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Research Article



STUDY THE IMINES EQUILIBRIUM REACTION THEORY AND THE ROLE OF VARIOUS SUBSTITUTES

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Abstract

Imines are a functional group or chemical compound with a carbon-nitrogen double bond. An amine can be processed through increasing nucleophilic substitution reaction of a ketone or aldehyde with ammonia or an amine leading to formation of a hemiaminal -C(OH)(NHR)-. This hemiaminal converts to an imine with losing water. The imines synthesis reaction is as an equilibrium reaction. The main problem in the synthesis of imine is the balance between the reactants and products. Given the importance of imines and their applications in the pharmaceutical and chemical industries, investigation the problem of equilibrium nature of imines reaction has been done by different factors. However, in this study, the effect of different substituents was examined. Therefore, the equilibrium reactions of imines synthesis were theoretically studied by Density Functional Theory (DFT) method using Gaussian software, to help forwarding the reaction and making it a one-way reaction, with examining the effect of various substituents. The results showed that the CF₃ electron-receiving substituent increases the speed of forward reaction and reduces the speed of backward reaction, while the electron donor substituents of CH₃ and C₂H₅ reduce the forward reaction rate and increase the speed of backward reaction.

Keywords: Imine, DFT, Gaussian, Balance Constant.

Introduction

The nitrogen analogs of ketones and aldehydes are called imines, azomethines, or Schiff bases, but imine is the preferred name and we use it here.[1] These compounds can be prepared by condensation of primary amines with ketones or aldehydes. The equilibrium constants are unfavorable, so the reaction is usually driven forward by removal of water. When secondary amines are heated with ketones or aldehydes in the presence of an acidic catalyst, a related reaction occurs, and the product is a substituted vinylamine or enamine.[2] There are other methods for preparing enamines from ketones that utilize strong chemical dehydrating reagents. For example, mixing carbonyl compounds and secondary amines followed by addition

of titanium tetrachloride rapidly gives enamines. This method is especially applicable to hindered amines.[3]. Triethoxysilane can also be used. Another procedure involves converting the secondary amine to its N-trimethylsilyl derivative. Owing to the higher affinity of silicon for oxygen than nitrogen, enamine formation is favored and takes place under mild conditions.[4]

Definition of Imine

Imine and other nitrogenous compounds are carbonyl compounds. In other words, the combination of nitrogen and carbon-nitrogen double bond of love that exists between them.[5][6].

Imine can be divided into two main categories:

- Imine having no substituent on the nitrogen and the nitrogen substituent.
- Imine that the nitrogen or carbon substituted with an aryl group is called a Schiff base

Imine's stability: Imine no substituent on the nitrogen unstable. Iman that all the alkyl substituent on the nitrogen and carbon and hydrogen, substituted aryl difficult than Iman have been prepared and are less stable.[7]

Ways to reduce their Imine: So far, a variety of methods are used to reduce Iman is that they can be classified as follows:

- The ways in which a metal is used.
- The ways in which transition metal complexes have been used.
- Methods using an organic compound as a reducing agent has been done.[8]

Physical Properties

UV and visible spectrum Imine gives us a lot of information. Raman spectra of Imine are known, Raman spectra of alkyl amines alkylidene specific absorption near 1670 that the double bond carbon -

nitrogen. Among the recent techniques such as infrared and microwave techniques for forming Imine can be mentioned, however, the main problem originates in the balance between synthesis Imine reactive substances and products. To overcome this problem of aromatic solvents are used at high temperatures, which is sensitive to moisture And also using different catalysts that have very high costs And reaction time increases. However, it cannot be synthesized some desired Imine.[9][10].

Materials and Methods

Gaussian03 and GaussianView software was used for the calculation. First of all molecules in a combined total of about 15 are designed using the software Gaussian parameter B3LYP DFT method for raising the theoretical level and Basis Set 6-11G energy efficiency and optimal ordering and Computation thermodynamic opt freq command is obtained.

Results

After optimization of all molecules entering the reaction and to obtain their energy, offering the following table.

