



Original Research Article

The dichlorocyclopropanation of 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene using water soluble multi-site phase transfer catalyst-A kinetic study

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ABSTRACT

Keywords

Multi-site phase transfer catalysts, Dichlorocyclopropanation, 3-methyl-1-cyclohexene;4-vinyl-1-cyclohexene, Kinetics

The present study focuses the attention towards the utility of “multi-site” phase transfer catalyst (MPTC), is demonstrated by studying hydroxide-ion initiated reaction like dichlorocarbene addition to olefins. The formation of the product was monitored by GLC. Dichlorocyclopropanation of 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene catalysed by multi-site phase transfer catalyst carried out in biphasic medium under pseudo-first-order conditions by keeping aqueous sodium hydroxide and chloroform in excess. The effect of various experimental parameters on the rate of the reaction has been studied. Also thermodynamic parameters such as ΔS^\ddagger , ΔG^\ddagger and ΔH^\ddagger were evaluated; based on the experimental results, a suitable mechanism is proposed. It also deals in greater detail on the kinetic aspects of chosen reactions. An attempt has been made to compare the ability of MPTC-I with MPTC-II and single-site PTC for dichlorocarbene addition to olefins like 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene.

Introduction

The reaction of chloroform with strong bases to generate synthetically useful dichlorocarbene normally requires anhydrous conditions to avoid its rapid hydrolysis (Reeves *et al.*, 1976). Thus addition of chloroform to a mixture of 3-methyl-1-cyclohexene and aqueous 25% sodium hydroxide solution gives 60-70% yield in the presence of a phase transfer catalyst such as tridecyl methyl ammonium chloride or benzyl triethyl ammonium chloride. The remarkable increase in yield of the dichlorocarbene adduct reflects the ability of the quaternary salt to cause $:CCl_2$

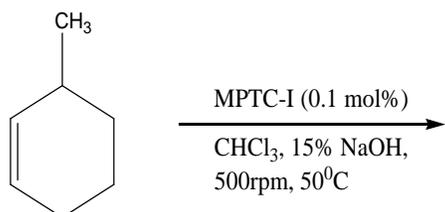
to be generated in, or transferred to the organic phase, where its reaction with 3-methyl-1-cyclohexene is much greater than with water addition of dichlorocarbene to 3-methyl-1-cyclohexene gave only normal dichlorocyclopropane product. Makosza and Bialecka (1977) formulated the mechanism of the olefin (cyclohexene) dichlorocyclopropanation under phase transfer conditions as reaction of $CHCl_3$ with OH^- at the aqueous organic phase boundary, from where it is then taken in to the organic phase by the quaternary cation. Soluble phase transfer catalysts for

dichlorocarbene addition to cyclohexene with concentrated aqueous sodium hydroxide as the base were first reported by von Doering *et al.*, 1980 and were investigated in detail by Makosza, 1978. The phase transfer catalyzed dichlorocarbene addition reaction of 3-methyl-1-cyclohexene was thought to proceed by rate-limiting generation of the dichlorocarbene and hydroxide ion at the aqueous / organic interface.

The reaction of chloroform with 4-vinyl-1-cyclohexene (Starks and Napier, 1976) in the presence of sodium hydroxide gives an excellent yield of a product $C_9H_{12}Cl_2$ which contains the bicyclo [4.1.0] heptane (norcarane) skeleton. In the early work, we have observed that dichlorocarbene addition reaction was carried out with excess of 3-methyl-1-cyclohexene; dichloronorcarane product was obtained in a yield of about 63% under single-site PTC conditions. The present detailed investigation of this reaction permitted us to develop a new method for the preparation of 7,7-dichloro-3-methyl-

