

SHORT
COMMUNICATIONS

1,3-Migration of Hydrogen in 1,3-Dioxane Carbocation

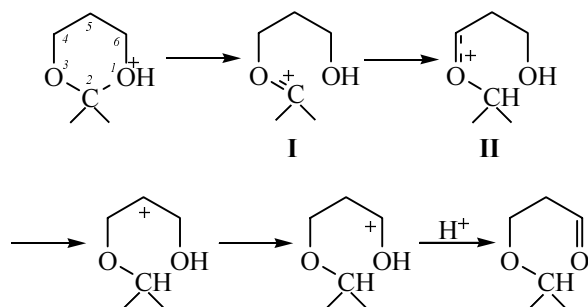
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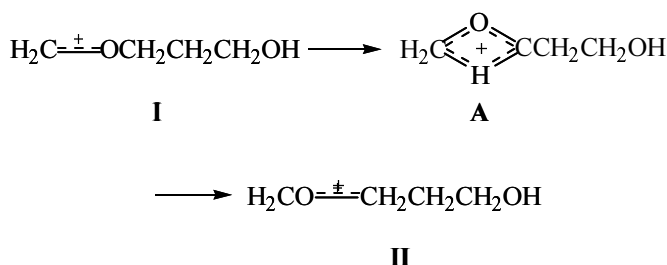
Received February 26, 2003

At temperature higher than 250°C in the presence of catalysts 1,3-dioxanes are converted into β -alkoxyaldehydes. It is assumed that the key stage of the process is 1,5-migration of hydrogen within a catalytic complex formed by coordination of both oxygen atoms of the 1,3-dioxane to the catalytic site [1].

On the other hand an information exists on possible occurrence of 1,3-hydride shift in alkoxy-carbocations **I** arising at dissolution of 1,3-dioxanes in acid media [2]. It is presumable that the β -alkoxyaldehyde forms as a result of successive 1,3 and 1,2 intramolecular hydrogen migrations.



The key stage of this scheme is 1,3-migration of a hydrogen atom that can be described as follows:



Conformations of ion **I** were calculated within the framework of AM1 and Hartree–Fock methods in the valence-split basis with polarization d -orbitals (6-31G**).

The narrow range of heats of formation (less than 2 kcal mol⁻¹) indicates that all conformations may exist in solution. In all conformations hydrogen atom at C² and migrating hydrogen H¹⁰ at C⁴ are located in the plane C²O³C⁴ ($\varphi = 0.5 \pm 0.5$ and $179.5 \pm 0.5^\circ$ respectively).

It should be noted that despite sterical hindrances the minimum of heat of formation corresponds to the eclipsed conformation of the carbocation **I** (ΔH_f 93 kcal mol⁻¹) where the C⁶ is located antiperiplanar with respect to O³ atom (φ 116°).

In all conformations considered atom H¹⁰ located in axial position at the C⁴ atom is involved into the migration process. This hydrogen, the single one among substituent atoms, is oriented in the plane C²O³C⁴, and the distance H¹⁰–C² is 2.5 Å, a lot shorter than the distances between the C² atom and other hydrogens.

The HOMO is built up of antibonding combination of p -orbitals belonging to O¹ and C⁶ atoms and s -orbitals of the hydrogen attached to C⁶, and LUMO is combined from antibonding p -orbitals of C² and O³ atoms, where the contribution into LUMO from AO of C² atom amounts to 50% (see figure). This structure underlies the 1,3-migration of hydrogen.

In transition state **A** the orientation of hydrogen atoms at C² atom changes as compared to that in ion **I** since simultaneously with the rearrangement a methylene group rotation occurs accompanied with the bond C–O cleavage. Note that in ion **A** atoms C²O³C⁴, and H¹⁰ are located in the same plane, and the bond angles at the atoms O³, C², and C⁴ are altered. The bond angle C²O³C⁴ decreased by over 30° confirms that **A** moiety constitutes a four-membered transition state.

The electron density redistribution in transition state **A** concerns only atoms taking part in building up the four-membered state. The charges on atoms C² and C⁴ get leveled, and the negative charge on O³ increases.

