

# Selective double bond isomerization of allyl phenyl ethers catalyzed by ruthenium metal complexes

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Received 16 July 2005; received in revised form 19 September 2005; accepted 5 October 2005

Available online 9 November 2005

## Abstract

The  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  complex catalysts were studied for the double bond isomerization of methyl chavicol and eugenol in the polar aprotic (DMSO, acetonitrile), polar protic (ethanol, methanol, *n*-propanol, iso-propanol, *n*-butanol, iso-butanol, *n*-hexanol) and non-polar (benzene, toluene, *n*-hexane, cyclohexane, tetrahydrofuran) solvents. The highest conversion of methyl chavicol (99.7%) with 95.4% selectivity of *trans*-anethole was observed in ethanol using  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyst. However, 94.2% conversion of methyl chavicol with 98.6% selectivity of *trans*-isomer was observed using methanol as a solvent in  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$ . The kinetics of isomerization of methyl chavicol and eugenol using  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  catalysts in ethanol or methanol involving the effect of substrate concentrations, catalyst amount, solvents and temperature on the initial rate of reaction was studied in details. The initial rates of reaction were observed to increase on increasing the initial concentrations of methyl chavicol, eugenol and catalysts. However, the initial rate of reaction decreased on increasing the solvent concentration. Activation energies for the isomerization of methyl chavicol were calculated using  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  catalysts and were found to be 4.3 and 6.0 kJ/mol, respectively. Activation energy for the isomerization of eugenol was found to be 6.9 kJ/mol using  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalyst. The  $\text{RuCl}_2(\text{PPh}_3)_3$  complex was recycled five times for the isomerization of methyl chavicol and eugenol. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Methyl chavicol; *trans*-Anethole; Eugenol; Isomerization; Kinetics; Ruthenium

## 1. Introduction

The allyl phenyl ethers have unique importance in the perfumery, fragrance and food industries and among the allyl phenyl ethers, the *trans*-anethole and isoeugenol have high industrial demand as intermediates for the synthesis of various perfumery chemicals [1–3]. Besides, *trans*-anethole also finds application in alcoholic beverage industry, food industry and in the formulation of oral sanitation products. It is one of the precursors for the synthesis of anisic aldehyde, synthetic intermediate for fragrance and flavor industries. The total annual global production of *trans*-anethole is approximately 0.75 million metric tonnes. *trans*-Isoeugenol which is also known as 2-methoxy-4-(1-propenyl) phenol, is widely used in manufacture of perfumeries, stabilizers and antioxidants for plastic and rubber industries. It is also used in antiseptic and analgesic medicines, as well as for the production of vanillin.

Generally, most of the *trans*-anethole is extracted from the natural sources like anise oil (80–90%), star anise oil (>90%), anise seeds and fennel oil (80%). The demand of *trans*-anethole in the world market increased rapidly during last few years due to its growing applications in various products. The production of *trans*-anethole from the natural sources was not sufficient enough to fulfill the increased demand, therefore, other alternative routes starting from anisole [4] and methyl chavicol [5] have been developed. The synthesis of *trans*-anethole from anisole is not favorable from industrial viewpoint due to multi-step involvement. Therefore, the single step preparation of anethole (mixture of *trans*- and *cis*-isomers) from methyl chavicol via double bond isomerization has drawn a special attention from both industrial and academic perspectives [6–12]. Presently, *trans*-anethole is commercially produced by double bond isomerization of methyl chavicol using liquid bases like KOH and/or NaOH in stoichiometric amounts at 473 K reaction temperature. Under these conditions 56% conversion is achieved in 12h reaction time with a *trans*:*cis* (anethole) ratio of 82:18 in the product mixture.

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Additionally, the anethole obtained from certain natural sources and synthesized from methyl chavicol is always accompanied with the *trans*- and *cis*-isomers (mostly *cis*-isomer >15%). Thermodynamically, *trans*-isomer is more stable as compared to *cis* and commercially *trans*-isomer is an important valuable product for various applications. According to food regulatory instructions, more than 1% *cis*-isomer cannot be tolerated due to its toxicity and sharp, unpleasant taste. On the other hand, present commercial process using liquid base like KOH or NaOH produce *trans* to *cis* ratio of anethole is 82:18. Therefore, isomerization process is required in which either *cis*-isomer is converted into *trans*-isomer in the same reaction conditions, or to develop a suitable catalyst that can restrain the formation of *cis*-isomer to minimum quantitative amounts in order that a fractional distillation may be effective to separate the remaining *cis*-isomers from product mixture [8].

Interestingly, isoeugenol at the commercial level is also being produced by the prolonged heating of the eugenol with the stoichiometric amount of liquid base like KOH in the presence of alcohol, mostly higher alcohols, at higher temperature [13–15].

Thus, the existing commercial processes for the synthesis of *trans*-anethole from methyl chavicol and *trans*-isoeugenol from eugenol via double isomerization reaction possess demerits like use of strong liquid base in large amount, longer reaction time, lower conversion of reactant, lower selectivity of *trans*-isomer, higher reaction temperature, post synthesis work-up in separation of spent KOH from reactants/products mixture, hazardous post reaction effluent disposal problems and separation of *cis*-isomer from the products mixture. However, recently we have successfully demonstrated the applicability of solid base catalysts [11] like basic alumina, exchanged zeolites and hydro-talcites, which overcome some of these drawbacks. In another study, the applicability of transition metal complexes as catalysts was also shown for the isomerization of methyl chavicol to *trans*-anethole [16,17].

In this present study, we are reporting selective double bond isomerization of methyl chavicol to *trans*-anethole and eugenol to *trans*-isoeugenol using  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  as catalysts. The detailed kinetic study comprises the effect of concentration of reactants, catalysts, solvents and reaction temperature on the rate of reaction. The effect of various solvents, reusability of the catalyst has also been studied.

## 2. Experimental

### 2.1. Materials

*trans*-Anethole (99.8%), methyl chavicol (98%), eugenol (98%), *trans*-isoeugenol (99.7%) and tetradecane (98%) were procured from Lancaster, UK and used without further purification. All the solvents (analytical grade) were purchased from Ranbaxy Fine Chemicals Limited, India. Ruthenium trichloride ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ), triphenylphosphine ( $\text{PPh}_3$ ) and triphenylarsine ( $\text{AsPh}_3$ ), were procured from E. Merck, USA.

