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Kinetics Reaction and Mechanism of Thiozole with Sodium Methoxide in CSTR Reactor

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Abstract

Sulphur and nitrogen containing organic compounds are gaining importance in synthetic and pharmaceutical fields. Thiazoles are a heterocyclic organic compound is well known intermediates in thesynthesis of clinically important heterocycles such as 4-thiozolidinones and benzothiozoles. Thiazoles are found in medicaments like vitamin-B, sulphathiozoles, promizole, niridazole, aminotrizole and tetramisole. Therefore, and because of the importance of these compounds, the understanding and study of the mechanism and kinetic of their reactions are particularly important.

Keywords: Kinetics reaction; Thiozole; Sodium meth-oxide; CSTR reactor

Introduction

To Fairly Study the Reaction kinetics and mechanism of any chemical reaction, it is mainly to study the rate of the reaction through studying transitional reactions involved as step reactions in case of multistep reactions. Also performing energy profile and thermodynamics study to determine the reaction enthalpy whether it favors endothermic or exothermic reaction [1]. Through these studies of rates, kinetics, mechanism and reactions pathway investigations, greatly helps in chemical engineers in reactors design and provide clear way of a certain reaction behavior [1]. Within a certain type of reactor, the physical and chemical properties of both products and reactants have to be studied closely to be able to study the kinetics for the reactor in request [1]. Thiazoles are a heterocyclic organic compounds, it's used mainly as a fungicide, biocide and in dyes industries, Thiazoles possess the following formula (C_3H_3NS) they are characterized by a pale yellow color in their liquid state at room temperature [2]. Actually the Thiazole as an aromatic compound cant undergoes reaction with methoxide groups solely except for sever conditions which can't be obtained in CSTR reactors, and the obtained compounds is not for importance and contain many un identified complexes, on the other hand halides derivatives of thiazoles compounds can undergoes nuncleophillic aromatic substitution upon reacting with MeOH group [3]. Through this paper, the reaction kinetics and mechanism of Cholronitrothiazole, mononitrothiazole and Dichlorothiazole with Sodium meth-oxide as will be discussed as shown by Metzger [2], The following figures shows the structural formula of these compounds (Figure 1). Reaction of 2-Chloro-5nitorthiazole with sodium meth-oxide yields the production of 2-methoxy-5-nitrothiazole, the reaction is carried in an equi-molar ratio of both meth-oxide salt and 2-Chloro-5nitorthiazole to avoid low yield product of 2-methoxy-5-nitrothiazole [2]. In case of using excess amount of sodium meth-oxide reaction's yield goes down to about 30% with amounts of un-identified complexes on the other hand using an equi-molar of both reactants the reaction's yield is about 90% [3].

Substituted Atom Position

The position of halogens atom in the penta rings of thiazoles molecule affects the reaction yield products and the leaving group from the thiazole ring [2]. For example, In case of 2-nitro-5-chlorothiazole when reacted with sodium meth-oxide the leaving group is the halogen atom as shown in Figure 2 below. On the other hand, when of 2-Chloro-5-nitorthiazole reacts with the Sodium meth-oxide the methoxy group will replace nitro Group (good leaving group) as shown in Figure 3. In case of 2, 5- dichlorothiazole reaction with sodium methoxide the halogen atom will be replaced on position 5 as (leaving group) as shown in Figure 4. It's clear that the attack of the methoxide group is always targeted towards the position no.5 Carbon bond giving the corresponding methoxy-thiazole this reaction is known as ring-addition reaction which shows very slow rate of processing and could be enhanced by adding DMSO (Dimethyl Sulfoxide) solvent for faster rate of reaction [2].

