

Phase transfer catalysis: Kinetics and mechanism of hydroxide ion initiated dichlorocarbene addition to styrene catalysed by triethylbenzylammonium chloride[†]

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Abstract. The kinetics of dichlorocarbene addition to styrene was studied under phase-transfer catalytic conditions using aqueous sodium hydroxide as the base and triethylbenzyl ammonium chloride as the phase-transfer catalyst. The reaction was carried out at 40°C under pseudo first-order condition by keeping aqueous sodium hydroxide and chloroform in excess. The progress of the reaction was monitored by gas chromatography. The effects of various experimental conditions on the rate of the reaction were studied and based on the results obtained a suitable mechanism has been proposed.

Keywords. Phase-transfer catalysis; dichlorocarbene addition; styrene.

1. Introduction

The catalytic effect of lipophilic quaternary ammonium and phosphonium salts in aqueous–organic reaction systems has solved the problems normally associated with two-phase reactions (Weber and Gokel 1977; Starks and Liotta 1978; Montanari *et al* 1982; Dehmlow and Dehmlow 1983). This type of phase transfer catalysis (PTC) has been extensively applied in the synthesis of a wide variety of organic compounds by displacement, alkylation, arylation, addition, oxidation, reduction, elimination, condensation and free radical polymerization. The advantages of soluble PTC include fast reaction rate at mild experimental conditions, high selectivity of the product, moderate operating temperature, saving on expensive anhydrous aprotic solvents, use of aqueous sodium hydroxide instead of alkali metal alkoxide and applicability to industrial production.

In phase-transfer catalysis, the role of the catalyst is to extract the reactive anion from an aqueous phase into organic phase (Starks and Owens 1973; Herriott and Picker 1975; Landini *et al* 1978). In such systems the effectiveness of phase-transfer catalyst was shown to depend mainly on the organophilicity of the catalyst with other structural factors which are much less important. In contrast the hydroxide ion-initiated reactions performed under PTC conditions attain maximum reactivity generally with catalysts of low organophilicity (Dockx 1973; Dehmlow and Lissel 1976). Among the

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phase transfer catalysts, quaternary ammonium ions are inexpensive, readily available, highly effective and stable in strong alkaline medium.

Investigations were carried out on dichlorocarbene addition reactions conducted in aqueous-organic two-phase systems in the presence of an onium phase-transfer catalyst. C-H insertion reactions of dichlorocarbene generated from potassium tertiary butoxide and chloroform or with sodium methoxide/trichloroacetic ester were rare and gave poor yields. But dichlorocarbene generated in phase-transfer catalysis from chloroform, concentrated sodium hydroxide and triethylbenzylammonium chloride (TEBA) displayed an enhanced reactivity since it is formed in the immediate vicinity of the substrate and is less likely to undergo undesirable side reactions with the solvent or with itself.

Dihalocyclopropanes are very useful compounds from which many other important organic compounds such as cyclopropanes, allenes etc., are prepared. So far no report is available on the kinetics of dichlorocarbene addition to styrene giving cyclopropane. In this paper we report a systematic kinetic investigation on the dichlorocarbene addition to styrene under PTC/OH⁻ conditions and discuss the mechanistic implications of the results. We have studied the effects of various experimental parameters, viz., stirring speed, substrate amount, catalyst amount, concentration of sodium hydroxide and temperature, on the rate of the reaction. Further it was our interest to compare the activity of the soluble phase-transfer catalyst with the insoluble polystyrene-bound triethylbenzylammonium chloride under biphasic and triphasic conditions respectively in the reaction of dichlorocarbene addition to styrene. The activity of the recovered triphasic catalyst was also investigated and compared with that of the original catalyst.

2. Experimental

2.1 *Synthesis of polymer-supported triethylbenzylammonium chloride*

Crosslinked poly(styrene-co-vinylbenzyl chloride) was prepared in well-defined bead form following a modified suspension copolymerization literature procedure (Balakrishnan and Ford 1982). A 50 g sample of sieved copolymer was swelled in 150 ml of acetonitrile in a 250 ml three-necked flask fitted with a condenser, thermometer and nitrogen inlet. 20 ml of triethylamine was added quickly to the reaction flask. The whole set-up was placed in an oil bath over a magnetic stirrer. Nitrogen was passed for about 30 minutes. The mixture was refluxed at 80°C for 48 h with continuous sweep of nitrogen into the reaction flask. The catalyst was filtered, washed with acetonitrile, methanol, acetone and anhydrous methanol and dried in vacuum at 60°C.