### 2.2. Synthesis and characterization of metal complexes

The metal complexes,  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  were synthesized using reported methods [18].

#### 2.2.1. Synthesis of $\text{RuCl}_2(\text{PPh}_3)_3$

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (0.2 g) was dissolved in methanol (50 ml) and six-fold excess (1.2 g) of  $\text{PPh}_3$  was added. The solution was refluxed for 4 h under  $\text{N}_2$  (or Ar) atmosphere. The resulting reddish brown crystals of the complex were washed with methanol followed by diethyl ether and dried in vacuum (yield 75%).

#### 2.2.2. Synthesis of $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (0.2 g) was dissolved in methanol (50 ml) and six-fold excess (1.2 g) of  $\text{AsPh}_3$  was added. The solution was refluxed for 2 h under  $\text{N}_2$  (or Ar) atmosphere. The resulting green crystals of the complex were washed with methanol followed by diethyl ether and dried in vacuum (yield 70%).

All the metal complexes were characterized by Bruker Avance DPX 200 MHz FT-NMR ( $^1\text{H}$ ,  $^{31}\text{P}$ ) spectroscopy and Perkin-Elmer Spectrum GX FT-IR spectroscopy. The  $^{31}\text{P}$  NMR spectrum of  $\text{RuCl}_2(\text{PPh}_3)_3$  (in  $\text{CD}_2\text{Cl}_2$ ) gave a singlet at 41.42 ppm which confirms the formation of the complex. The appearance of  $\nu(\text{Ru}-\text{P})$  and  $\nu(\text{Ru}-\text{As})$  bands at 517 and  $474 \text{ cm}^{-1}$ , respectively, confirmed the formation of corresponding ruthenium complexes. C, H, N elemental analysis was done using Perkin-Elmer CHNS/O 2400 analyzer. Metal Complexes; C, H calculated (found):  $\text{RuCl}_2(\text{PPh}_3)_3$ : C 67.7 (67.5); H 4.7 (4.5) and  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$ : C 52.2 (52.1); H 4.0 (4.1).

### 2.3. Isomerization reaction and products analysis

Typically, isomerization reaction was carried out in a 50 ml oven dried double necked round bottom flask in which pre-calculated amount of metal complex catalyst, solvent and tetradecane as an internal standard were taken. One neck of the flask was fitted with refluxing condenser and another neck of the flask was blocked with silicon rubber septa. The entire experimental set-up was kept in an oil bath equipped with temperature controlling unit. After attaining the reflux temperature (358 K) of the mixture, the reactants were fed into the flask with the help of a glass syringe via silicon rubber septa. After the set reaction time, the reaction mixture was cooled to room temperature and filtered. For the kinetic studies, the samples (0.01 ml) were taken out during the experiment by glass syringe at different time intervals. The analysis of these samples were carried out using gas chromatography (Shimadzu 17A, Japan), having 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and flame ionization detector (FID). The initial column temperature was increased from 373 to 433 K at the rate of 5 K/min using nitrogen as a carrier gas. The temperature of injection port and FID were kept 513 and 573 K, respectively, during product analysis. The retention times for different compounds were determined by injecting pure compounds under identical gas chromatography conditions. The reaction mixture of isomerization of methyl chavicol and eugenol was further characterized by FT-NMR.

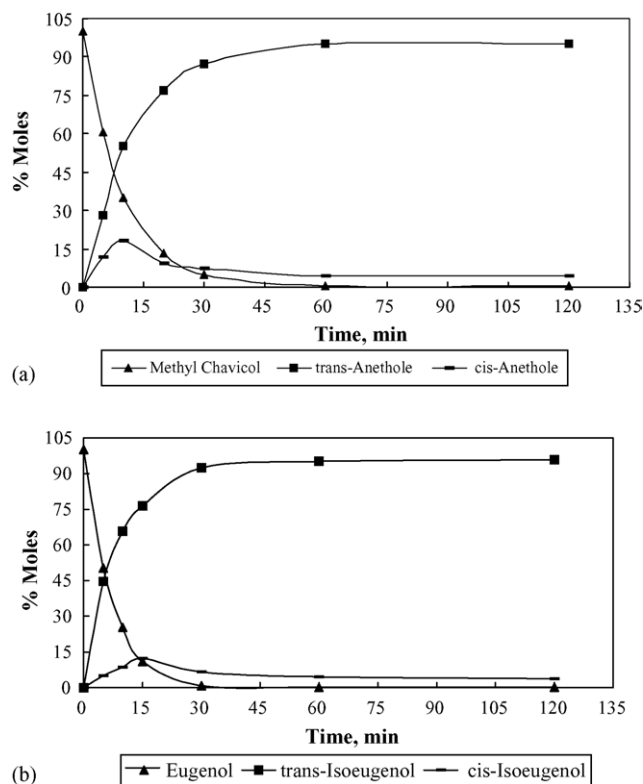


Fig. 1. (a) Concentration profile of methyl chavicol isomerization and products. Reaction conditions: [methyl chavicol]=6.75 mmol,  $[\text{RuCl}_2(\text{PPh}_3)_3]=5.2 \times 10^{-3}$  mmol, [solvent] (ethanol)=65.22 mmol, reaction time=2 h, 358 K. (b) Concentration profile of eugenol isomerization and products. Reaction conditions: [eugenol]=6.75 mmol,  $[\text{RuCl}_2(\text{PPh}_3)_3]=5.2 \times 10^{-3}$  mmol, [solvent] (ethanol)=65.22 mmol, reaction time=2 h, at 358 K.

#### 2.4. Kinetic analysis and reproducibility

The parameters, which might have pronounced effect on the rate of isomerization reaction include, concentration of reac-

tants, catalysts, solvents and the reaction temperature. Therefore, the kinetic experiments were carried out by varying these parameters. In each case, the changes in concentration of reactant were determined by gas chromatography at fixed time intervals. The initial rate of reaction was calculated by plotting the concentration of reactant in the range of initial period wherein the concentration of the reactant did not change significantly (<10%) with time, which gave a polynomial fit and the analysis was carried out by differential method. Under the kinetics experimental conditions, *trans*- and *cis*-isomers were only the major products formed during all the isomerization reaction.

