

BRIEF COMMUNICATIONS

QUANTUM-CHEMICAL STUDY OF THE HYDROGENATION
AND HYDROGENOLYSIS OF XYLOSEB. Sh. Kedel'baev, N. N. Imankulov, A. M. Kuatbekov,
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A wealth of experimental data, which frequently contradicts itself, has been accumulated on the hydrogenation and hydrogenolysis of sugars [1-3]. This is especially true of the mechanism of these processes.

Quantum-chemical studies are very valuable for determining the sequence of steps and direction of reactions. They enable the "study" of short-lived intermediates, i.e., radicals, ions, and ion-radicals, that often cannot be studied experimentally. We used a semi-empirical MINDO3 method [4], which is highly recommended for studying oxygen-containing hydrocarbons [5].

Therefore, we performed quantum-chemical calculations in order to answer the separate questions about the mechanisms of hydrogenation and hydrogenolysis of monoses, in particular, xylose.

Any pentose or hexose can be represented by four structural forms [6]: two cyclic (pyranose and furanose) and two open (hydroxyaldehyde and endiol) [2]. All four structural forms of xylose were calculated in order to establish the electronic structure and analyze the stability and reactivity of the molecules.

The geometric structure and charge distribution of the structural forms of xylose are shown in Fig. 1. Figure 1a and -b show that the C_2-C_3 bond is noticeably shortened on going from the hydroxyaldehyde to the endiol form. This is consistent with its strength. Numerous experimental data confirm this. The effect of the C_1-C_2 double bond explains it.

An analysis of the geometric structure and charge distribution of the cyclic hemiacetal structures suggests that the decrease in the number of C atoms in the ring on going from xylopyranose to xylofuranose causes a significant decrease in the C_2-C_3 bond. This may be explained by the higher energetic stability of the xylofuranose.

The calculated heats of formation and total energies indicate that the cyclic forms are more stable than the open ones, which are more reactive. Of the two cyclic forms, xylofuranose is the more stable one; of the two open ones, the endiol. These data confirm many conclusions about the very high reactivity of the hydroxyaldehyde monoses [7]. The energy of the lowest unoccupied and molecular orbital under otherwise equal conditions enables the activity of the molecule toward reduction, such

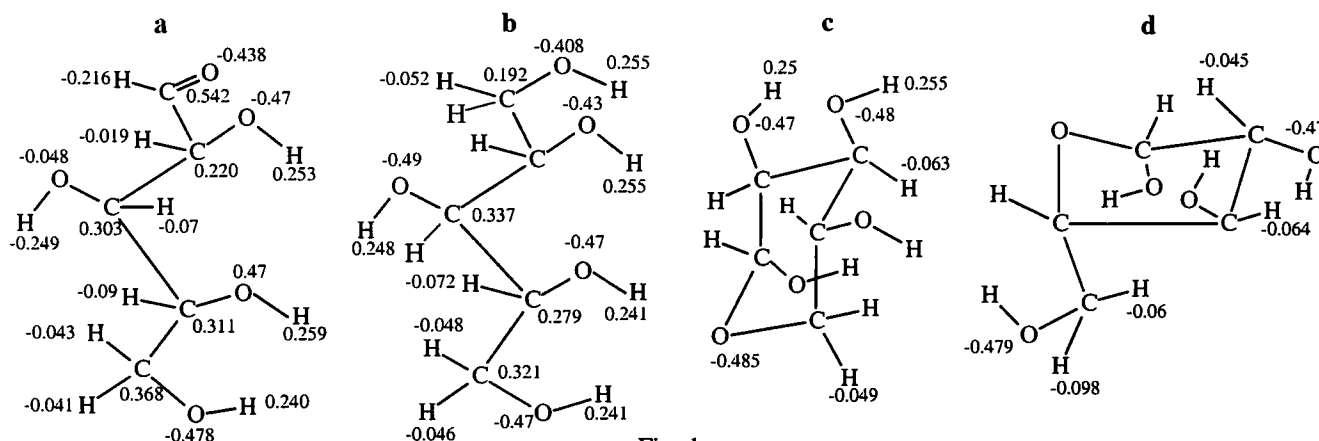


Fig. 1

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as hydrogenation and hydrogenolysis, to be estimated. The energy characteristics of the xylose structural forms are given below:

Structural form	Heat of formation, kcal/mol	Total energy, eV	Electron affinity (LUMO energy), eV
Hydroxyaldehyde	-187.951	-2338.458	0.695
Endiol	-223.110	-2339.983	1.222
Pyranose	-226.952	-2340.150	0.414
Furanose	-237.507	-2340.607	1.098

The calculated electron affinities (LUMO energy) show that the pyranose and hydroxyaldehyde forms should be the most active toward reduction. This is consistent with the lowest energy for the LUMO compared with the other forms. The final product of xylose hydrogenation is xylitol. Therefore, we calculated the energy of xylitol and determined the hydrogenation energy using the formula

$$\Delta E_{\text{reaction}} = \sum E_{n_{\text{products}}} - \sum E_{n_{\text{reactants}}}$$

where E_n is the total energy of the molecules.

