Educator Insights: A Journal of Teaching Theory and Practice
Volume 2, Issue 4, April 2026
brightmindpublishing.com
ISSN (E): 3061-6964

MECHANISM OF THE DEHYDRATION PROCESS IN REACTIONS INVOLVING DIOLS AND FACTORS AFFECTING THE REACTIVITY OF HYDROXYL GROUPS

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Abstract
This article investigates dehydration reactions of organic compounds containing two hydroxyl groups in an acidic medium. Particular attention is given to the mechanism of water elimination and the factors determining which hydroxyl group participates in the reaction. It is shown that under the influence of sulfuric acid, protonation occurs at the hydroxyl group with higher reactivity, leading to the formation of a water molecule from that group. The effect of oxygen isotopes on the reaction pathway is also discussed, indicating that hydroxyl groups containing lighter isotopes may participate more readily in dehydration processes. The obtained results are important for understanding the mechanisms of organic synthesis reactions.

Keywords: Diols, dehydration, hydroxyl group, isotope effect, protonation, sulfuric acid.

Introduction

In organic chemistry, compounds containing a hydroxyl group constitute an important class, as they actively participate in many chemical reactions. In particular, compounds containing two or more hydroxyl groups—diols and polyhydroxyl compounds—play a special role in organic synthesis processes. The

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chemical properties of such compounds depend not only on the number of functional groups but also on their position within the molecule and their mutual interactions.

One of the important reactions involving diols is the dehydration reaction. During the dehydration process, a molecule of water is eliminated from the compound, resulting in the formation of new unsaturated compounds or rearranged products. This process is often carried out in the presence of strong mineral acids, including sulfuric acid. The reaction mechanism consists of several stages: first the protonation of the hydroxyl group occurs, followed by the departure of a water molecule and the formation of a carbocation.

In compounds containing two hydroxyl groups, one important question is which hydroxyl group actually loses water during the reaction. This process is not random but is determined by several physicochemical factors. In particular, the stability of the resulting carbocation, electronic effects, steric hindrance, and the acidity of the reaction medium play significant roles.

Modern studies have also shown that the isotopic composition may influence the dehydration process. In particular, when oxygen isotopes (^{16}O and ^{18}O) are present, changes in the reaction rate and mechanism may be observed. This phenomenon is explained by the kinetic isotope effect. Studies have shown that bonds containing lighter isotopes have a higher probability of participating in reactions.

The purpose of this work is to study the mechanism of the dehydration reaction in organic compounds containing two hydroxyl groups, analyze the factors that determine which hydroxyl group loses water, and scientifically substantiate the effect of isotopes on this process.

Main Part

In organic chemistry, compounds containing two hydroxyl groups—diols—represent an important class and often participate as intermediates in many reactions. The chemical properties of diols depend on their molecular structure, the position of the hydroxyl groups, and the reaction medium. In particular, dehydration reactions occurring in the presence of strong acids are among the most important reactions of diols.

A dehydration reaction is an elimination reaction that proceeds with the removal of a water molecule from a compound. It is typically carried out in the presence