To ensure the reproducibility of isomerization of methyl chavicol and eugenol using metal complex catalysts in the solvent, repeated experiments were carried out under identical reaction conditions. The results obtained, including conversions and selectivities were found to be within less than 1% variation, confirming the reproducibility of the results. In order to check the material balance of the reaction, the moles of products formed and moles of reactant consumed were compared. A typical concentration profile of reactant consumption and products formation are shown in Fig. 1a (for methyl chavicol isomerization) and Fig. 1b (for eugenol isomerization).

### 3. Results and discussion

#### 3.1. Solvent effect

The nature of the solvent used has potential influence in the isomerization reaction of the methyl chavicol and eugenol, as seen from the conversion and selectivity data given in Tables 1 and 2. The conversion of methyl chavicol was observed 4.7 and 8.2% (Table 1; Runs 1 and 12) in highly polar aprotic solvents, such as DMSO and acetonitrile, respectively, using  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyst. Whereas in case of  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  catalyst the conversion of methyl chavicol was observed 2 and 6% using DMSO and acetonitrile,

Table 1  
Effect of solvents on the isomerization of methyl chavicol

Run	Solvents	$\text{RuCl}_2(\text{PPh}_3)_3$ catalyst		$\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$ catalyst*		Refluxing temperature (K)
		Conversion of methyl chavicol (%)	Selectivity of <i>trans</i> -anethole (%)	Conversion of methyl chavicol (%)	Selectivity of <i>trans</i> -anethole (%)	
1	DMSO	4.7	80.9	2.0	82.0	470
2	Chloroform	58.5	60.4	72.5	93.4	338
3	Benzene	63.0	82.4	58.2	92.3	357
4	Toluene	82.8	77.4	90.6	93.0	388
5	Cyclohexane	87.4	77.8	34.3	92.2	359
6	<i>n</i> -Butanol	98.8	94.2	92.6	96.2	395
7	<i>n</i> -Hexane	67.7	86.7	20.6	93.7	345
8	Ethanol	99.7	95.4	93.8	97.2	358
9	Methanol	86.7	94.0	94.2	98.6	358
10	iso-Propanol	99.6	94.3	92.1	96.5	358
11	iso-Butanol	99.2	94.0	93.0	95.8	385
12	Acetonitrile	8.2	84.6	6	90	358
13	Tetrahydrofuran	69.5	88.7	66.4	95.4	343
14	Dichloromethane	61.7	86.2	52.7	93.4	321

Reaction conditions: [methyl chavicol]=6.75 mmol, [solvent]=65.22 mmol, [solvent\*]=93.75 mmol, [catalyst]= $5.2 \times 10^{-3}$  mmol, [catalyst\*]= $5.88 \times 10^{-3}$  mmol, reaction time=3 h at refluxing temperature.

Table 2  
Effect of solvents on the isomerization of eugenol

Run	Solvents	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub> catalyst		RuCl <sub>3</sub> (AsPh <sub>3</sub> ) <sub>2</sub> -CH <sub>3</sub> OH catalyst*		Refluxing temperature (K)
		Conversion of eugenol (%)	Selectivity of <i>trans</i> -isoeugenol (%)	Conversion of eugenol (%)	Selectivity of <i>trans</i> -isoeugenol (%)	
1	DMSO	5	76	2	90	470
2	Benzene	74.2	71.6	7	85	357
3	Toluene	97.5	85	43	88	388
4	Cyclohexane	64.3	74	15	77	359
5	<i>n</i> -Hexane	54	78.6	11	75	345
6	Ethanol	99.8	95.6	14	82	358
7	Methanol	93.6	84.2	2	92	358
8	iso-Propanol	99.8	95.2	33	81	358
9	<i>n</i> -Propanol	99.7	94	11	85	372
10	iso-Butanol	99.7	94.6	21	82	385
11	<i>n</i> -Butanol	99.5	92.2	38	87	395
12	<i>n</i> -Hexanol	98.2	91	27	82	413
13	Acetonitrile	5.4	91	2.5	83	358
14	Tetrahydrofuran	99.1	87	4	80	343
15	Dichloromethane	39	82	48	68	321
16	<i>n</i> -Decane	96.6	84	35	81	433

Reaction conditions: [eugenol] = 6.75 mmol, [solvent] = 65.22 mmol, [solvent\*] = 93.75 mmol, [catalyst] =  $5.2 \times 10^{-3}$  mmol, [catalyst\*] =  $5.88 \times 10^{-3}$  mmol, reaction time = 3 h at refluxing temperature.

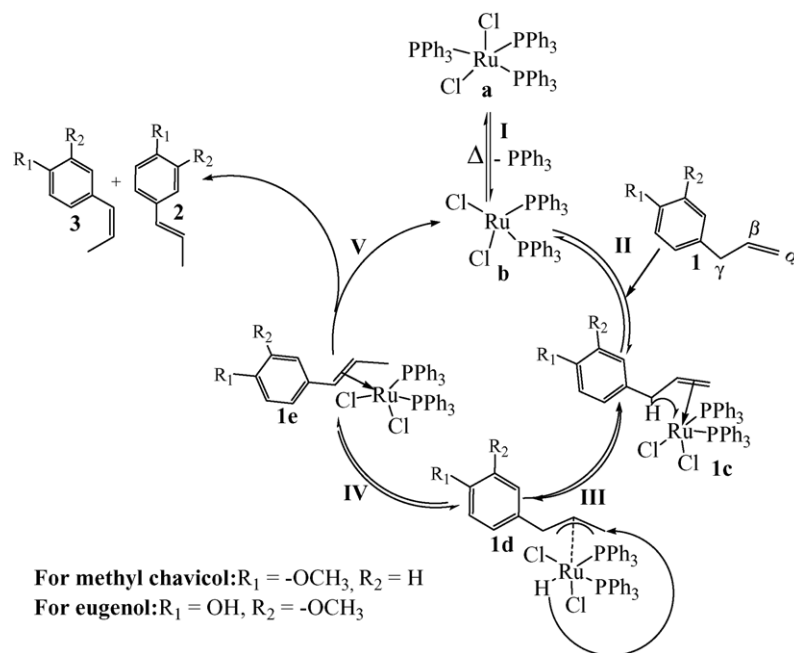
respectively. Similar behavior with the highly polar aprotic solvents was observed during the double bond isomerization of eugenol to isoeugenol. The conversion of the eugenol was found 5% in DMSO as a solvent using RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyst (Table 2; Run 1).

