



# Ab initio study of 1,3-dioxanes formation from formaldehyde dimer and alkenes



O.Yu. Kupova\*, I.V. Vakulin<sup>1</sup>, R.F. Talipov<sup>1</sup>

Department of Bioorganic Chemistry, Bashkir State University, Zaki Validi St., 32, Ufa 450074, Republic of Bashkortostan, Russia

## ARTICLE INFO

### Article history:

Received 13 December 2012  
Received in revised form 24 February 2013  
Accepted 25 February 2013  
Available online 19 March 2013

### Keywords:

Ab initio calculation  
Transition state  
Prins reaction  
1,3-Dioxanes  
Formaldehyde oligomers  
Alkenes

## ABSTRACT

Some features of adding formaldehyde dimer to alkenes with formation of alkyl-substituted 1,3-dioxanes by the Prins reaction in the gas phase are studied at the MP2(fc)/6-31G(d,p) computational level. The structure of the transition states and key intermediates is revealed and thermochemical reaction parameters are determined. It is shown that 1,3-dioxanes are mostly formed from the  $\pi$ -complex obtained in the result of formaldehyde dimer interaction with alkenes without intermediate formation of a  $\sigma$ -complex. Here the transformation of  $\pi$ -cation can be considered as a pseudo synchronous process. The synchrony degree and activation energy are considerably determined by the presence of alkyl substituents at the double bond.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

As a multireaction, the Prins reaction is a convenient technique of oxygen-containing heterocycles formation [1,2]. However, in some cases this multipathing is considered to be a drawback. For instance, the first stage of the isoprene synthesis by the “dioxane” method [3] is accompanied by the formation of a large number of by-methyldihydropyrans (up to 20%) [4–6], thus, decreasing the efficiency of this method. Obviously, in order to increase the selectivity of the first stage a mechanism of alkenes and formaldehydes interaction should be refined.

Products formation by way of cascade involvement of one or two molecules of formaldehyde monomer [7,8] is considered one of the generally accepted mechanisms of the Prins reaction (see Fig. 1).

Experimental [9] and theoretical data [10,11] clearly demonstrate that the presence of formaldehyde oligomers (FOs) is a prerequisite for the 4-alkyl-1,3-dioxanes formation, whereas FO are much more reactive than the monomer. It is assumed that the FO addition at the double bond can be described as sequential, or pseudo synchronous [12] (see Fig. 2).

The implementation of the two mechanisms corresponds to the experimental data on a stereoselective Prins reaction for a series of cycloalkenes [13].

In the work we studied some features of formaldehyde oligomers and alkenes interaction resulting in the formation of 1,3-dioxanes. The geometric and orbital structures of the reactions transition states depending on the alkene structure are considered. A formaldehyde dimer (FD) served an example for FO calculation.

## 2. Methods of calculations

PC GAMESS v7.1 programs [14] were used in carrying out quantum and chemical calculations. Searching for the equilibrium geometry of the transition states was carried out by MP2(fc)/6-31G(d) [15–17] approximation. Verification of the transition state was made by calculating vibrational parameters for the obtained transition state geometry with the subsequent analysis of the calculated frequencies of the IR spectrum, as well as modeling the found transition state into the starting materials and final products by means of the IRC procedure. The degree of asynchrony in the cyclization reaction was calculated by the method [18].

## 3. Calculation results and discussion

Due to the calculation results, the section of the potential energy surface corresponding to the formation of 4-alkyl-1,3-dioxane from FD and alkenes (1–5) is presented as follows (Fig. 3):

It is shown that this reaction proceeds in two stages without an intermediate  $\sigma$ -cation formation. The  $\pi$ -cation (1b–5b) is directly transformed into the 1,3-dioxane structure (1d–5d) though the

\* Corresponding author. Tel.: +7 347 272 63 70.

E-mail address: [olgakupova@gmail.com](mailto:olgakupova@gmail.com) (O.Yu. Kupova).

<sup>1</sup> Tel.: +7 347 272 63 70.

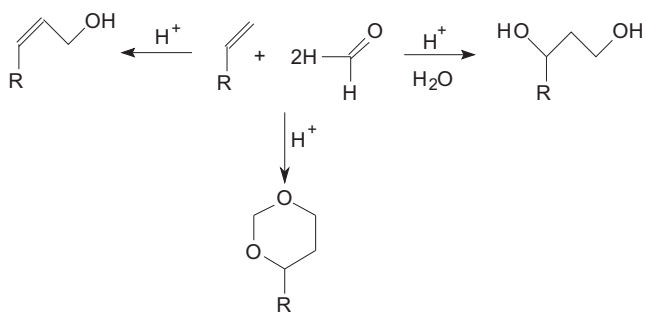


Fig. 1. The Prins reaction products [8].

