S_1 and T_1 states also coincide ($F_2 = F_4 = 0.92$). Similarly to the other biradical states studied previously [5, 6], the singlet–triplet splitting in this case is small: 3.7 kcal mol^{-1}.

Along with the above-considered excitation to the biradical state $(S{\cdot}T)_1$ with the degraded double bond, the bicyclohexene molecule can undergo two-electron excitation to the quintet state with full cleavage of the carbon–carbon double bond. For this state, we obtained an unexpectedly low energy of 12.4 kcal mol^{-1} (calculation

methods RHF, ROHF/DH), which is very close to the experimental activation energy of the dimerization, 11.5 kcal mol^{-1}. This means that the neutral nonradical molecule of bicyclohexene at room temperature readily undergoes thermal electronic excitation and transforms into a chemically active bisbiradical species with the free valence indices $F_5 = F_6 = 1.91$ (Figs. 1, 2), which subsequently undergoes virtually activationless addition to other monomer molecules with the formation of a dimeric or polymeric product. The quintet monomer molecule is characterized by zero dipole moment and has the geometric parameters of the hydrocarbon ring close to those of cyclohexane (Fig. 1).

Coincidence of the activation energy with the excitation energy of the quintet suggests participation of this species in the dimerization. However, the possibility of a prototropic rearrangement, i.e., of hydrogen atom transfer from methylene groups to biradical centers in biscarbenes, which leads to the formation of double bonds in the six-membered ring, is against this hypothesis. As seen from Fig. 2, hydrogen transfer itself is not accompanied by a significant change in the energy (it only slightly decreases) but leads to the formation of double bonds with a sharp decrease in the energy due to recombination of radical centers on the adjacent carbon atoms.

Bicyclohexene dimers. Two products of bicyclohexene dimerization, **II** and **III**, have been isolated experimentally. In addition, the existence of a hypothetical intermediate **IV** (Fig. 1), described only theoretically [2], is suggested. It is believed that, in the primary step of the dimerization, interaction of two molecules of **I** yields experimentally unobserved biradical dimer **V** (Fig. 3), which at alow concentration of **I** undergoes monomolecular transformation into **II** or **III** and at a concentration exceeding 0.01 M initiates the polymerization. The heat of formation of **V** from two molecules of monomer **I**, calculated by RHF/DH and

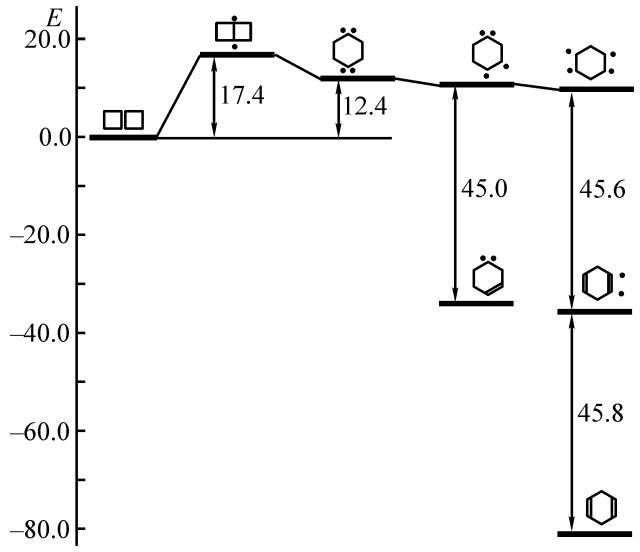

Fig. 2. Energy levels of bicyclo[2.2.0]hex-1(4)-ene in the ground, triplet, and quintet excited states and of prototropic species formed by intramolecular hydrogen transfer.

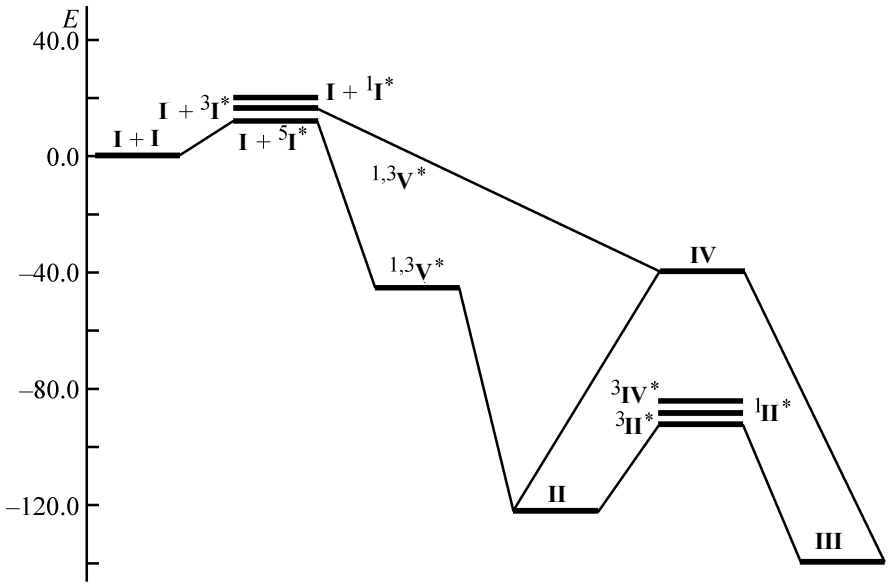

Fig. 3. Energy scheme of thermal reactions of bicyclo[2.2.0]hex-1(4)-ene dimerization. (**V**) Experimentally unobserved biradical dimer.