Kinetics and Mechanism Study

Monohalogenothiazol with sodium meth-oxide reaction mechanism

The bond between the halogen atom and the carbon atom in the thiazole ring shows different degrees of reactivates. According to the bond location (2, 4, 5) and the reagent used, the 2-chlorothiazoles shows normal substitution reaction with the nucleophilic groups as CH_3O- in sodium-methoxide reagent to give the normal subistituted product, the mechanism of such reaction could be explained by the following reaction shown in Figure 5 [2]. The high reactivity of 4-halogenothiazoles with sodium-methoxide related to the aromaticity for thiazole and the presence of π-bond in the ring of thiazole compounds. As a matter of fact it was found that the halegeno-thiazole compounds can also show reactivity towards positions (2, 5) also under certain reaction conditions. The reactivity to position with sodium-methoxide in methanol solution takes the following sequence: 5-chlorothiazole >2-chlorothiazole >4chlorothiazole. The following table (Table 1) shows the Relation between Halogen atom location and type in thiazol ring and the Rate Constant with Sodium Methoxide [2].

Cholorothiazol with sodium methoxide reaction rate study for CSTR

The Reaction Rate studies for all halegens, nitro halegens and nitro thiazoles were all carried out at 50 °C degrees and normal atmospheric

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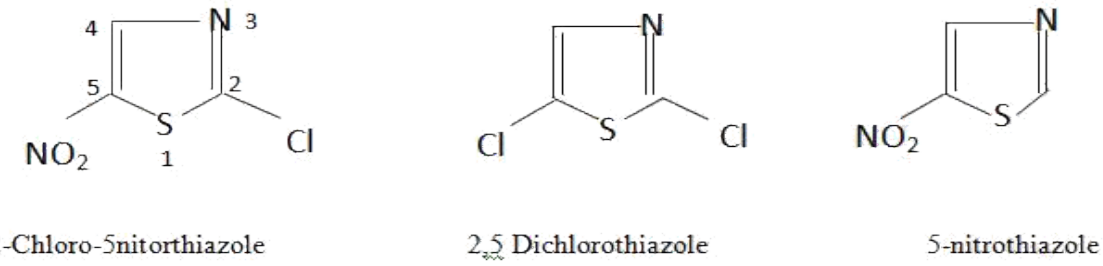

Figure 1: Reaction of 2-Chloro-5nitorthiazole.

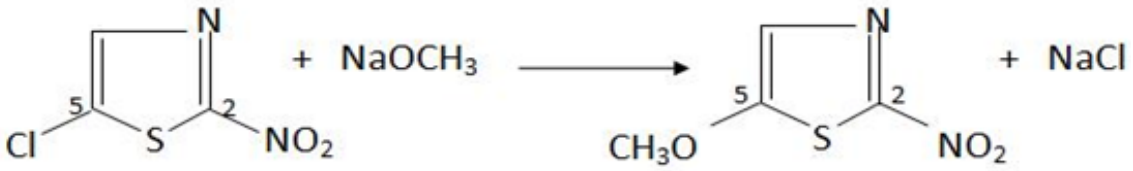

Figure 2: Reaction of 2-nitro-5-chlorothiazole.

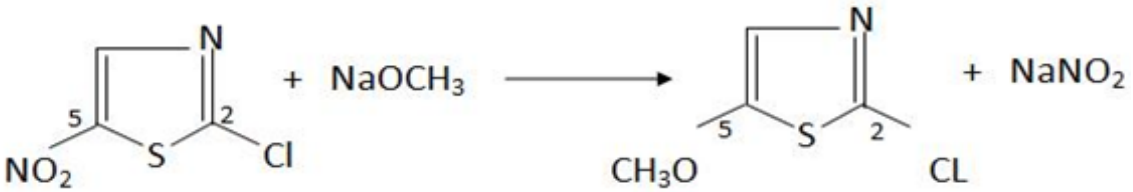

Figure 3: 2-Chloro-5-nitorthiazole reaction with Sodium meth-oxide.