Volume 2, Issue 4, April 2026
brightmindpublishing.com
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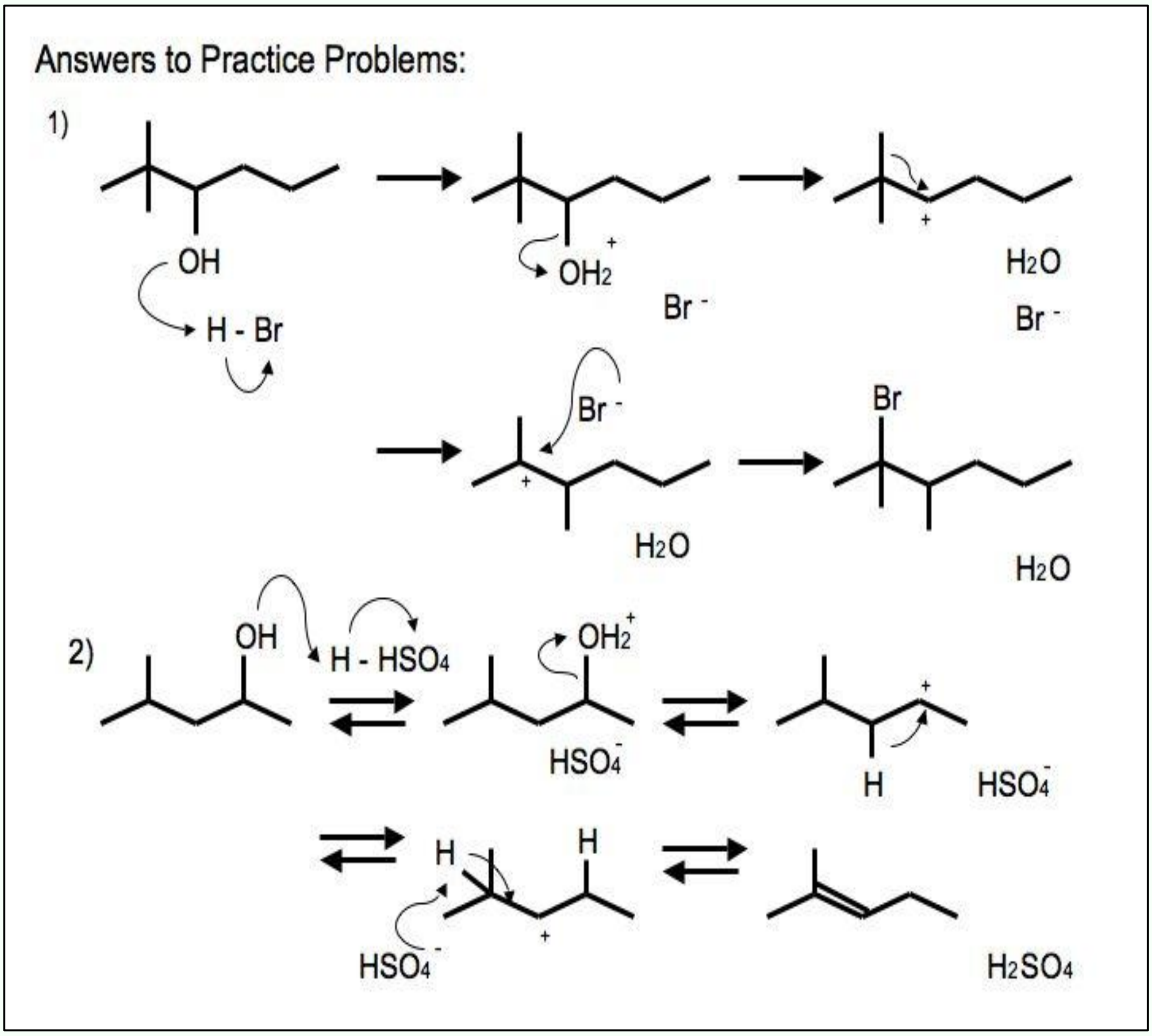
of strong mineral acids such as sulfuric acid (H_2SO_4) or phosphoric acid (H_3PO_4). In this reaction, the acid acts as a catalyst and increases the rate of the reaction. Since diols contain two hydroxyl groups, an important question arises: from which hydroxyl group does the water molecule depart during the reaction? In order to answer this question, it is necessary to examine the reaction mechanism. The dehydration reaction usually proceeds through three main stages:

Stage 1: Protonation

At the beginning of the reaction, the strong acid donates a proton to the oxygen atom of the hydroxyl group. As a result, the hydroxyl group becomes protonated and forms an oxonium ion:

$R–CH(OH)–CH_2OH + H_2SO_4 \rightarrow R–CH(OH)–CH_2OH_2^+ + HSO_4^–$



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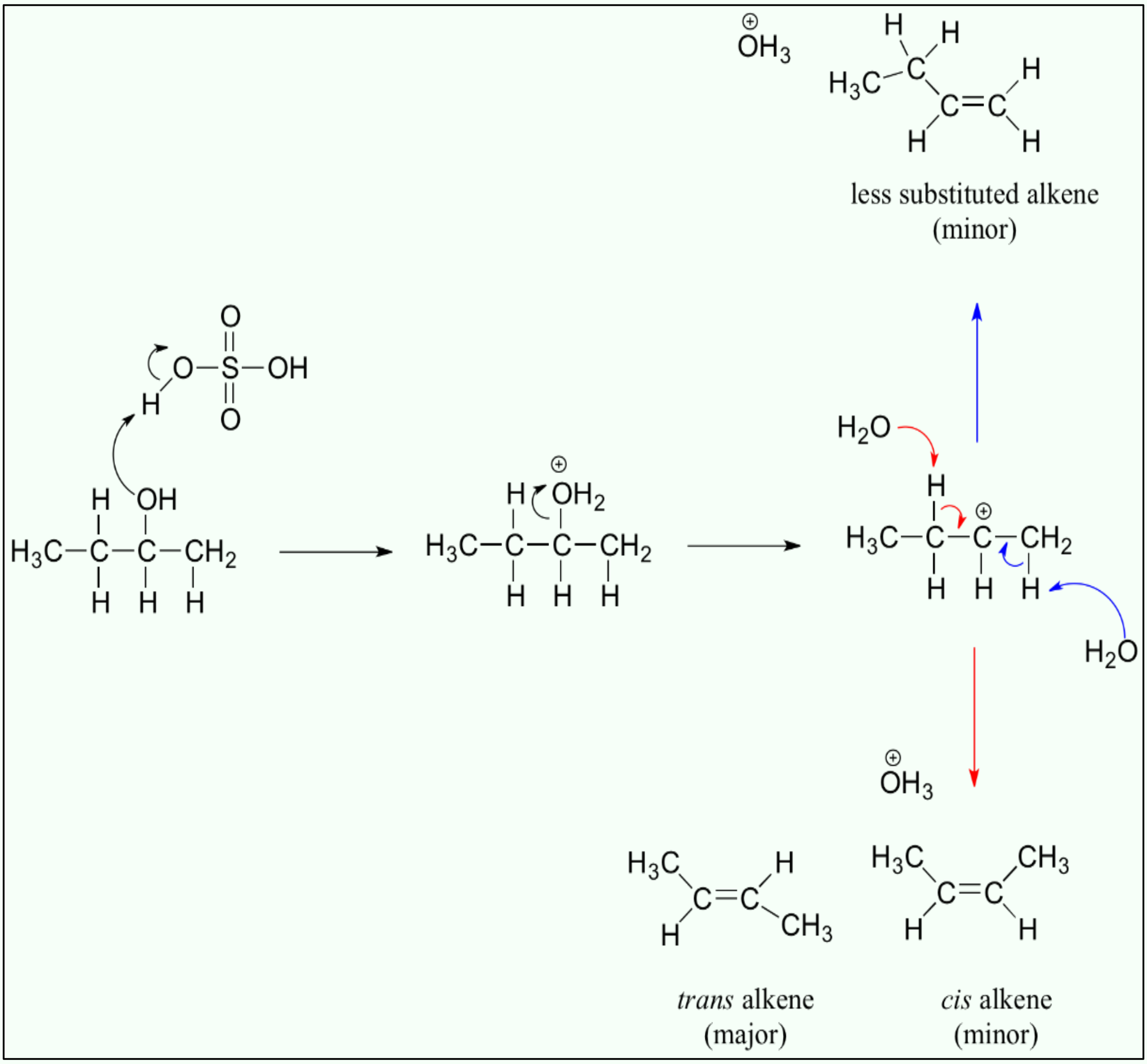

This stage is very important because the ordinary OH group is not a good leaving group. However, the protonated OH_2^+ group is considered a good leaving group. Therefore, the subsequent stage of the reaction becomes easier.
Protonation also does not occur randomly. Sulfuric acid usually attaches to the oxygen atom with higher electron density. If the molecule contains two OH groups, the proton typically attaches to the oxygen atom where the electron density is higher.

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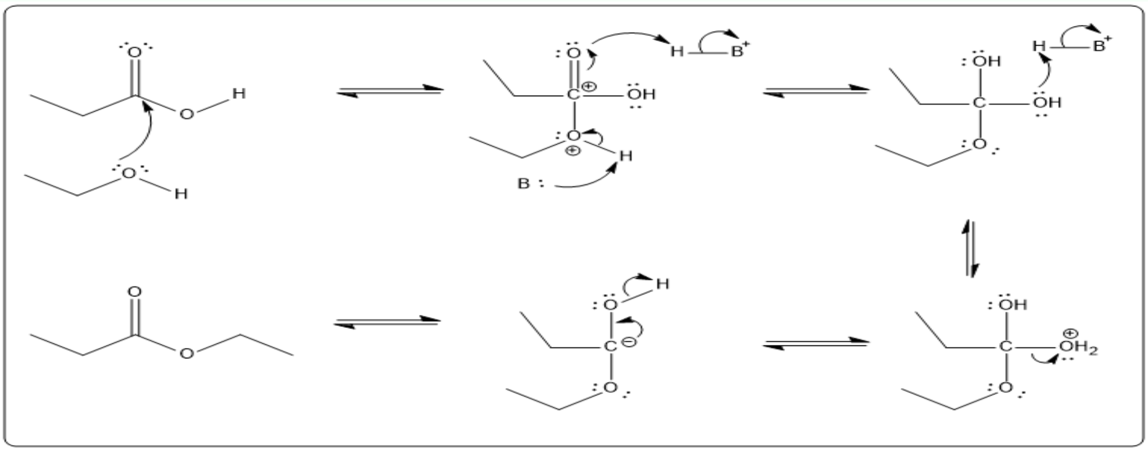
Stage 2: Water Elimination