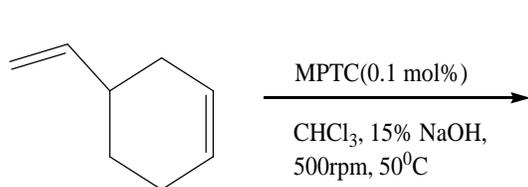
bicyclo[4.1.0]-heptane derivatives by the addition of dichlorocarbene to 3-methyl-1-cyclohexene; the method involves the reaction of 3-methyl-1-cyclohexene with chloroform in the presence of concentrated aqueous solution of sodium hydroxide (15% w/w) and catalytic amount of MPTC-I. The reaction proceeds exothermically when the reagents are mixed at 50⁰C and the yields of the product obtained by this method are very high usually about 100%, within one hour with no excess of the 3-methyl-1-cyclohexene required. The ratio of 3-methyl-1-cyclohexene to chloroform applied is 1: 10 in volume, depending on the availability of the olefin. In a similar way, the addition of dichlorocarbene with 4-vinyl-1-cyclohexene yielded 100% product within one hour under PTC conditions.

The dichlorocarbene addition with 3-methyl-1-cyclohexene and with 4-vinyl-1-cyclohexene were chosen to investigate the kinetic aspects using the new, water-soluble “multi-site” phase transfer catalyst (MPTC-I).



(Scheme-1)

7,7'-dichloro-3-methyl-bicyclo[4.1.0]-heptane



(Scheme-2)

7,7'-dichloro-4-vinyl-bicyclo[4.1.0]-heptane

Dichlorocarbene addition to 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene under PTC conditions

The kinetic experiments for the dichlorocarbene addition to 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene (schemes 1, 2) were conducted under biphasic conditions with excess of aqueous sodium hydroxide and chloroform under pseudo first order conditions. The reaction was studied at a stirring speed of 500rpm in the temperature range 40-60°C. Before the kinetic run was started, the catalyst was conditioned with aqueous sodium hydroxide and chloroform for 10 minutes. The substrate, 3-methyl-1-cyclohexene/4-vinyl-1-cyclohexene preheated at the appropriate temperature, was added to the reaction mixture. The samples were collected from the organic layer at regular intervals of time. The kinetics of dichlorocarbene was followed by estimating the formation of two different norcarane products namely 7,7'-dichloro-3-methyl-bicyclo[4.1.0]-heptane and 7,7'-dichloro-4-vinyl-bicyclo[4.1.0]-heptane using gas chromatographic technique. The effect of various experimental parameters such as stirring speed, substrate concentration, sodium hydroxide concentration and temperature on the reaction rate constants were studied. The kinetics was measured up to 30% of the formation of the product.

Effect of Stirring Speed

The effect of varying stirring speed on the rate of dichlorocarbene to 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene was studied in the range 100-800 rpm. From the plots of $\log(a-x)$ versus time, the pseudo-first order rate constants were evaluated. A plot of k_{obs} against stirring speed is shown in Fig. 1 (Table1). Balakrishnan et al, 2005, had documented the kinetic studies of dichlorocarbene addition to cyclohexene using aqueous sodium hydroxide and chloroform catalyzed by polymer supported phase transfer catalyst, obtained an yield of

89%. This reaction was also carried out by Winberg et al, 2007, using 50% aqueous sodium hydroxide and catalytic amount of TEBA (PTC) and obtained 72% yield of the norcarane product, 7, 7' -dichlorobicyclo [4.1.0]-heptane. In the present study, the rate constant is dependent on the stirring speed up to 500rpm and maintains constancy beyond the limit. The reaction is carried out in aqueous medium; the anion exchange equilibrium between the anions in the aqueous phase and those associated with quaternary salt in the organic phase was very relative to the organic phase transformation reaction. The mass transfer across the interface is regarded as evident from Fig. 1 at low stirring speed. At agitation level 500rpm, anion exchange equilibrium is very fast relative to the reaction and the substrate consumption rate becomes independent of the stirring rate as observed by Makosza et al, 1975, in the study of dichlorocarbene addition to cyclohexene catalyzed by triethyl benzyl ammonium chloride (TEBA) under PTC conditions. Doering, Wawrzyniewicz and Jawdosiak, 1985 reported independently a similar observation that reflected kinetic control by chemical reaction in which $[Q^+X]$ is at a steady-state concentration. Below 500rpm the requirement for sufficiently rapid mass transfer of the reacting anion is not met and diffusion controlled kinetics is observed.