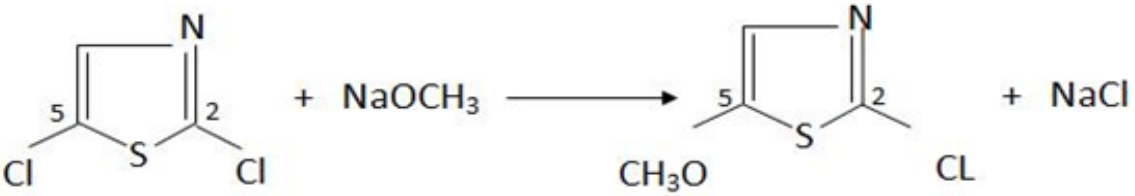

Figure 4: 2,5- dichlorothiazole reaction with sodium methoxide.

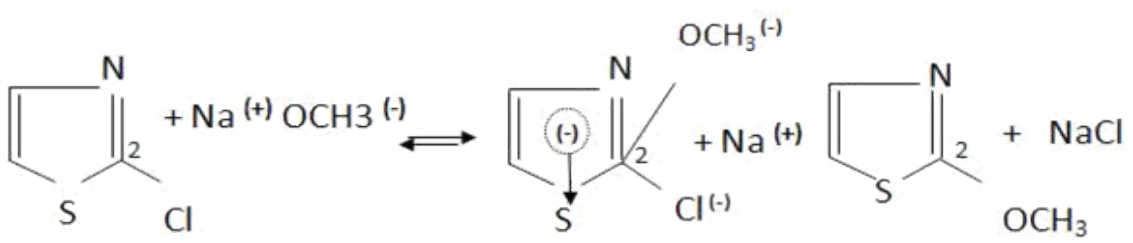

Figure 5: 2-chlorothiazoles shows normal substitution reaction with the nucleophilic groups.

pressure to obtain the maximum yield out of the reaction, so the CSTR reactor will be equipped with steam jacket to provide constant temp of 50 °C the following figure shows the steam jacketed CSTR Figure 6 [2].

Reaction conditions: The reaction carried on at atmospheric pressure with temperature of 50 °C in a MeOH (methanol) solution [2].

Reaction rate: Almost all thiazole reactions shows 2nd order reaction, and hence, the reaction rate for the reaction of 2-Cholorothiazol with Sodium Meth-oxide can be calculated as follow [2]:

$Cl\text{-}C_3H_2NS + NaOCH_3 \rightarrow OCH_3\text{-}C_3H_2NS + NaCl$

For second order:

Reaction Rate (R)=$K[Cl\text{-}C_3H_2NS] \times [NaOCH_3]$

$[Cl\text{-}C_3H_2NS]$=concentration of 2- chlorothiazole in mol L^{-1}=3 $[NaOCH_3]$=concentration of sodium methoxide in mol L^{-1}=5.4

Note that Sodium Methoxide concentration chosen based on the most abundant commercial concentration in the market.

Calculation Of rate constant [K] K=Ae-Ea/RT

lnK=LnA - Ea/RT R=8.31 J $K^{-1}mol^{-1}$

E=30672 J mol^{-1}

T-50 C=323 K

Ref. [4] found out experimentally the following Values Pre Exponential Factor A=0.002236

By substituting in the previous equation K=8.1 × 10^{-6} L $mole^{-1}$ sec^{-1}

Therefore Reaction Rate (R)=1.3122 × 10^{-6} mol L^{-1} s^{-1}

Reaction Yield: The reaction yield for these reactions was measured experimentally and found to be is 80% [5].

Mononitrothiazol reaction mechanism

The 2-nitrothiazole reacts sodium meth-oxide, leading to the normal substitution product, 2-methoxythiazole, the reaction shows high rate of reaction and high yield products. The 5-nitrothiazole reacts with excess sodium meth-oxide in dimethylsulfoxide molar solution decomposes rapidly showing ring-opening reaction [3]. All electrophilic substitution reactions in monoitrothiazoles are inhibited due to presence of the nitro group attached in either 4, 5 positions, Except for the 2-nitrothiazolereaction yields normal substitution reaction easily and with high rates Figure 7 [2].