Table (1) Reactions by energy optimization software with Gaussian

1	Aceton + Ammonia = Imine (propan-2-imine)
	Imine (propan-2-imine) = Aceton + Ammonia
2	Aceton + Methylamine = N-(propan-2-ylidene)methanamine
	N-(propan-2-ylidene)methanamine = Aceton + Methylamine
3	Aceton + Dimethylamine = N,2-dimethylprop-1-en-1-amine
	N,2-dimethylprop-1-en-1-amine = Aceton + Dimethylamine
4	Aceton + Ethanamine = N-(propan-2-ylidene)ethanamine
	N-(propan-2-ylidene)ethanamine + Ethanamine = Aceton + Ethanamine
5	Aceton + diethylamine = N,N-diethylprop-1-en-1-amine
	N,N-diethylprop-1-en-1-amine = Aceton + diethylamine
6	Aceton + trifluoromethanamine = trifluoro-N-(propan-2-ylidene)methanamine
	trifluoro-N-(propan-2-ylidene)methanamine = Aceton + trifluoromethanamine
7	Aceton + bis(trifluoromethyl)amine = N,N-bis(trifluoromethyl)prop-1-en-2-amine
	N,N-bis(trifluoromethyl)prop-1-en-2-amine = Aceton + bis(trifluoromethyl)amine

Table (2) to calculate the internal energy reversible and irreversible reactions and equilibrium constants

	rev G	irrev G	revK	irrevK
Reaction 1	154253.33	-154253.325	9.19878e-28	1.08 e-27
Reaction 2	1938.8995	-1938.8995375	0.4573	2.19
Reaction 3	5835.509	-5835.509	0.09489	10.54
Reaction 4	-5835.151696	5835.151696	10.97237229	0.091137994
Reaction 5	-5805.399204	5805.399204	10.41431004	0.08926446
Reaction 6	-5804.452838	5804.452838	10.83496446	0.092293796
Reaction 7	-5788.08785	5788.087852	10.34179654	0.096694998

Table (3) to calculate the Gibbs free energy reversible and irreversible reactions and equilibrium constants

	rev G	irrev G	revK	irrevK
Reaction 1	2660.912	-2660.912	0.341677343	2.926738
Reaction 2	1920.57145	-1920.572	0.46065655	0.7751829
Reaction 3	5827.4392343	- 5827.4392343	0.095194533	10.504805
Reaction 4	-5634.29553	5634.29553	10.103959	0.09897111
Reaction 5	-5628.568492	5628.568492	9.696919356	0.103125535
Reaction 6	-5583.768416	5583.768416	9.89654277	0.101045387
Reaction 7	-5635.162067	5635.162067	9.722760187	0.102851451

Conclusion and Discussion

As we know, the reaction equilibrium towards the formation of the reaction product is not going well and it is difficult purification. Imine without the nitrogen substituent in organic chemistry are unstable due to Non-bonding orbital electron of the nitrogen substituent on the Imine that all nitrogen and carbon and hydrogen, alkyl group, a substituted aryl difficult than Imine have made they are less stable. Friendship core game is almost proportional to the property. Derivatives of ammonia, like you nucleus and the electron lone pair of electrons in the reaction of their friends. "Friendship core" represents a stretch for a carbon atom in a Lewis base is an elimination reaction and "character acting" too much stretch for proton gives back. Like the nucleus have a negative charge, are usually more reactive than the neutral core of love. Thus substituted by electron-

lethal, friendship and more negative with increasing nuclear operator and the intermediate compound was rapidly increasing, and in the case of electron-donor substituent, the opposite is happening. In this research, the theory of the equilibrium reactions to synthesize various substituted Imine's role (CH₃, C₂H₅, CF₃) on Imine for further reaction and its one-sided deal. After careful review of the results of calculations performed and the reaction equilibrium constant, we came to the result that the reaction rate can be substituted with change, change. In response to electron donor substituent (C₂ H₅), the equilibrium constant was greater than the equilibrium constant of the reversible reaction resulting in the formation of the reaction product was greater, so is the substituted suitable for Imine.

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