2.2 *Typical kinetic experiments*

In a 150 ml three-necked round bottomed flask, 20 ml of 40% w/w aqueous NaOH, 44.4 mg (1.5 mol% based on substrate) of the catalyst and 10 ml (124.98 mmol) of chloroform were added. The contents were conditioned for about 10 minutes at 40°C and 1 ml of hexadecane was added as an internal standard. The reaction mixture was stirred very slowly by a mechanical stirrer. 1.5 ml of styrene preheated to 40°C was

added to the reaction mixture. The instant of half-delivery of styrene was taken as the zero time. The stirring speed was increased to 500 rpm by adjusting the speed with the tachometer. Phase separation was almost immediate after stopping the stirring. The samples were collected from the organic layer at regular intervals of time. A pinch of anhydrous CaCl_2 was taken in the sample tubes to absorb the moisture present in the organic layer if any. Samples were analysed using a gas chromatograph (Varian 3700 model, vista CDS 401 data system, with thermal conductivity detector) at 180°C (column temperature) (5% SE-30 Chrom WHP 80×100 , $2\text{m} \times 1/8''$ stainless column). The reaction was followed by estimating the disappearance of styrene, for which the retention time was 0.58 min.

The retention times for other compounds were found to be chloroform–0.43 min, 1-phenyl-2,2-dichlorocyclopropane–1.35 min, and hexadecane–3.70 minutes. The reaction was followed upto 88% conversion.

A similar procedure was adopted for the experiment carried out with the triphase catalyst using 237 mg of the insoluble polystyrene-supported triethylbenzylammonium chloride catalyst.

3. Discussion

The reaction of styrene with chloroform in the presence of aqueous sodium hydroxide and catalytic amount of triethylbenzylammonium chloride was carried out under pseudo first-order conditions taking chloroform and aqueous sodium hydroxide in excess. Since triethylbenzylammonium chloride (TEBA) was found to be an optimum catalyst for alkylation and carbene addition reactions (Starks and Liotta 1978), the catalyst structure was not varied in the reaction.

In general, the functional groups of the quaternary cation affect the dissolution of the catalyst in the organic phase. Further, the phase-transfer of the anion also affects the reaction rate in the two-phase reaction. Therefore, a proper choice of phase-transfer catalyst is very important in promoting the reaction rate. Unfortunately, a universal guideline is not available for selecting the proper phase-transfer catalyst to enhance the reaction rate. Thus common phase-transfer catalyst, triethylbenzylammonium chloride, was employed in our present study.

The kinetic profile of the reaction was run under varying conditions of stirring speed, catalyst concentration, aqueous sodium hydroxide concentration, substrate concentration and temperature.

All the reactions were carried out at a stirring speed of 500 rpm and at 40°C unless otherwise mentioned.

Standard reaction conditions were studied by taking 20 ml of 40% w/w aqueous sodium hydroxide (14.2 M), 44.4 mg of triethylbenzylammonium chloride (1.5 mole% based on the substrate), 10 ml of chloroform (124.98 mmol) and 1.5 ml of styrene (13.09 mmol). The kinetics of the reaction was monitored by a gas chromatograph using the internal standard method. The observed rate constants are evaluated from the plots of $\log(a-x)$ vs time and are presented for each variation.

Since the ratio of styrene to chloroform in the organic phase of the reaction mixture is 1:10 and since styrene is very soluble in chloroform, no loss of styrene was noticed during the experiments. It is very clear from the control experiment that the loss of styrene is $< 1\%$. The best first-order plots obtained confirm the above fact.

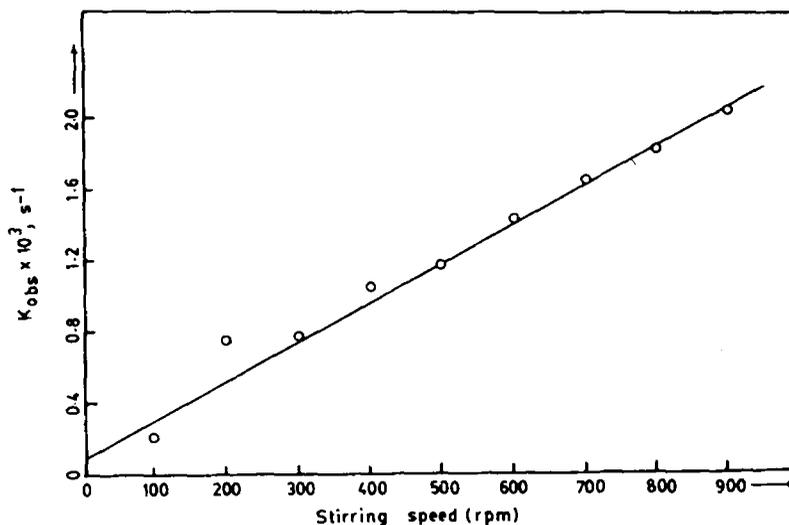


Figure 1. Effect of stirring speed on observed rate constant.