**Table 1**  
Energy parameters of dioxane formation reactions, kJ/mol.

Alkene	$\Delta_r G^*(a-c)$	$\Delta_r G(b-a)$	$\Delta_r G(d-a)$	$\Delta_r G^*(c-b)$
1	138.7	110.9	-7.4	27.7
2	99.2	92.6	-27.6	6.6
3	72.2	87.9	-30.5	18.5
4	66.2	36.9	-33.8	29.3
5	114.7	67.8	-35.3	46.9

reacting with terminal alkenes, propylene and butane-1 and amount to 99.2 and 72.2 kJ/mol accordingly. In increasing the number of alkyl substituents at the double alkene bond, the Gibbs activation energy slightly grows (for butane-2 and isobutylene). Such character of changes in the activation energy of the alkene structure is well explained by a steric factor.

Besides, such potential energy surface points to the fact that the limiting stage of the alkene reacting with FD is the formation of  $\pi$ -cation.

The structure of transition states (1c–5c) indicating the values of interatomic distances and bond orders of the reaction are presented in Fig. 4.

According to the data presented in almost all transition states the formation of the C–C bond of 1,3 dioxane cycle is accomplished earlier than the O–C bond one. So the C2–C4 in the transition

corresponding transition states. (1c–5c). The calculated values of the thermodynamic parameters are presented in Table 1.

According to the Gibbs free energy values, a dioxane (1d–5d) formation is thermodynamically favorable; it slightly increases while the number of alkyl substituents at the double bond grows. Thus, the Gibbs free energy value for ethylene amounts to -7.4 kJ/mol, whereas this value for butene-2 is -35.3 kJ/mol.

The calculated values of the Gibbs activation energy reaction show that ethylene is hard to be reacted ( $\Delta_r G^*(a-d) = 138.7$  kJ/mol). The lowest values of the activation energy are achieved in

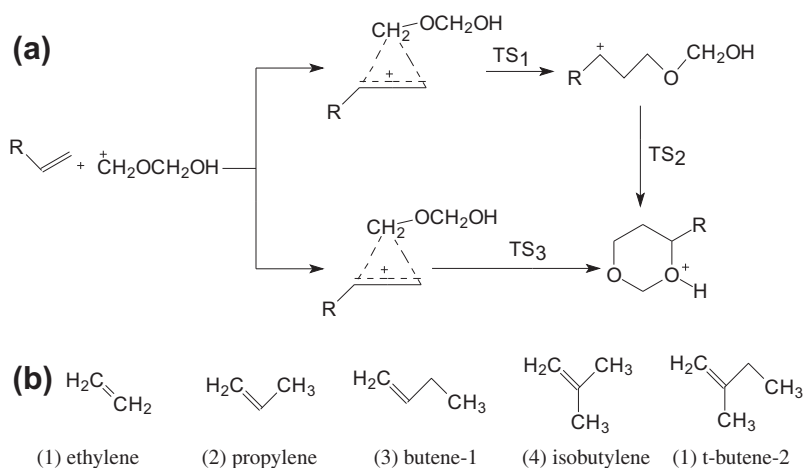


Fig. 2. (a) Possible schemes of dimer formaldehydes and alkenes addition; (b) list of examined alkenes.

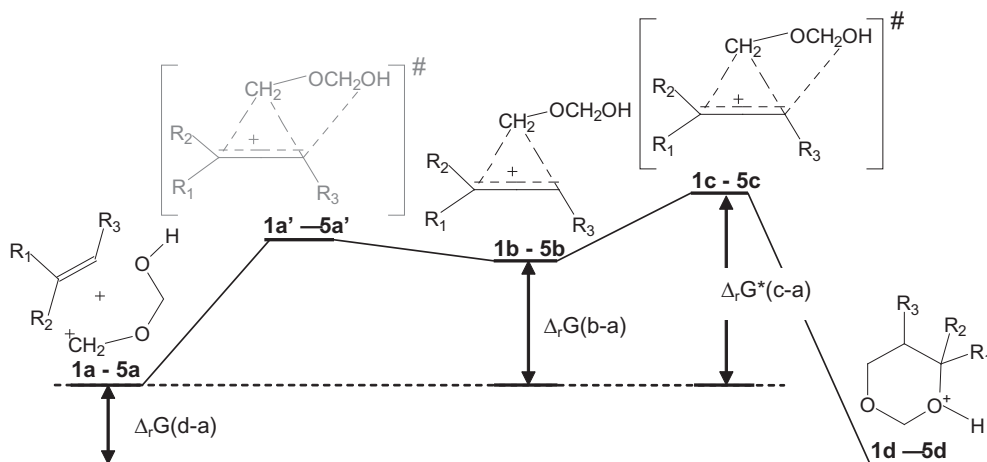


Fig. 3. Potential energy surface of the Prins reaction.

Download English Version:

<https://daneshyari.com/en/article/5394183>

Download Persian Version:

<https://daneshyari.com/article/5394183>

[Daneshyari.com](https://daneshyari.com)