Hence the independence of the reaction rate constants on the stirring speed above 500rpm in the present study is indicative of extrication mechanism. The behavior is in short contrast to reactions operative through interfacial mechanism, where the reaction rate is directly proportional to the stirring speed.

Parham, 1983, reported the continuous increase in the rate of dichlorocarbene

addition even up to stirring speeds of 1200rpm. It has also been reported that the rate of an interfacial reaction is proportional to the stirring speed in the range of 600 to 1400rpm. The interfacial area per unit volume of dispersion increased linearly with increasing speed till a stage is reached where there is no significant increase in the interfacial area per unit volume of dispersion with the corresponding increase in the speed. Thus increasing the stirring speed changes the particle size of the dispersed phase. Above certain stirring speed (500rpm), the particle size does not change. The constancy of the rate constants is observed not because the process is necessarily reaction rate limited but because the mass transfer rate has reached constant value. Therefore Fig. 1 (Table 1) is indicative of an extraction mechanism and not of a real "phase Transfer".

Effect of Substrate Amount

Kinetic experiments were performed by varying the amount of 3-methyl-1-cyclohexene from 6.34-25.36mmol and 4-vinyl-1-cyclohexene from 3.87-23.24 mmol and keeping other reagents such as chloroform and NaOH in excess. Pseudo-first order rate constants are evaluated from the linear plots of $\log(a-x)$ versus time. The observed reaction rate constants decrease as the amount of substrate increases Fig. 3 (Table 1).

The decrease in rate may be attributed to the proportionate decrease in the number of catalytic active sites available. The results suggest that the concentration of the substrate in the organic phase is not important and the concentration of the substrate at the inter-phase may be vital. Similar observation was earlier reported by Balakrishnan et al, 2004, in the study of dichlorocarbene to cyclohexene with NaOH and PS-PTC under tri-phase conditions.

Effect of catalyst amount

The amount of catalyst was varied from 0.05-0.25 mol% for the dichlorocarbene addition to 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene (based on the substrate amount) and the experiments were conducted using 15% w/w aqueous NaOH solution. The pseudo first order rate constants are calculated from the plots of $\log[a-x]$ versus time. The rate constants are dependent on the amount of catalyst used in each reaction. The increase in rate constants is attributed to the increase in the number of active sites. Control experiments were performed and no product was detected even after 2 hours of the reaction. Only a catalytic amount (0.1 mol% based on the substrate) is required in order to obtain good yields of the product emphasizing the indispensability of the catalyst. Sasson et al, 1987, evaluated first order rate constants for the dichlorocarbene addition to cyclohexene using N, N-di-n-butyl piperidinium iodide as the catalyst.

Abilogarithmic plot of reaction rate constants versus the concentrations of catalyst gave a straight line having a slope of 4.6 for 1-methyl-1-cyclohexene and 1.35 for 4-vinyl-1-cyclohexene (Table 1, Fig.2). In the study of dehydrobromination of ethylbromide, zero order kinetics with respect to the catalyst was observed.

Effect of sodium hydroxide concentration

The rate of dichlorocarbene addition to 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene strongly depends on the strength of sodium hydroxide; kinetic experiments were carried out employing 3.41-7.89M aqueous NaOH for both the olefins. Pseudo-first order rate constants are evaluated from the plots of $\log(a-x)$ versus time. The reaction rate constants

tremendously increased with increase in basicity of hydroxide ion. Bilogarithmic plots of the reaction rate against sodium hydroxide concentrations give a straight line having a slope of 1.3 for 3-methyl-1-cyclohexene and 1.8 for 4-vinyl-1-cyclohexene (Table 1, Fig.4).