The highest conversion (99.7%) of methyl chavicol with 95.4% selectivity for *trans*-anethole was observed in moderate polar protic solvents such as ethanol followed by iso-propanol (99.6% conversion, 94.3% selectivity), *n*-butanol (98.8%, 94.2%) and iso-butanol (99.2%, 94%) in RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyzed isomerization reaction. While, in case of RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>2</sub>-CH<sub>3</sub>OH catalyzed reaction, the highest conversion of methyl chavicol (94.2%) with 98.6% selectivity for *trans*-anethole was observed in methanol (Table 1; Run 9) followed by other polar protic solvents. Similar behavior was observed in case of double bond isomerization of eugenol (Table 2) to isoeugenol catalyzed by RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> complex. The highest conversion (99.8%) of eugenol with 95.6% selectivity for *trans*-isoeugenol was observed in moderate polar protic solvents, such as ethanol followed by iso-propanol (99.8% conversion, 95.2% selectivity), *n*-propanol (99.7%, 94.0%), iso-butanol (99.7%, 94.6%) and *n*-butanol (99.5%, 92.2%) in RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyzed isomerization reaction. However, significantly lower conversion and selectivity of eugenol to isoeugenol were observed in RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>2</sub>-CH<sub>3</sub>OH catalyzed reaction.

The non-polar solvents showed better performance as compared to the highly polar aprotic solvents for the double bond isomerization of methyl chavicol and eugenol. The highest conversion (87.4%) of methyl chavicol was observed using cyclohexane as a solvent followed by toluene (82.8%) in RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyzed isomerization reaction. Whereas RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>2</sub>-CH<sub>3</sub>OH catalyst showed 90.6% conversion of methyl chavicol with 93.0% selectivity of *trans*-anethole with

toluene as a solvent. The non-polar solvents gave slightly lower conversion as compared to polar protic solvents, for the isomerization of eugenol using RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyst. The conversion of eugenol was observed 99.1% in tetrahydrofuran, 97.5% in toluene and 96.6% using *n*-decane as solvent. However, lower selectivities of *trans*-isomer were observed in case of non-polar solvents, as compared to polar protic solvents. For example, the selectivity of the *trans*-isomer was found to be 87% in tetrahydrofuran, 74.2% in toluene and 84% in *n*-decane. The selectivities of *trans*-isomers were also influenced significantly by the nature of solvents used in the isomerization reactions. The maximum selectivity of *trans*-isomers was observed with alcoholic solvents, while the solvent systems other than alcohols have given relatively lower selectivity for the *trans*-isomers and the magnitude of selectivity were almost similar with all the solvent systems other than alcohols.

The double bond isomerization catalyzed by transition metal complexes follows, generally, two types of mechanistic pathways [16], one is  $\pi$ -allylic mechanism (1,3-hydrogen shift) and other is the alkyl mechanism (1,2-hydrogen shift). Generally, metal hydride complexes follow the alkyl mechanism. The key feature of the  $\pi$ -allylic mechanism is the  $\beta$ -C-H activation, a step that includes the three-carbon arrangement in  $\pi$ -bonding to the metal. In this mechanism, the proposed active catalyst species RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, is formed by the dissociation of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (step I) [19]. The next step II, is the interaction of  $\pi$ -allylic electron of **1** to form a  $\pi$ -complex **1c** with the coordinatively unsaturated metal complex, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The equilibrium step III gives  $\pi$ -allyl metal complex **1d** through allyl-H-migration (oxidative additions) from  $\gamma$ -carbon atom to metal. The hydride shift (reductive eliminations) from  $\pi$ -allyl metal-hydride complex **1d** to  $\alpha$ -carbon atom gives complex **1e** via next equilibrium step IV. The dissociation of active catalyst species from the complex **1e** results the formation of **2** and **3**.



Scheme 1. Possible mechanistic pathway for the isomerization of methyl chavicol and eugenol using  $RuCl_2(PPh_3)_3$  catalyst.

For the alkyl mechanism, 1,2-insertion of coordinated alkene to Ru–H bond or  $\beta$ -elimination might be the rate-determining step. While for  $\pi$ -allylic mechanism, the slowest step is oxidative addition, which leads to the formation of hydride- $\alpha$ -allyl complex. From the macroscopic point of view, factors such as the rate of homogenization of the pre-catalyst, formation of the active catalyst species, which is involved in the catalytic cycle may also strongly influence the overall rate of reaction [20]. These two factors are certainly connected with homogenization, which is in equilibrium with ligand dissociation and formation of the active catalyst species. There is an additional set of equilibrium reactions, like coordination of the catalyst by substrate, products or decomposition of products, which also influences the rate-determining step [20].

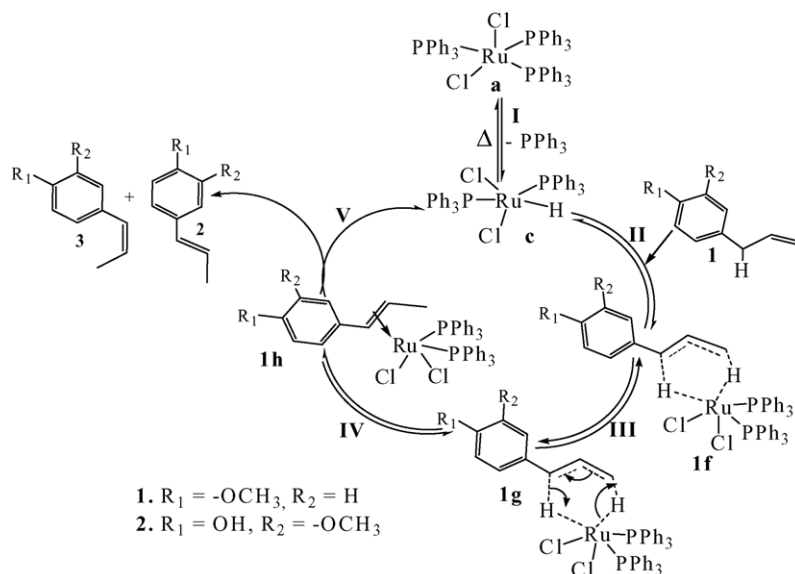
The higher conversion and selectivity obtained in alcohols may be attributed to easily transformation of the catalytic precursor **a** into the active catalyst species **c** in the reaction conditions (Scheme 2). In fact, the ruthenium hydride complex may be formed in a preliminary step through an oxidative addition of the alcohol to the complex, and this new hydride complex could be the catalytically active species having a very high activity towards double bond isomerization [21,22]. Higher catalytic activity of ruthenium hydride complex has also been reported during the double bond isomerization of 1,4-diarylbutenes [22], from the comparative activities of  $RuCl_2(PPh_3)_3$  and  $HRuCl(PPh_3)_3$  with the replacement of the former with  $HRuCl(PPh_3)_3$  showing 80-fold increase in the maximum rate of reaction. Effect of addition of 3% methanol to the reaction mixture of  $RuCl_2(PPh_3)_3$  and 1,4-diarylbutenes resulted into a 10-fold increase in the maximum rate of reaction and this increase in reaction rate has been attributed to formation metal hydride complex [22]. The formation of metal hydride is associated with the oxidative protonation of  $RuCl_2(PPh_3)_3$  in the