The results of the calculations, which are listed below, confirm that the hydroxyaldehyde form of xylose is the most reactive toward reduction. This is consistent with the lowest ΔE for the reaction:

Structural form	Hydrogenation energy, eV
Hydroxyaldehyde	-1.715
Endiol	-0.190
Pyranose	-0.023
Furanose	+0.434

The positive energy of hydrogenation for the xylofuranose indicates that energy must be expended for the hydrogenation to occur.

Several theories that are sometimes contradictory also exist for the hydrogenolysis of sugars and polyols [8-11]. We performed quantum-chemical calculations in this area also. We found that decomposition of the hydroxyaldehyde form of xylose from the two possible directions is more favored for formation of the hydroxyethanal and the glycerine aldehyde:

Compound	Product formed	Cleavage energy, eV
1. Xylose hydroxyaldehyde	a) dihydroxypropanol and hydroxyethanal	0.049
	b) methanal and trihydroxybutanal	0.764
2. Xylose	a) methanal and butenetetraol	0.788
	b) hydroxyethanal and propenetriol	0.166
	c) dihydroxypropanal and ethanediol	1.473
3. Xylitol	a) methanol and trihydroxybutanal	1.385
	b) ethanediol and dihydroxypropanal	1.244
	c) propanetriol and hydroxyethanal	-0.020
	d) butanetetraol and methanal	0.749

Three different directions are possible for decomposition of the endiol form of xylose. Of these, the most energetically favorable is formation of propenetriol and hydroxyethanal; the least, cleavage of the C_2-C_3 bond [12]. This has often been observed experimentally and is explained by the effect of the double bond, which weakens the β -bond and strengthens the α -bond relative to the double bond.

The study of xylitol decomposition showed that the most energetically favorable direction is that which forms glycerine

and hydroxyethanal. Comparison of the three decomposition reactions revealed that the most favorable in all instances is the one that forms hydroxyethanal (directions 1a, 2b, and 3c). It is interesting that the energetic favorability of the carbohydrate decomposition is determined not by the site of bond cleavage but by the structure of the products formed. A comparison of the data suggests that the indirect decomposition that proceeds through xylitol formation is the most probable for xylose hydrogenolysis.

Thus, energy characteristics of the four structural forms of xylose are calculated by a quantum-chemical method. Their reactivities toward hydrogenation and hydrogenolysis are determined. It is shown that the hydroxyaldehyde form of xylose is most reactive toward reduction. The energetic favorability of hydrogenolysis is determined by the structure of the products formed, in our instance, xylitol.

REFERENCES

1. A. P. Sergeev and B. L. Lebedev, *Usp. Khim.*, **23**, No. 6, 669 (1959).
2. N. K. Kochetkov, et al., *Chemistry of Carbohydrates* [in Russian], Khimiya, Moscow (1967).
3. A. Reverdin, *Über die reduktion and spaltung von Glukose*, Zurich (1944).
4. T. Clark, *A Handbook of Computational Chemistry. A Practical Guide to Chemical Structure and Energy Calculations*, John Wiley and Sons, New York (1985).
5. M. S. Erzhanova and T. B. Beisekov, *Alloy Catalysts for Furfurol Hydrogenation* [in Russian], Gylym, Alma-Ata (1992).
6. N. K. Nadirov and R. L. Slutskin, *Catalytic Hydrogenation and Hydrogenolysis* [in Russian], Khimiya, Moscow (1976).
7. B. V. Erofeev, et al., *Proceedings of the 4th International Congress on Catalysis*, Moscow (1968), Vol. 2, Nauka, Moscow (1970), p. 57.
8. A. A. Vasyunin, N. A. Vasyunina, and R. L. Slutskin, *Dokl. Akad. Nauk SSSR*, **169**, No. 5, 1077 (1966).
9. Yu. A. Zhdanov and G. N. Dorofeenko, *Chemical Transformations of the Carbon Framework of Carbohydrates* [in Russian], Akad. Nauk SSSR, Moscow (1962).
10. A. A. Balandin, in: *Multiplet Theory of Catalysis. Part 2. Energy Factors in Catalysis* [in Russian], MTU, Moscow (1964), p. 179.
11. Yu. A. Zhdanov, et al., in: *Chemistry and Biochemistry of Carbohydrates* [in Russian], Nauka, Moscow (1969), p. 22.
12. B. Sh. Kedel'baev, A. M. Ashirov, A. Zh. Tashimetova, and K. T. Kurbanbekov, *Nauka Obr. Yuzh. Kaz.*, No. 3, 10 (1998).