The structure of frontier molecular orbitals in ion **A** suffers significant changes compared with that of ion **I** (see figure). The HOMO is built up of antibonding combination of O^1 , C^6 , and hydrogen atoms attached to this carbon. HOMO lacks the bonding combination of p -orbitals from atoms C^2 and O^3 , the C^2-O^3 bond gets longer, its partially double character observed in ion **I** is removed. The LUMO is formed of antibonding combination of p -orbitals from atoms C^2 and C^4 .

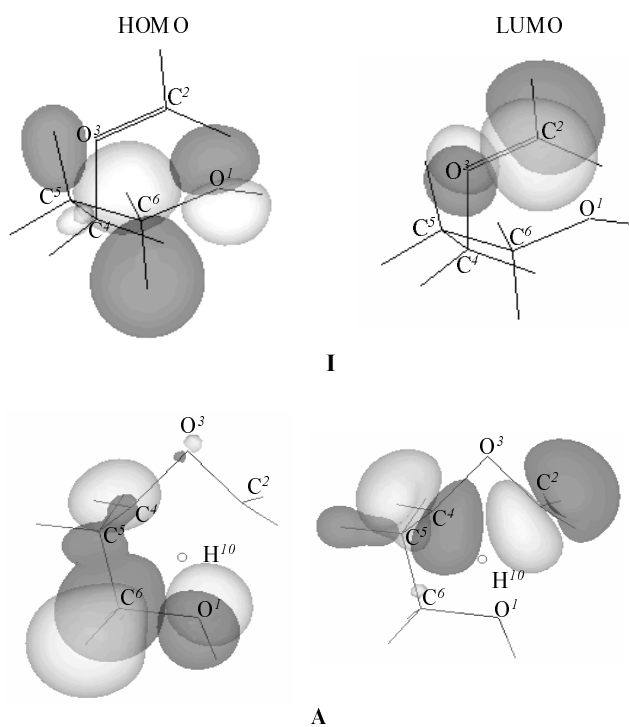
The calculation results show, firstly, that 1,3-migration of hydrogen is a concerted process where the bond C^2-H^{10} (l 1.444 Å) starts to form before the rupture of C^4-H^{10} bond (l 1.375 Å); secondly, that charge distribution on the atoms and the structure of the frontier molecular orbitals are independent of conformation.

The interaction of atom H^{10} with C^2 and C^4 carbons on a valence level, disappearance of the $C=O$ double bond due to leveling of bond lengths C^2-O^3 and O^3-C^4 and charges on atoms C^2 and C^4 , symmetrical structure of the frontier MO in the transition state, and also a presence of one negative eigenvalue in the matrix of force constants [3] confirm that we deal with a true transition state.

The performed calculations of 1,3 hydrogen migration show the existence of an energy barrier of 54 kcal mol⁻¹ (AM1). The barrier value is consistent with the results of previously performed calculations for 1,1-dimethoxymethane [4] and 1,1-diethoxymethane [5]. The refined calculation in 6-31G** basis with complete geometry optimization for carbocations **I**, **II**, and **A** afforded the barrier value of 53 kcal mol⁻¹. The data obtained permit a conclusion that the intramolecular 1,3-hydrogen shift is a probable reaction stage.

REFERENCES

1. Rondstedt, C. S. Jr. and Mantell, G. J., *J. Am. Chem. Soc.*, 1960, vol. 82, p. 6419.



Structure of frontier molecular orbitals in ion **I** and 1,3-transition state **A**.

- Akhmadinov, R.T., *Cand. Sci. (Chem.) Dissertation*, Ufa, 1981.
- Burshtein, K.Ya. and Shorygin, P.P., *Kvantovo-khimicheskie raschety v organicheskoi khimii i molekulyarnoi spektroskopii* (Quantum-Chemical Calculation in Organic Chemistry and Molecular Spectroscopy), Moscow: Nauka, 1989, p. 35.
- Klyuchareva, E.V., Shornikov, D.V., and Kantor, E.A., *Bashkirskii Khimicheskii Zhurnal*, 1999, vol. 6, no. 2–3, p. 46.
- Klyuchareva, E.V., Shornikov, D.V., and Kantor, E.A., *Bashkirskii Khimicheskii Zhurnal*, 1999, vol. 6, no. 2–3, p. 52.