In the case of the isomerization of allyl benzene, the effective kinetic order with respect to aqueous NaOH concentration was reported to be 4-8, where extraction mechanism is operative. Makosza reported the successful, application of two phase catalytic and ion-pair extractive methods in the reaction of carbanions and halocarbenes. The instability of some C-H acids in the presence of aqueous alkali (such as hydrolysis of esters of other functional groups) was pointed out. The remedy suggested was the use of less concentrated solution of the base. This requirement is met by employing MPTC-I as the optimum NaOH concentration is 15% as against 25% used in the case of TEABr. Generally quaternary salts are stable up to $\sim 150^{\circ}\text{C}$ but less stable at temperature 78°C , when strong alkalis were used. While employing MPTC-I, the need to use low concentration of alkali in spite of the fact that the reaction is in a great measure dependent on it reveals the higher activity and applicability of the MPTC-I.

Influence of temperature variation

The effect of varying temperature on the rate of dichlorocarbene addition to 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene was studied in the range of $40-60^{\circ}\text{C}$. The kinetic profile of the reaction is obtained by plotting $\log(a-x)$ versus time. The rate constants increase with the increase in temperature. The energy of activation is calculated from Arrhenius plot, $E_a=9.2\text{ Kcal mol}^{-1}$ for 3-methyl-1-cyclohexene and 11.5

Kcal mol^{-1} for 4-vinyl-1-cyclohexene (Table 1, Fig.5). The other thermodynamic parameters, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ are Evaluated and presented in Table2.

The very low activation energy indicates that the step (2) (ie., chemical reaction) is not the rate-determining step; on the other hand, these results are characteristic of diffusion control. At a given temperature, stirring speed and shape of the reaction vessel, there exists a definite rate of mass transfer between two phases on contact (the aqueous-organic phase boundary), which is also dependent on the catalyst concentration upon a certain value. It can be seen from the Table.1 and Fig.5 that the dependence of the reaction rate constants on the concentration of the catalyst is stronger at the lower concentration (in the present case, between 0.05-0.2 mol%) and is weakly dependent at higher catalyst concentrations (0.25mol%). In the concentration range examined, the dependence of k_{obs} on the [catalyst] does not attain linearity. Therefore it may be concluded that a process involving maximum rate of diffusion occurs in the present reaction and that the maximum rate of diffusion is being approached at the higher catalyst concentration (0.25mol %). At still higher concentration, the capacity of the system to accommodate diffusion of additional catalyst is smaller or negligible.

Similar observation was earlier reported by Rabinovitzetal, 1981, in the study of dehydrobromination of (2-bromoethyl) benzene where E_a is reported to be $12.4\text{ Kcal mol}^{-1}$. In general, E_a is equal to $0-10\text{ Kcal mol}^{-1}$ for diffusion-controlled processes and usually over 15Kcal mol^{-1} for chemical reaction controlled processes. A higher E_a value has been reported for the polystyrene bound trimethyl ammonium ion catalyzed reaction, which was controlled by strict intrinsic reactivity under tri-phase reactions.

Table 1- Effect of MPTC-1 on the rates of dichlorocarbene addition to 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene reactions

Type of Variation	variable parameters	Rates of the reaction ($k_{obs} \times 10^4, S^{-1}$)	
		3-methyl-1-Cyclohexene	4-vinyl-1-cyclohexene
Stirring Speed (rpm)	100	0.72	0.19
	200	0.81	2.75
	300	0.82	3.80
	400	1.25	5.21
	500	1.83	6.03
	600	1.86	6.05
	700	1.88	6.07
	800	1.88	6.07
Catalyst Amount (mmols)	0.05	1.04	1.98
	0.10	1.65	2.22
	0.15	1.98	3.87
	0.20	2.69	4.69
	0.25	3.29	5.02
Substrate Amount (mmols)	6.34	7.90	16.59
	8.45	5.74	12.46
	12.68	3.77	9.17
	16.91	3.15	5.28
	21.13	2.23	2.85
[NaOH] (M)	25.36	1.33	2.21
	3.41	1.01	1.30
	4.41	1.26	2.43
	5.49	2.02	3.68
	6.65	2.60	4.30
Temperature (K)	7.89	3.42	4.93
	313	0.75	1.30
	318	1.30	1.82
	323	1.98	3.26
	228	2.71	3.63
	333	3.27	4.32

Table.2 Thermodynamic parameters.