polar protic solvents, probably oxidative protonation of dissociated form  $RuCl_2(PPh_3)_2$ . Another important factor influencing the conversion of allyl phenyl ether is the rate of the dissolution of the catalyst precursor. General observations for ruthenium complexes, reveals that they dissolve faster in polar aprotic solvents, while in benzene they may even stay partially solidified till the end of the reaction period if the concentration of the complex is more. However, it may be noted that the proposed mechanisms in Schemes 1 and 2 needs to be confirmed by spectroscopic evidence of the actual intermediate species.

The lower conversion of substrate was found in highly polar solvents like DMSO, acetonitrile might be attributed to a competition between the solvent and the substrate for a coordinative place available on the catalyst. In this type of reactions, usually active solvents such as acetonitrile, DMSO were not performed well, due to the reason that, these solvents may react with the Ru complexes by oxidative addition to C–X bond, most likely deactivate the catalyst resulting in a decreased conversion [23]. Relatively strong coordination properties of DMSO, acetonitrile are the most important factors causing such a low conversion.

The conversion of methyl chavicol was increased up to 80% using the non-polar solvents, such as, toluene, cyclohexane, *n*-decane, benzene, chloroform, etc. This may be perhaps due to the coordination properties of these solvents. THF is usually the most effective solvent probably due to its coordinating properties.

In view of higher conversion and selectivity observed with ethanol as a solvent, further detailed kinetics has been studied using ethanol as a solvent for the double bond isomerization of methyl chavicol and eugenol using Ru/ $PPh_3$  complex catalyst. However, in the case of the isomerization of methyl chavicol using Ru/ $AsPh_3$  complex catalyst, methanol has been chosen as a solvent for the further detailed kinetic study as the



Scheme 2. Possible reaction mechanism for the isomerization of methyl chavicol and eugenol in protic polar solvents.

higher selectivity of *trans*-isomer was observed with methanol solvent.

### 3.1.1. Effect of solvent concentration

The effect of solvent concentration on the initial rate of reaction using  $RuCl_2(PPh_3)_3$  and  $RuCl_3(AsPh_3)_2 \cdot CH_3OH$  complex catalysts are shown in Fig. 2a and b, respectively, for the isomerization of methyl chavicol. From these figures, one can observe that the concentration of solvent plays an active role in inhibiting the rate of reaction.

At 10.87 mmol solvent concentration, the initial rate of reaction was found to be 21.67 mmol/(l s). Further, by increasing the solvent concentration 10.87–21.74 mmol, the initial rate of reaction was observed to decrease from 21.67 to 6.8 mmol/(l s). This trend was continued up to the solvent concentration 65.22 mmol, which resulted into the least value of the initial rate of reaction (1.67 mmol/(l s)). Initially, at the lower solvent concentration, the initial rate of reaction was found to be maximum. As the concentration of solvent increases, the initial rate of reaction decreased sharply. Therefore, further kinetic experiments were performed at 65.22 mmol ethanol concentration because in this region the initial rate of reaction was not significantly dependent on the solvent concentration.

In case of  $RuCl_3(AsPh_3)_2 \cdot CH_3OH$  complex catalyst, the initial rate of reaction decreases from 17.1 to 5.6 mmol/(l s) on increasing the solvent concentration 15.62–31.25 mmol. Therefore, for  $RuCl_3(AsPh_3)_2 \cdot CH_3OH$  catalyzed isomerization reaction, the methanol concentration was taken 31.25 mmol for all kinetic experiments.

Similar behavior of the solvent concentration on the initial rate of reaction using  $RuCl_2(PPh_3)_3$  complex catalyst was observed for the eugenol isomerization under studied experimental reaction conditions (Fig. 2a). The concentration of the solvent (ethanol) for the isomerization of eugenol to isoeugenol was taken 65.22 mmol for the kinetic experiments.

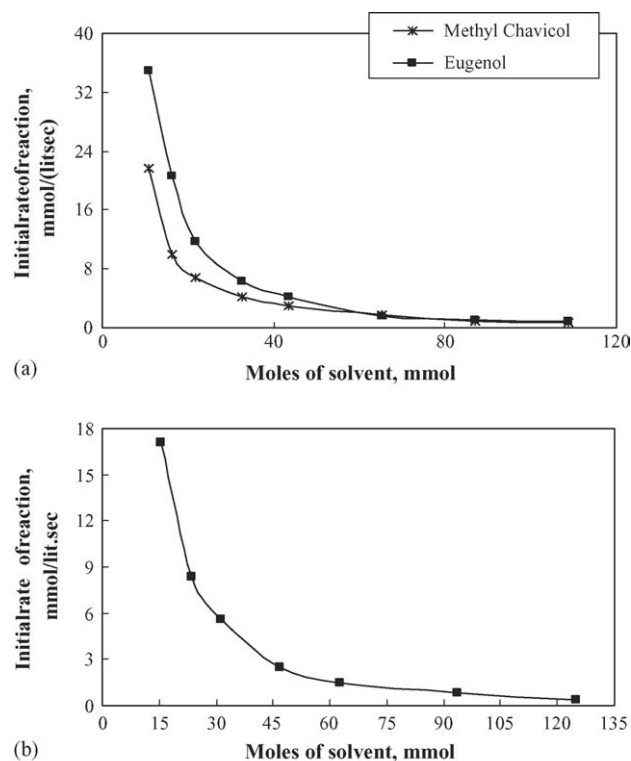


Fig. 2. (a) Effect of solvent concentration on the isomerization of methyl chavicol and eugenol using  $RuCl_2(PPh_3)_3$  complex catalyst. Reaction conditions: [reactant] = 6.75 mmol,  $[RuCl_2(PPh_3)_3] = 5.2 \times 10^{-3}$  mmol, [solvent] (ethanol) = 11.0–109.0 mmol, at 358 K. (b) Effect of solvent concentration on the isomerization of methyl chavicol using  $RuCl_3(AsPh_3)_2 \cdot CH_3OH$  complex catalyst. Reaction conditions: [methyl chavicol] = 6.75 mmol,  $[RuCl_3(AsPh_3)_2 \cdot CH_3OH] = 5.88 \times 10^{-3}$  mmol, [solvent] (methanol) = 15.0–125.0 mmol, at 358 K.