In the next stage, a water molecule is eliminated from the protonated hydroxyl group:

$R–CH(OH)–CH_2OH_2^+ \rightarrow R–CH(OH)–CH_2^+ + H_2O$



As a result, a carbocation is formed. This stage is the most important stage of the reaction because it determines which hydroxyl group actually participates in the reaction.

There is a well-known rule in chemistry:

A reaction always proceeds in the direction that forms the most stable carbocation.

The stability of carbocations increases in the following order:

tertiary carbocation > secondary carbocation > primary carbocation

Therefore, if the elimination of water from one OH group leads to the formation of a secondary carbocation, while elimination from another OH group leads to the formation of a primary carbocation, the reaction proceeds in the direction that produces the secondary carbocation.

Stage 3: Elimination or Rearrangement

From the formed carbocation, a hydrogen atom may be eliminated, resulting in the formation of a double bond:

$R–CH^+–CH_3 \rightarrow R–CH=CH_2 + H^+$

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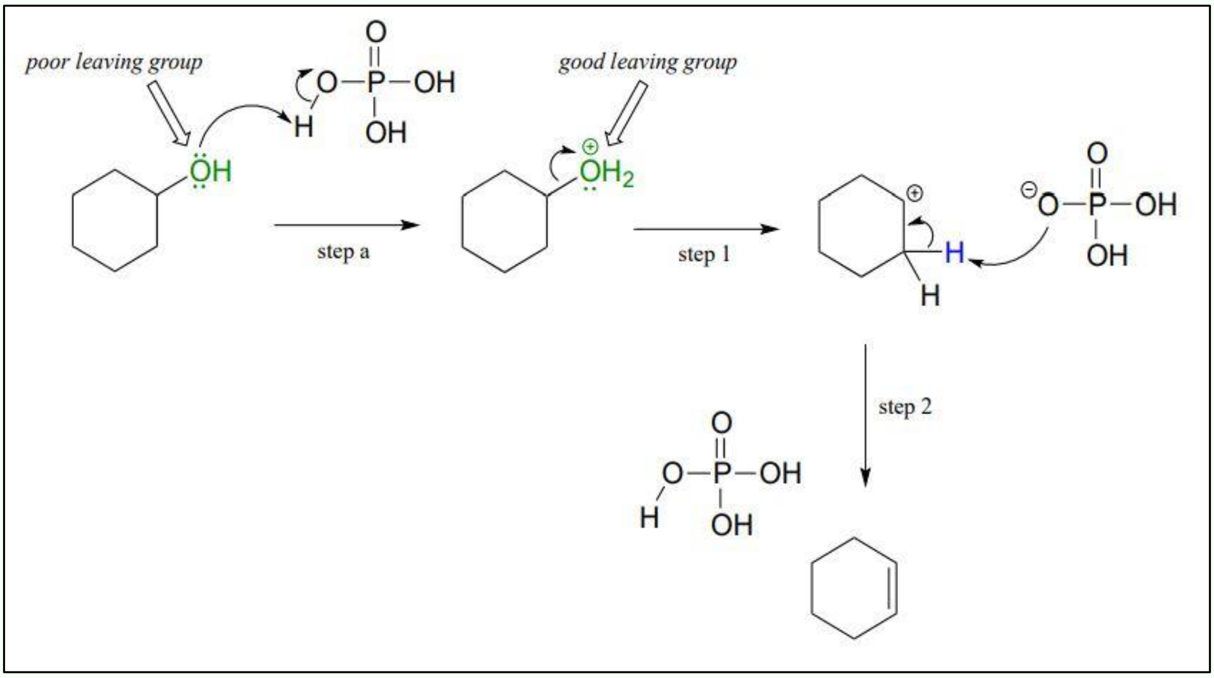


As a result, an alkene is formed and the acid is regenerated.