Substrate	E_a Kcalmol ⁻¹	ΔH^\ddagger Kcalmol ⁻¹	$-\Delta S^\ddagger$ CalK ⁻¹ mol ⁻¹	ΔG^\ddagger Kcalmol ⁻¹
3-methyl-1-cyclohexene	9.2	8.5	181.0	56.9
4 – vinyl-1-cyclohexene	11.5	10.8	175.6	55.2

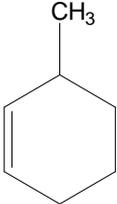
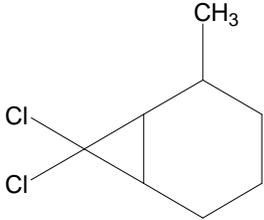
Table.3 Comparison of reaction rate constants with different catalysts.

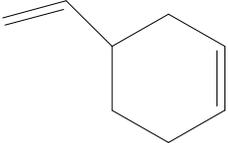
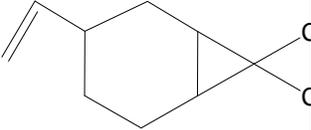
Entry	Catalyst	Amount (mol %)	$k_{obs} / 10^{-4}, S^{-1}$	
			3-methyl-1-cyclohexene	4-vinyl-1-cyclohexene
A	None	None	Nil*	Nil*
B	MPTC-I	0.1	3.08	5.35
C	MPTC-II	0.1	2.01	3.16
D	SPTC	0.1	0.45	2.00

*No Conversion after 3 hours

“MULTI-SITE”PHASE TRANSFER CATALYST-I’SACTIVITY INHYDROXIDE-ION INITIATED REACTIONS.

The results shown in **Table.4** establish the synthetic utility of the new MPTC-I under PTC / OH⁻ conditions.

S.No	Substrate with experimental conditions	Products (S)	% Conv. ^a with Reaction time	Spectral data ^b	reference
1	3-methyl-1-cyclohexene (0.60min)  <ol style="list-style-type: none"> Subs. amount: 2.0 ml Cat.amount: 0.1mol% Solvent: CHCl₃; 20 ml [NaOH]: 15% w/w, 25ml(4.41m) Temp: 50°C 	Product (1.49 min) 	100.00; One hour	¹ H-NMR (CDCl ₃ /TMS) δ =2.33 (s,3H) 1.71-1.29(m,10H)	O’Donnell, Etal,2007

<p>2</p>	<p>4-vinyl-1-cyclohexene (0.60 min.)</p>  <p>1. Subs. amount: 2.0 ml 2. Cat. amount: 0.1 mol% 3. Solvent: CHCl₃; 20 ml 4. [NaOH]: 15% w/w, 25ml (4.41M) 5. Temp. 50°C</p>	<p>Product (1.49 min.)</p> 	<p>100.00; One hour</p>	<p>¹H-NMR (CDCl₃/TMS) δ = 1.98-0.949 (m,8H) 1.91-1.78 (dd,2H)</p>	<p>Fedorynski, Etal,1993</p>
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a: Conv.by Gaschromatography, b: for known compounds only selected spectral data given.
Table: 4. Hydroxide-ion initiated reactions under the PTC conditions using the new MPTC-I.

Fig. (1). Effect of stirring speed variation for the dichlorocarbene addition to (A) 3-methyl-1-cyclohexene and (B) 4-vinyl-1-cyclohexene.