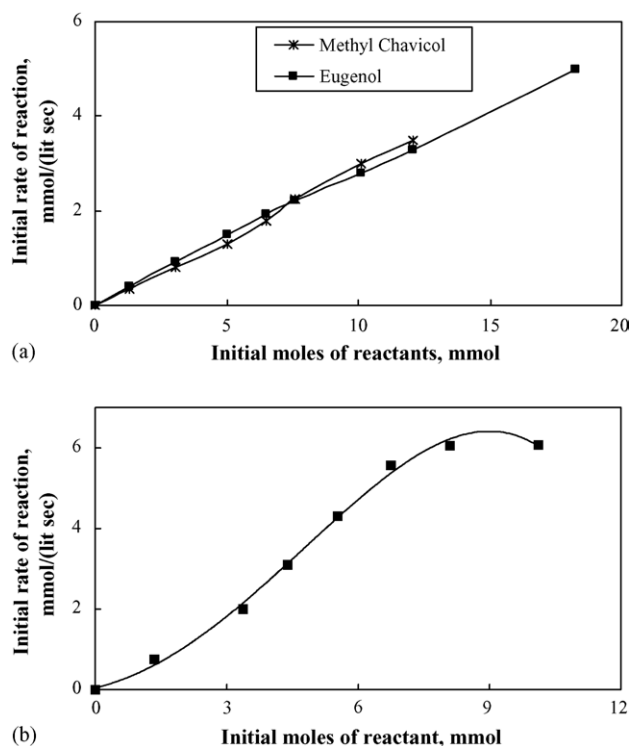


Fig. 3. (a) Effect of reactants concentration on the isomerization of methyl chavicol and eugenol using  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalyst. Reaction conditions: [reactant] = 1.35–18.27 mmol,  $[\text{RuCl}_2(\text{PPh}_3)_3] = 5.2 \times 10^{-3}$  mmol, [solvent] (ethanol) = 65.22 mmol, at 358 K. (b) Effect of methyl chavicol concentration on the isomerization of methyl chavicol using  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  complex catalyst. Reaction conditions: [methyl chavicol] = 1.35–10.15 mmol,  $[\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}] = 5.88 \times 10^{-3}$  mmol, [solvent] (methanol) = 31.25 mmol, at 358 K.

### 3.2. Effect of various parameters on the rate of reaction

#### 3.2.1. Effect of reactants concentration

**3.2.1.1. Effect of methyl chavicol concentration.** The effect of initial concentration of methyl chavicol on the initial rate of reaction using  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalyst is shown in Fig. 3a. The initial rate of reaction showed positive order dependence on the concentration of methyl chavicol and found to it to increase linearly by increasing the concentration of methyl chavicol. In the present study, the maximum rate of reaction was found 3.5 mmol/(l s) at 12.1 mmol

methyl chavicol concentration using  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalyst.

The effect of the initial concentration of methyl chavicol on the initial rate of reaction using  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  catalyst was also studied (Fig. 3b). The trend of the dependence of the initial rate of the reaction upon the concentration of methyl chavicol was observed to be some what different than  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyst system. Firstly, the initial rate of reaction was found to be increased linearly in the methyl chavicol concentration range 0.75–8.1 mmol and after that it remained constant with further increase in the concentration of methyl chavicol.

**3.2.1.2. Effect of eugenol concentration.** The effect of initial concentration of eugenol on the rate of reaction using  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalyst is shown in Fig. 3a. The trend observed was almost similar like the isomerization of methyl chavicol using  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyst. The initial rate of reaction increased from 1.5 to 5.0 mol/l, on increasing the concentration of eugenol 5–18.3 mmol. The initial rate of reaction was found to be linearly dependent on the concentration of eugenol in entire range of experiments.

**3.2.1.3. Effect of reactants concentration and time on selectivity of *trans*-isomers.** The trend of the formation of *trans*-isomers was also studied and the results obtained are shown in Table 3. The selectivity of *trans*-anethole was observed to increase from 70.4 to 95.4% by increasing the reaction time up to 60 min. After that, the selectivity of *trans*-anethole was observed to be independent on the reaction time even it is double. Initially, the lower selectivity of *trans*-isomer was observed due to simultaneous formation of the *cis*-isomer (Scheme 1). As the time increases, the concentration of the reactant decreased, at the lower concentration of methyl chavicol (<10%), the conversion of the *cis*-isomer to the *trans*-isomer was started, due to thermodynamically instability of *cis*-isomer. It was interesting to observe that the selectivity of *trans*-anethole is independent of the concentration of methyl chavicol. There is no significant changes in the selectivity of *trans*-anethole were observed even the concentration of the methyl chavicol increased from the 3.4 to 10.2 mmol.

Some relatively interesting results were found for the double bond isomerization of eugenol to isoeugenol using

Table 3  
Effect of reaction time and concentration of reactant on the selectivity of *trans*-isomer

Time (min)	Selectivity of <i>trans</i> -isomer (%)					
	Moles of methyl chavicol (mmol)			Moles of eugenol (mmol)		
	3.4	6.8	10.2	3.1	6.2	12.4
5	70.4	70.7	70.5	89.7	90.1	89.8
10	83.3	82.5	83.5	88	88	87.9
15	84.5	84.1	84.4	85	85.6	85.1
30	91.2	91.4	90.8	93.3	92.5	92.2
60	95.4	95.4	95.3	95.5	95.6	95.5
120	95.4	95.4	95.4	95.5	95.6	95.6

Reaction conditions: [solvent] (ethanol) = 65.22 mmol,  $[\text{RuCl}_2(\text{PPh}_3)_3] = 5.2 \times 10^{-3}$  mmol, reaction time = 2 h at 358 K.