3.1 Effect of stirring speed

The effect of stirring speed on the rate of dichlorocarbene addition to styrene was studied in the rate of 0–900 rpm in the presence of 44.4 mg of triethylbenzylammonium chloride as catalyst and 20 ml of 40% w/w aqueous sodium hydroxide. 1.5 ml of styrene (13.09 mmol) was added at zero time. The rate of the reaction increases sharply with increase in stirring speed (figure 1). From the plots of $\log(a-x)$ vs time, the pseudo first-order rate constants are evaluated. At zero rpm, the reaction rate is comparatively slower than at higher stirring speeds. The increased rates are attributed to the increase in the interfacial area. The strong rate dependence on the speed of stirring is a clear indication of the interfacial mechanism. The other kinetic experiments were conducted at 500 rpm in order to get reproducible results. Similar observations were reported (Chiellini *et al* 1980) for the heterogeneous ethylation of phenylacetonitrile in aqueous organic medium in the presence of tetrabutylammonium bromide. The rate of the reaction increased steadily with increase in the stirring speed from 35 to 1950 rpm. These observations support the interfacial mechanism. Contrary to the observations reported above, Rabinovitz *et al* (1983) studied the kinetics of isomerization of allylbenzene under phase transfer catalysis conditions and observed that the reaction rate increases with increase in the stirring speed upto 300 rpm and thereafter the rate becomes independent of stirring speed. This observation supports the hydroxide ion extraction mechanism.

3.2 Catalyst amount

The effect of variation of the amount of the catalyst on the rate of dichlorocarbene addition to styrene was studied by varying the amount of the catalyst from 14.8 to 74.0 mg (0.5 to 2.5 mol% based on the substrate). The rate of the reaction is directly proportional to the amount of the catalyst added. A bilogarithmic plot of the observed rate constant against the concentration of the catalyst gives a straight line over a

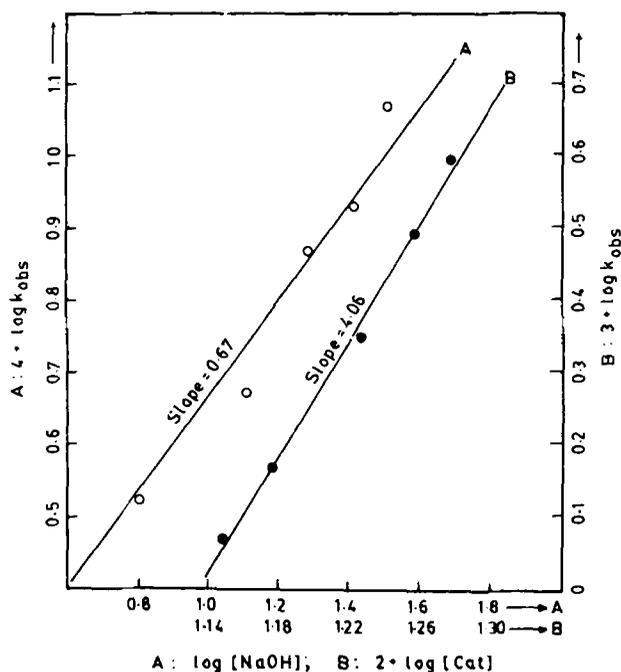


Figure 2. Effect of [NaOH] and catalyst amount on the observed rate constant.

wide range of concentrations and the slope is found to be 0.67 (figure 2). The increased rates are due to the increase in the number of active sites. Control experiment was carried out in the absence of the catalyst under similar conditions and less than 1% conversion was observed within three hours. This fact also supports the interfacial mechanism. A similar observation was reported in the alkylation of phenyl acetonitrile (Makosza and Bialecka 1977). The slope of 0.67 suggests that the chemical reaction between the ion pair and the organic substrate is not the sole rate determining step.

3.3 Sodium hydroxide concentration

The reaction rates were measured at different concentrations of NaOH ranging from 14.2 to 19.0 M. The observed rate constants increase with increase in NaOH concentration. A bilogarithmic plot of the reaction rate against NaOH concentration gives a straight line having a slope of 4.0 (figure 2). The drastic increase in the reaction rate is due to the increase in the basicity of the hydroxide ion (Chiellini *et al* 1980).

Recently a study on the efficiency of different bases for the alkylation of benzamide has been reported (Dehmlow and Lissel 1978). The effect of NaOH concentration on the heterogeneous ethylation of phenylacetonitrile was reported by Chiellini *et al* (1980). The order with respect to NaOH concentration was found to be 5.3 in the concentration range 11–19 M.