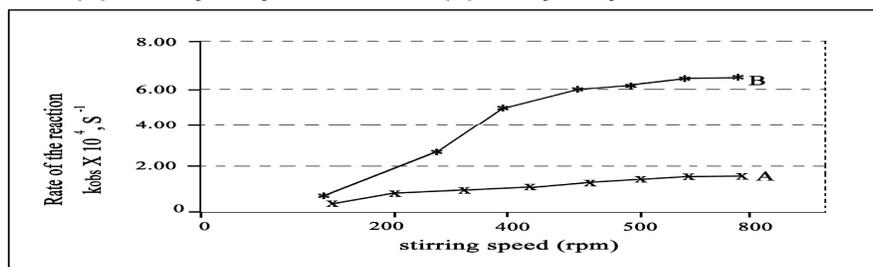


Fig.(2). Effect of catalyst amount for the dichlorocarbene addition to (A) 3-methyl-1-cyclohexene and (B) 4-vinyl-1-cyclohexene.

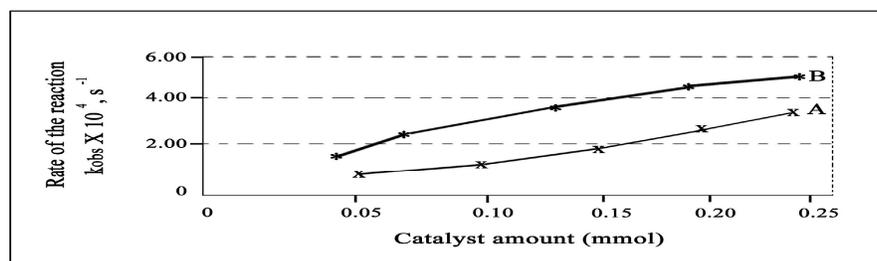


Fig. (3). Effect of variation of substrate amount for the dichlorocarbene addition to (A) 3-methyl-1-cyclohexene and (B) 4-vinyl-1-cyclohexene.

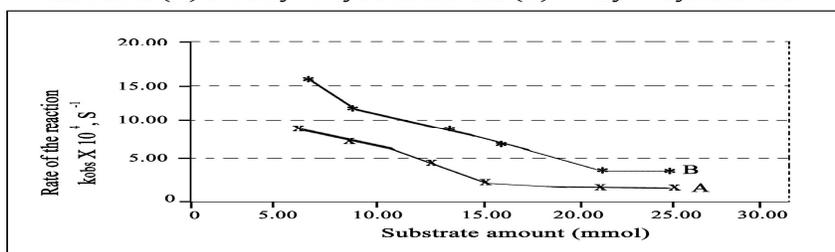


Fig (4) Effect of variation of concentration of NaOH for the dichlorocarbene addition to (A) 3-methyl-1-cyclohexene and (B) 4-vinyl-1-cyclohexene.

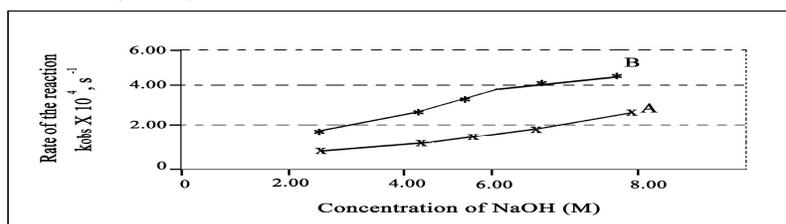
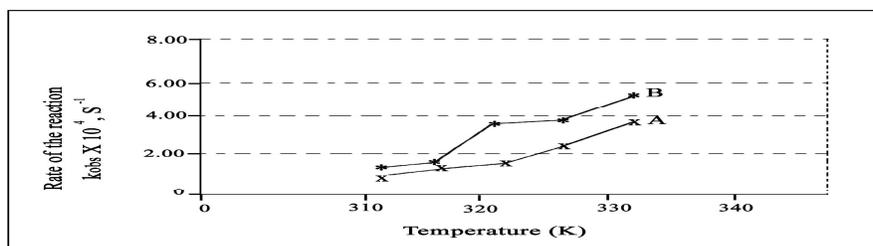


Fig. (5) Effect of Variation of temperature for the dichlorocarbene addition (A) 3-methyl-1-cyclohexene (B) 4-vinyl-1-cyclohexene.