$\text{RuCl}_2(\text{PPh}_3)_3$  catalyst. At the lower reaction time (5 min), the higher selectivity of *trans*-isomer was observed. As the reaction time increases from 5 to 15 min, the selectivity of the *trans*-isomer decreased 89.7–80% at the 3.1 mmol of eugenol concentration, due to enhanced formation of *cis*-isomer. Initially, the slow formation of the *cis*-isoeugenol has favored the higher selectivity of *trans*-isomer. As time increases, the formation of the *cis*-isomer increased, however, in this case also, when the concentration of reactant decreased, the *cis*-isomer was converted to the *trans*-isomer. Again there was no significant changes in the selectivity of *trans*-isoeugenol were observed even the concentration of the eugenol increased from the 3.1 to 12.4 mmol.

### 3.2.2. Effect of catalysts concentration

The effect of the catalyst concentration on the initial rate of reaction for isomerization of methyl chavicol using  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  catalyst is shown in Fig. 4a and b, respectively. The initial rate of reaction linearly increased with increasing the catalyst concentration up to  $8.0 \times 10^{-3}$  mmol (2.4 mmol/(1s)). However, after  $8.0 \times 10^{-3}$  mmol catalyst concentration the extent of increment of the initial rate of reaction was less as the initial rate of reaction increased from 2.4 to 2.75 mmol/(1s) by increasing the

concentration of  $\text{RuCl}_2(\text{PPh}_3)_3$  complex from  $8.0 \times 10^{-3}$  to  $31.3 \times 10^{-3}$  mmol.

The effect of the catalyst concentration on the initial rate of reaction for isomerization of eugenol using  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalyst is shown in Fig. 4a. The observed trend on the effect of catalyst concentration on the initial rate of reaction showed that, initially, the rate of reaction linearly dependence on the catalyst concentration up to  $6 \times 10^{-3}$  mmol, after that the initial rate of reaction was observed to be increased slowly with increasing catalyst concentration. The similar type of the trend was observed when methyl chavicol was used as reactant as described above.

### 3.3. Rate constant and activation energy

The effect of the temperature on the rate of reaction for the isomerization of methyl chavicol and eugenol using  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  complex catalysts are shown in Fig. 5a and b, respectively. It was observed that the initial rate of reaction increased by increasing the reaction temperature in case of isomerization of methyl chavicol using  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalyst. The lower conversion of methyl chavicol and lower selectivity of *trans*-anethole was found below refluxing temperature of the reaction mixture. Similar types of trends in conversion

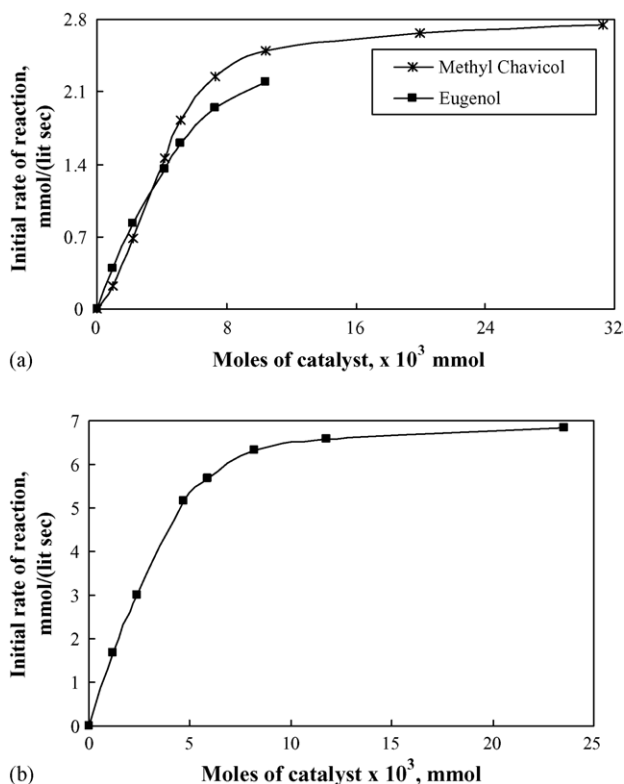


Fig. 4. (a) Effect of catalyst concentration on the isomerization of methyl chavicol and eugenol using  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalyst. Reaction conditions: [reactant] = 6.75 mmol,  $[\text{RuCl}_2(\text{PPh}_3)_3] = 1 \times 10^{-3}$ – $31.3 \times 10^{-3}$  mmol, [solvent] (ethanol) = 65.22 mmol, at 358 K. (b) Effect of catalyst concentration on the isomerization of methyl chavicol using  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  complex catalyst. Reaction conditions: [methyl chavicol] = 6.75 mmol,  $[\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}] = 1.2 \times 10^{-3}$ – $23.5 \times 10^{-3}$  mmol, [solvent] (methanol) = 31.25 mmol, at 358 K.

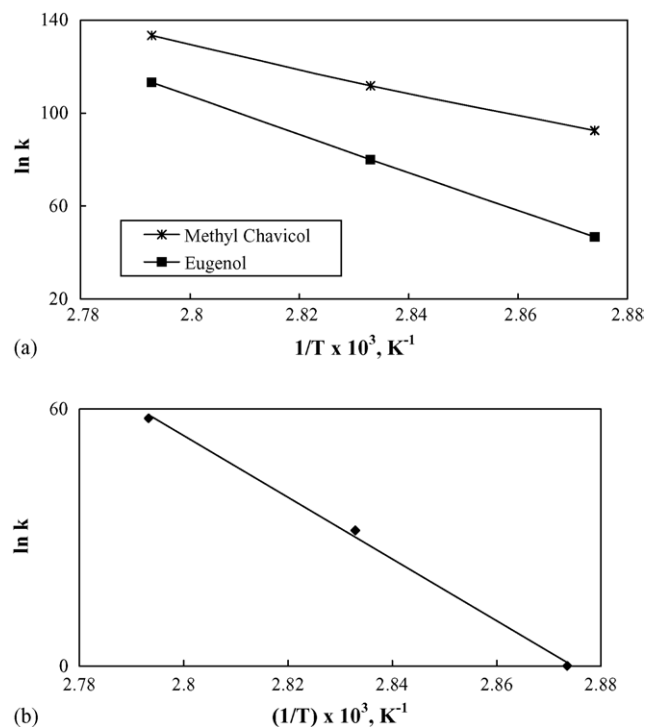


Fig. 5. (a) Arrhenius plot for the isomerization of methyl chavicol and eugenol using  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalyst. Reaction conditions: [reactant] = 6.75 mmol,  $[\text{RuCl}_2(\text{PPh}_3)_3] = 5.2 \times 10^{-3}$  mmol, [solvent] (ethanol) = 65.22 mmol, temperature = 348–358 K. (b) Arrhenius plot for the isomerization of methyl chavicol using  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$  complex catalyst. Reaction conditions: [methyl chavicol] = 6.75 mmol,  $[\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}] = 5.88 \times 10^{-3}$  mmol, [solvent] (methanol) = 31.25 mmol, temperature = 348–358 K.