Other basic reactions: The aminothiazole could be obtained through catalytic chemical reduction of the 5-nitrothiazole, the 5-nitrothiazole, it could be also reduced to 5-aminothiazole but with low purity.

Figure 6: Steam jacketed CSTR.

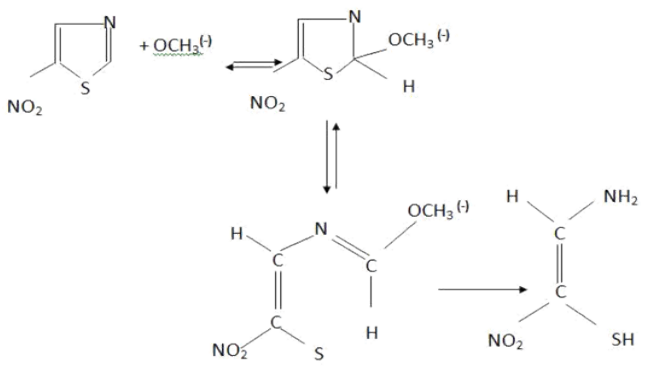

Figure 7: 5-nitrothiazole reacts with excess sodium meth-oxide.

Reaction conditions: To avoid the rapid decomposition and ring-opening reaction in DMSO The reaction is to be carried out at atmospheric pressure with temperature of 50°C in a MeOH (methanol) solution [2].

Reaction order: Almost all thiazole reactions shows 2nd order reaction, and hence, the reaction rate for the reaction of 2-Cholorothiazol with Sodium Methoxide can be calculated as follow main Reaction [2]:

NO_2-C_3H_2NS+$NaOCH_3$ → OCH_3-C_3H_2NS+$NaNO_2$

For Second order=2

=5.4

Reaction Rate (R)=K[NO_2-C_3H_2NS] × [$NaOCH_3$] [NO_2-C_3H_2NS] : concentration of 2-nitrothiazole in mol L^{-1} [$NaOCH_3$]=concentration of sodium methoxide in mol L^{-1}.

-Note that NaMeOH concentration is chosen according to most abundant commercial concentration in the market.

Calculation Of rate constant [K]:

K=Ae-Ea/RT

lnK=LnA - Ea/RT R=8.31 J $K^{-1}mol^{-1}$

E=2500 J mol^{-1}

T-50 C=323 K

Ref. [4] found out experimentally the following Values

Pre Exponential Factor A=0.002236

By subistuting in the previous equation

K=3.224 × 10^{-6} L $mole^{-1}$ sec^{-1}

Therefore, Reaction Rate (R)=1 × 10^{-6} mol L^{-1} s^{-1}

Note that the reaction for both of and shows almost near values of rate of reactions

Halgen nitrothiazole reaction mechanism

The 2-Halogeno 5-nitrothimoles can also undergoes nucleophilic substitution reactions on 2-halogeno-5-methoxythiazoles, these compounds are mainly used as biocides for due to their biological activity [3]. According to the previously shown reaction mechanism of mono halegeno thiazole and mono nitro thiazoles nucleophilic during substitution reaction, also the 2-halogeno 5-nitrothimoles easily converted to 2-halogeno-5-methoxythiazoles. Taking into account that in case of using excess amount of sodium methoxide reagent the reaction yield is too low and many side reactions takes place, while using equi-molar leads to high quantity of product yields that reaches 80% [5].