The activation energy for the dichlorocarbene addition to cis 1, 4-poly butadienewas reported to be 21 K cal mol⁻¹ and for this an interfacial mechanism was proposed (Selvaraj, Rajendran, 2011). The activation energy of intra particle diffusion of anion exchange resins in aqueous solutions is of the order of 5-10 K cal mol⁻¹. The observed energy of activation for the dichlorocarbene addition to 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene are 9.2 and 11.5 Kcal mol⁻¹ and hence a hydroxide ion extraction mechanism is proposed for the reaction under study which is governed by diffusion control.

Comparison of reaction rate constants

A comparison of reaction rate constants of the two dichlorocarbene additions can be attempted since all the reactions were

conducted at identical reaction conditions taking 2.0ml substrate, 20ml chloroform, 0.1mol% catalyst (MPTC-1, MPTC-II and SPTC) and 15% w/w NaOH. The reactions were run at 50^oC with a stirring speed of 500rpm.The observed rate constants ($k_{obs}/10^{-4}, S^{-1}$)for 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene are found to be 2.65 and 7.03 respectively (Table.3). These values are in an approximate ratio 3: 1 (4-vinyl-1-cyclohexene: 3-methyl-1-cyclohexene).

The reaction rate of 4-vinyl-1-cyclohexene is three times faster than 3-methyl-1-cyclohexene which can be attributed to the electron-rich nature due to the possibility of secondary orbital interaction of the vinyl group in 4-vinyl-1-cyclohexene which readily attached to the electron-deficient

dichlorocarbene. Also the transition state of 4-vinyl-1-cyclohexene is far less hindered than 3-methyl-1-cyclohexene which makes 4-vinyl-1-cyclohexene more reactive than 3-methyl-1-cyclohexene.

MPTC-I : α , α^1 , α^{11} -tris(triethyl ammonium methylene bromide) β -hydroxyl ethylbenzene (Shanmugan, Balakrishnan, 2007), MPTC -II : 2-Benzylidene-N,N,N,N¹,N¹,N¹-hexa ethyl propane- 1,3-di ammonium dichloride (Balakrishnan, Paul Jayachandran,1995), SPTC : Single -site phase transfer catalyst (TEBAB)

In Table 3, the results reflect a comparative trend among the different catalysts used. Based on the observed rate constants, it is evident that the MPTC-I is 60% and 75% more active than the MPTC-II and "single-site" TEBAB respectively. Control experiments of dichlorocarbene additions to olefins in the absence of the catalyst resulted in <1% conversion in three hours. As is evident from Table 4, the new MPTC catalyst-I is found to perform extremely well for hydroxide-ion initiated reaction systems resulting in excellent yields of the products. All the dichlorocarbene additions reactions were conducted at identical reaction conditions taking 20ml chloroform, 0.1 mol% catalyst (MPTC-I) and 15% w/w NaOH. The reactions were run at 50°C with a stirring speed of 500rpm. The reaction, viz., dichlorocarbene addition to olefins such as 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene in the presence of MPTC-I resulted in 100% conversion within one hour.

Mechanism

The mechanism of hydroxide-ion initiated reactions, like dichlorocarbene addition reactions which were performed under phase transfer catalyzed conditions (PTC/OH⁻

systems), has been the subject of much discussion. The anion (: CCl₂) which is derived from chloroform is sensitive towards the aqueous NaOH concentration may be explained by a combination of several major factors, the mass law, the salting out effect and the basicity of the hydroxide ion. Past studies have also revealed that the nature (singlet or triplet) and reactivity of dichlorocarbenes depend significantly on the mode and medium of generation as well as whether the substituents are directly bound or conjugated with carbenes. The rate-determining step of the reaction involves the attack of dichlorocarbene on the olefins such as 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene. The kinetically controlled step is greatly influenced by the orientation of all the relevant factors around the dichlorocarbene anion during the attack. From GC studies, it is clear that there is no norcarane product, at all hydroxide ion concentration and this may be due to the association of the active site and site the electrophilic nature of: CCl₂.