Effect of the isotope effect

In modern organic chemistry, isotope effects are widely used to explain reaction mechanisms. If the oxygen atoms in the hydroxyl groups of a diol molecule consist of different isotopes, for example:

^{16}O – light isotope

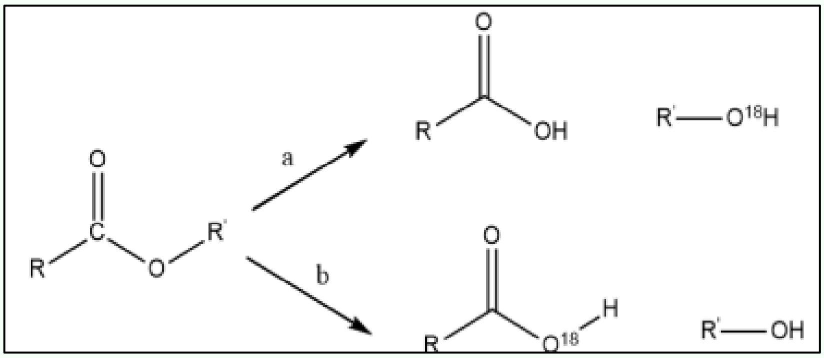
^{18}O – heavy isotope

then in the reaction, the bond containing the lighter isotope usually breaks faster. This occurs because bonds containing lighter isotopes:

have higher vibrational energy;

require less energy for bond cleavage;

lead to a higher reaction rate;



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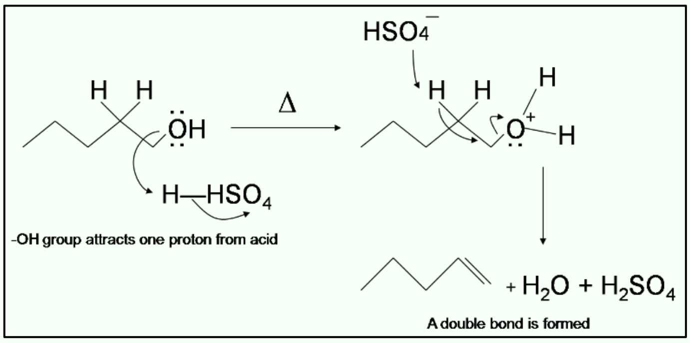
This phenomenon is called the **kinetic isotope** effect.

Scientific studies show that if one of the two OH groups contains ^{16}O and the other contains ^{18}O, the hydroxyl group containing ^{16}O usually reacts first and forms water.

Selective effect of sulfuric acid

Sulfuric acid is not only a proton donor but also a strong dehydrating agent. It has the ability to remove water from molecules.



Main effects of H_2SO_4

1. Protonation
2. Facilitation of water elimination
3. Acceleration of carbocation formation
4. Shifting the reaction equilibrium toward the products

When sulfuric acid protonates a particular OH group, water is usually eliminated from that hydroxyl group. This determines the regioselectivity of the reaction.

Main factors affecting the reaction direction. In the dehydration reactions of diols, the following factors play an important role:

Electronic effects: If an electron-donating group is located near the OH group (+I effect), the carbocation becomes more stable.

Steric effects: Bulky groups may hinder protonation.

Intramolecular hydrogen bonding: In some diols, internal hydrogen bonds influence the reaction.

Isotopic composition: Lighter isotopes can accelerate the reaction.

Temperature: Higher temperatures accelerate the dehydration process.

ISSN (E): 3061-6964

Conclusion

In this study, the dehydration reactions of organic compounds containing two hydroxyl groups in an acidic medium were theoretically analyzed. The investigation showed that the elimination of water in reactions involving diols is not a random process but is determined by several physicochemical factors.

It was found that in the first stage of the reaction, the hydroxyl group becomes protonated under the influence of sulfuric acid, forming a good leaving group—a water molecule. In the next stage, water is eliminated and a carbocation is formed. The direction of the reaction mainly depends on the stability of the carbocation formed.

The results also showed that if a molecule contains two hydroxyl groups, water is usually eliminated from the hydroxyl group that forms the most stable carbocation. This process can be explained by protonation selectivity and electronic effects.

Analysis of the isotope effect revealed that the hydroxyl group containing the lighter isotope may participate in the reaction more rapidly. This phenomenon is explained by the kinetic isotope effect and serves as an important scientific basis for understanding the elementary stages of the reaction.

The obtained results are important for a deeper understanding of the mechanism of dehydration reactions of diols, for controlling organic synthesis processes, and for explaining reaction selectivity. These findings may also serve as a theoretical basis for the synthesis of complex organic compounds in future studies.

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