ROHF/DH methods, is –44.4 kcal mol^{-1} (–28 kcal mol^{-1} according to [2]). Because of large thermal effects of the subsequent formation of dimers **II** and **III** (Fig. 3), –121.9 and –138.6 kcal mol^{-1}, respectively (RHF/DH), experimental detection of biradical **V** is hardly probable.

The experimental detection of hypothetical dimer **IV** as reaction product is also improbable because of its high energy, –38.50 kcal mol^{-1} relative to the level of the starting compound **I**, which should inevitably lead to its transformation into stable structure **II** or **III** (Fig. 3). The molecule of **IV** has a high point symmetry group, D_{2h}. Attempt to calculate the excited state of dimer **IV** leads to an unexpected result: The triplet state of **IV** appears to lie lower than the ground state by 35.2 kcal mol^{-1} (Fig. 3), and the minimum of the corresponding singlet state is not revealed.

Presumably, hypothetical species **IV** and experimentally observed dimers **II** and **III** are formed from different precursors. In the first case, such a precursor is the excited monomeric molecule of **I** in the triplet configuration ^{3}**I***, which undergoes addition to the molecule of **I** in the ground electronic state S_0. Two carbon atoms of the molecule of ^{3}**I***, C^2 and C^4, bearing the maximal free valence indices, are bonded with the corresponding atoms of the second molecule to form a slightly distorted (according to RHF calculations) four-membered ring linking two monomer molecules (Fig. 1). However, the internal strain in the molecular structure strongly increases the energy of hypothetical dimer **IV** relative to stable structures **II** and **III**. As a result, the concentration of **IV** decreases to such an extent that is experimental detection becomes impossible.

In the second case, the probable precursor of dimer **II** or **III** is bicyclohexene in the quintet electronic configuration ^{5}**I***. The distance between the C^5 and C^6 atoms in the cyclohexane steric configuration (Fig. 1) is 2.7 Å, and approximately the same distance (2.4 Å) is observed between the corresponding carbon atoms in the reaction product **II**. Cleavage of the intramolecular double bond in bicyclohexene upon quintet excitation and appearance of two unpaired electrons on each of the C^5 and C^6 atoms lead in the dimerization event to the formation of two intermolecular double bonds. The distance between them in the molecule of **II** is as short as 2.395 Å [3]. Close contacts between the carbon atoms of the double bonds in **II**, in the opinion of Wiberg et al. [2], appreciably affect the stability of the molecule and its physical properties such as the ionization potential and electronic absorption spectrum.

Another dimerization product detected, compound **III**, is formed by sigmatropic Cope rearrangement of the primary product **II**. The reaction is accompanied by a decrease in the symmetry from D_{2h} to C_2. The number of atoms and of single and double bonds in **III** is the same as in **II**, but the modes of atom connection are different. Rearrangements of such a kind are traditionally considered within the framework of the Woodward–Hoffmann theory based on the principle of conservation of orbital symmetry. In this study we suggest another approach [4] according to which thermochemical reactions, including Cope rearrangement, occur via electronically excited molecular or intermolecular states.

In the case under consideration, product **II** transforms in heating (to 100°C) into **III** with an activation energy of 28.7 kcal mol^{-1} [2] via a certain reaction state understood as electronically excited state of dimerization products. Our calculations show that compound **III** has a lower energy compared to **II** (Fig. 3), in agreement with thermochemical measurements made in [2], although the calculated data of [2] suggest opposite ratio of the energies of products **II** and **III**. The experimental activation energy of 28.7 kcal mol^{-1} should be apparently compared to such calculated quantity as the energy of the relaxed excited state of the less stable product, compound **II**. Indeed, the excitation energy of **II**, equal to 30.5 kcal mol^{-1}, is close to the above-indicated activation energy. In the excited state, the molecule of **II** transforms into a biradical with the maximal free valence indices $F = 0.96$, concentrated on the carbon atoms of the degraded double bond. Specifically in this state, as can be assumed, the electron density and molecular structure undergo rearrangement.

Thus, bicyclo[2.2.0]hex-1(4)-ene is a brilliant example of the effect of internal chemical strain on the reactivity of molecules. Considerable deviation of the C–C–C bond angles from the mean values characteristic of saturated compounds (109.5°) and close HH contacts (1.76 Å) make the molecular structure strained. The strain energy transforms into the molecular excitation energy. The energy of the lowest electronic states determining the reactivity of molecules under the action of structural deformations decreases to an enormous extent (by 1–4 eV according to estimates), and the corresponding levels shift to the range of thermal values (<1 eV) and are efficiently populated under common conditions.

CONCLUSIONS

(1) The mechanism of dimerization of strained bicyclo[2.2.0]hex-1(4)-ene was examined from the standpoint of biradical states. The correspondence was revealed between the experimental activation energy of dimerization, equal to 11.5 kcal mol^{-1}, and the calculated energies of excitation into the quintet (12.4 kcal mol^{-1}) and triplet (17.4 kcal mol^{-1}) states.

(2) The experimental activation energy of thermal Cope rearrangement of bicyclo[2.2.0]hex-1(4)-ene dimerization products (28.7 kcal mol^{-1}) corresponds to the calculated energy of excitation to the biradical state of the high-symmetry product (30.5 kcal mol^{-1}).

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