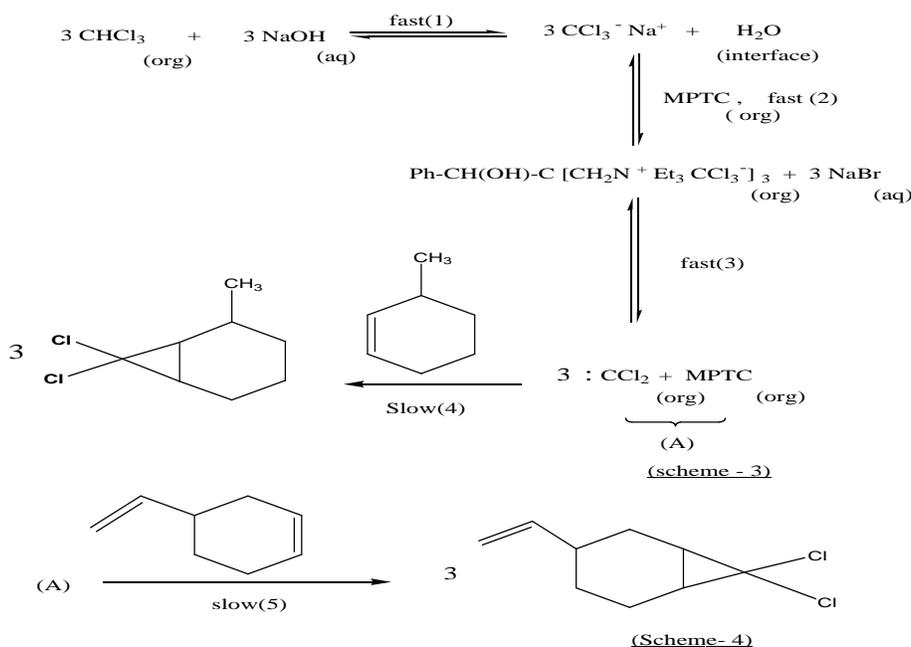
Two major mechanisms have been proposed for PTC reactions, the Stark's extraction mechanism (Starks, 1971) and the Masoksa interfacial mechanism (Makosza, 1972). Reactions proceed through the extraction mechanisms are characterized by 1. increased reaction rate with increased organophilicity or with larger symmetrical tetra alkyl ammonium ions, 2. independence of reaction rate on stirring speed above a certain value and 3. linear dependence of reaction rate on catalyst concentration. In contrast, reaction believed to proceed through the Makosza's interfacial mechanism are characterized by

1. Maximum reactivity with relatively hydrophilic quats (Yang et al, 2010), usually
2. Increased reaction rate with stirring speed even up to 1950rpm (Wang et al, 2006) and

3. Fractional kinetic order with respect to catalyst (when interfacial steps are at least partially rate limiting).

From the observed experimental results, it would be concluded that the dependency of the kinetic data on the stirring speed up to 500rpm, the dependency of the rate of

dichlorocarbene addition to 3-methyl-1-cyclohexene /4-vinyl-1-cyclohexene on quat structure, stirring speed and concentration of the catalyst is consistent with that found for the extraction mechanism. The mechanism for the dichlorocarbene addition to 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene may be written as.



In summary, a multi-site phase transfer catalyst was used, its catalytic efficiency was investigated by following dichlorocyclopropanation of 3-methyl-1-cyclohexene and 4-vinyl-1-cyclohexene. The kinetic parameters such as stirring speed, substrate amount, sodium hydroxide concentration and temperature were found to influence the rate constant (k_{obs}) values remarkably.

The energy of activation (E_a) and other thermodynamic parameters such as ΔS^\ddagger , ΔG^\ddagger and ΔH^\ddagger were evaluated for the dichlorocarbene addition to 3-methyl-1-

cyclohexene and 4-vinyl-1-cyclohexene from the experimental evidence; it is obvious that the reaction follows an interfacial reaction mechanism. The tri-site phase transfer catalyst MPTC-I, exhibits higher reactivity than the conventional MPTC-II and single-site PTC (BTEAB).

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