2-Chloro-5-nitorthiazole reaction rate Study for CSTR

Reaction conditions: The reaction carried on at atmospheric pressure with temperature of 50 °C in a MeOH (methanol) solution [2]. Almost all thiazole reactions shows 2nd order reaction, and hence, the reaction rate for the reaction of 2-Cholorothiazol with Sodium Methoxide can be calculated as follow Main Reaction [2]:

Cl-C_3H-NO_2-NS+$NaOCH_3$ → OCH_3-C_3H-Cl-NS+$NaNO_2$

For Second order Reaction rate:

(R)=K × [Cl-C_3H-NO_2-NS] × [$NaOCH_3$] [Cl-C_3H-NO_2-NS]=concentration of 2-Chloro-5-nitorthiazole in mol L^{-1}

[$NaOCH_3$]=concentration of sodium methoxide in mol L^{-1}=5.4

Note that sodium methoxide concentration chosen according to most abundant commercial concentration in the market.

Calculation Of rate constant [K]

K=Ae-Ea/RT

lnK=LnA - Ea/RT R=8.31 J $K^{-1}mol^{-1}$

E=5324 J mol^{-1}

T-50 C=323 K

[4] Found out experimentally the following Value

Pre Exponential Factor A=0.01

By subistuting in the previous equation

K=9 × 10^{-6} L $mole^{-1}$ sec^{-1}

Therefore Reaction Rate (R)=11.2 ×10^{-6} mol L^{-1} s^{-1}

Polyhalegenothiazole reaction mechanism

The two atoms in case of 2-halogenothiazoles could be replaced by the nucleophilic group, for the position 2 it was found that it was more reactive than 4 or 5 positions this could be due to the aza active bond located on the carbon atoms which shows more reactivity toward nucleophilic groups [2]. Thiophenol and 2-halogenothiazoles have opposing reaction scheme on the contrary to the nucleophilic groups in this case the activator groups in thiazole ring are the halogen leaving groups while the electron donors group was found to be the phenol groups, that's why in this type of reactions the rate is very slow even if the solution used is DMSO which shows high rate rate reaction I nucleophilic subistution reactions.

Polynitrothiazole reaction mechanisms

The reaction of with 2,5-nirothiazole is found to give very low yield of methoxythiazole, even in case of using an equi-molar solution of sodium meth-oxide reagent the reaction is very slow and almost no occurrence of products While in case of using excess of sodium, meth oxide solution the reaction occurs with low yield of methoxythiazole accompanied by many inter-stage un identified cyclic compounds as shown in the following Figure 8 [2].

Results and Discussion

In this study, the reaction kinetics and mechanism of Cholronitrothiazole, mononitrothiazole and Dichlorothiazole with Sodium meth-oxide were discussed. Kinetic measurements were carried out at constant concentrations of reactants and temperatures, the stoichiometric study indicates that using equi-molar of reactants leads to high quantity of product yields that reaches 80%). Almost all thiazole reactions shows 2nd order reaction. The rates of reaction were measured and the results are summarized in Table 1.

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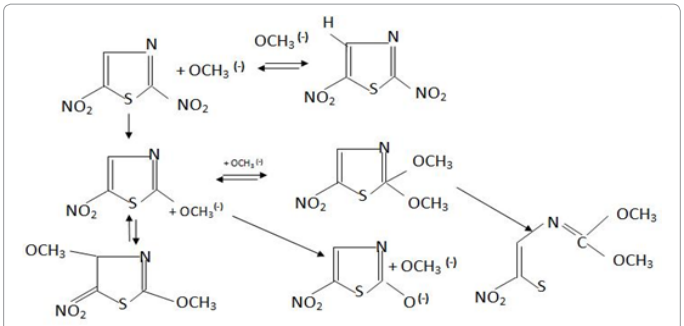

Figure 8: Polynitrothiazole Reaction Mechanisms.

Halogen atom Type and Position in Thiazole Ring	Rate Constant (k) $Sec^{-1}M^{-1}$ × 10^{-6}
2-Cl	0.81
4-Cl	0.05994
5-Cl	1.863
2-Br	1.053
4-Br	0.1296
5-Br	2.268

Note: Rate constant detected @50°C.

Table 1: Relation between Halogen atom location and type in thiazol ring and the Rate Constant with Sodium Methoxide [2].

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