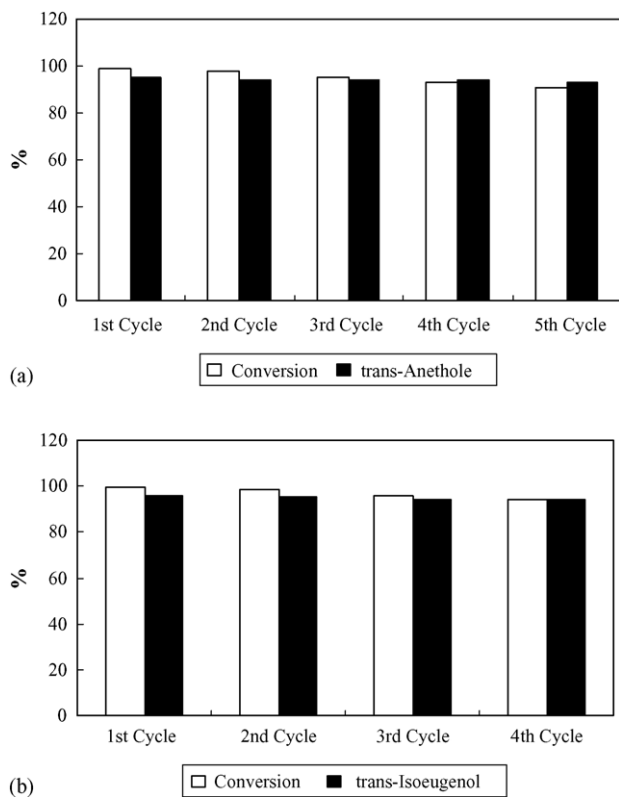


Fig. 6. (a) Reusability of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> complex catalyst for the isomerization of methyl chavicol. Reaction conditions: [methyl chavicol] = 6.75 mmol, [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] = 5.2 × 10<sup>-3</sup> mmol, [solvent] (ethanol) = 65.22 mmol, reaction time = 2 h, at 358 K. (b) Reusability of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> complex catalyst for the isomerization of eugenol. Reaction conditions: [eugenol] = 6.75 mmol, [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] = 5.2 × 10<sup>-3</sup> mmol, [solvent] (ethanol) = 65.22 mmol, reaction time = 2 h, at 358 K.

and selectivity were found in the case of isomerization of methyl chavicol using RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>2</sub>·CH<sub>3</sub>OH complex and isomerization of eugenol. Activation energies for the isomerization of methyl chavicol under experimental conditions were found to be 4.3 ± 0.08 kJ/mol (Fig. 5a) with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyst and 6.0 ± 0.12 kJ/mol (Fig. 5b) with RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>2</sub>·CH<sub>3</sub>OH catalyst. For the isomerization of eugenol, the activation energy was found to be 6.9 ± 0.13 kJ/mol (Fig. 5a) using RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> complex catalyst, which is less than the reported value for rhodium(III) chloride system (42.6 kJ/mol) [13] and for KOH system (148 kJ/mol) [15].

From above detailed kinetics studies, it was observed that the RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> complex showed the higher conversion and reasonably excellent selectivity for the isomerization of methyl chavicol and eugenol. Therefore, one reaction was performed in larger scale of methyl chavicol ([methyl chavicol] = 3.48 mol, [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] = 2.2 mmol, [ethanol] = 32.61 mol, time = 2 h at 358 K). The result was found identical as the previously observed for the isomerization of 1 g (6.75 mmol; Run 8; Table 1) methyl chavicol. The catalyst was recycled up to five times for the isomerization of methyl chavicol (Fig. 6a) and eugenol (Fig. 6b). There were not observed any considerable changes in the conversion and selectivity of respective isomers up to fifth cycles in both of the cases.

## 4. Conclusions

The regioselective synthesis of *trans*-anethole from methyl chavicol via double bond isomerization of methyl chavicol using RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>2</sub>·CH<sub>3</sub>OH complex catalysts with details kinetics studies has been reported for the first time. The effect of different solvents on the conversion and selectivity towards *trans*-anethole were studied for the isomerization of methyl chavicol to *trans*-anethole. The highest conversion (99.7%) with selectivity (95.4%) for *trans*-anethole was observed in the ethanol followed by iso-propanol and methanol in relatively lesser reaction time using RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyst. Similar results were observed for eugenol isomerization in alcoholic solvents using RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyst. However, in case of RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>2</sub>·CH<sub>3</sub>OH catalyzed isomerization of methyl chavicol, the highest conversion (94.2%) with selectivity (98.6%) for *trans*-anethole was observed in the methanol followed by iso-propanol and ethanol. Clearly, it was observed that the rate of reaction increased on increasing methyl chavicol, eugenol and catalyst concentrations. The rate of reaction was found strongly dependent on the solvent concentration. The rate of reaction decreased with increasing the solvent concentration. Activation energies for the isomerization of methyl chavicol under experimental conditions were found to be 4.3 kJ/mol with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalyst and 6.0 kJ/mol with RuCl<sub>3</sub>(AsPh<sub>3</sub>)<sub>2</sub>·CH<sub>3</sub>OH catalyst. For the isomerization of eugenol, the activation energy was found to be 6.9 kJ/mol using RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> complex catalyst. The catalyst was recycled five times without significant loss in conversion and selectivity for isomerization of methyl chavicol and eugenol.

## Acknowledgements

Authors are highly thankful to Dr. P.K. Ghosh, Director, CSMCRI, Bhavnagar, India, for encouragement of this publication and CSIR Network Program on Catalysis, CSIR, New Delhi, India, for the financial supports.

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