3.4 Substrate amount

Kinetic experiments were performed by varying the amount of styrene from 1.0 to 1.5 ml (8.73 to 13.09 mmol) maintaining the other reactants such as chloroform (10 ml)

and 40% aqueous NaOH (14.2 M) in excess. The observed pseudo first-order rate constants decrease as the amount of the substrate increases. These results suggest that the concentration of the substrate in organic phase is not important and that at the interface may be vital. The kinetics are not simple with respect to substrate in the reaction in which the interfacial mechanism is operative (Dehmlow and Baharona Naranjo 1982; Halpern *et al* 1984).

3.5 Effect of temperature

The effect of temperature on the rate of dichlorocarbene addition to styrene was studied by employing 44.4 mg of the catalyst at 500 rpm taking aqueous NaOH and chloroform in excess. The kinetic profile was studied by keeping the temperature at 30, 35, 40 and 45°C. The observed rate constants increase with temperature. The activation energy is evaluated from the plot of $\log k$ vs $1/T$ (figure 3) and is found to be $10.4 \text{ kcal mol}^{-1}$. The other thermodynamic parameters, viz. ΔS^\ddagger and ΔG^\ddagger , are evaluated as -38.9 eu and $21.8 \text{ kcal mol}^{-1}$ respectively.

The energy of activation for the heterogeneous ethylation of phenylacetonitrile was reported to be 20 kcal mol^{-1} and for this an interfacial mechanism was proposed (Chiellini *et al* 1980). The energy of activation for the dehydrobromination of (2-bromoethyl)-benzene in the presence of tetraoctylammonium bromide was reported to be 8 kcal mol^{-1} and for this the extraction mechanism was proposed (Halpern *et al* 1984).

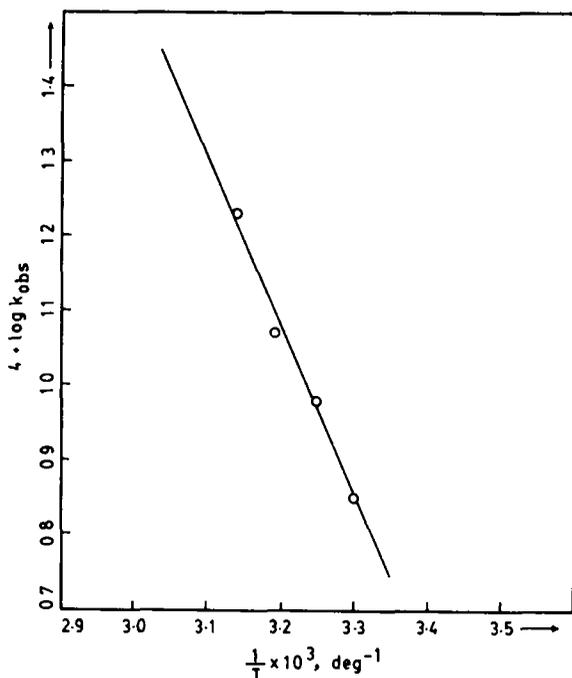


Figure 3. Arrhenius activation energy.

Table 1. Comparison of biphase and triphase reaction rates.

Catalyst	$k_{\text{obs}} \times 10^5 (\text{s}^{-1})$
Soluble triethylbenzylammonium chloride	118.00
Insoluble polystyrene bound triethylbenzylammonium chloride	2.99
Recovered insoluble catalyst	2.18

3.6 Polymer-supported triethylbenzylammonium chloride

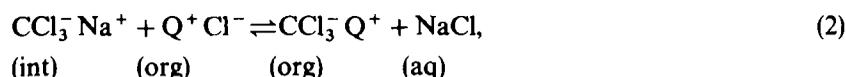
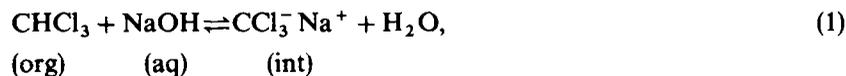
An experiment was carried out using microporous, insoluble polystyrene-supported triethylbenzylammonium chloride under triphase conditions. 2% crosslinked, -200 mesh, 18–20% ring substituted catalyst was used. The other experimental parameters were maintained as for biphase conditions. The catalyst activity of the triphase catalyst was evaluated from the plot of $\log(a-x)$ vs time and compared with that of biphase reaction (table 1). From the table it may be observed that the triphase reaction rate is nearly 40 times slower than that of the biphase system. The slower rate was attributed to the diffusional limitations of the rates in the triphase reactions (Ford and Tomoi 1984).

One of the most important advantages of a triphase catalyst over the two-phase catalyst is that it can be easily separated from the reaction mixture by simple filtration and it can be recycled. The catalytic activity of the recovered catalyst is compared with that of the original catalyst for a single run (table 1). The activity of the recovered catalyst is slightly lower than that of the original catalyst. The ratio of rate constant with the recovered catalyst to the rate constant with the original catalyst i.e. k_r/k_o was found to be 0.73. The decrease in the activity of the recovered catalyst may be due to the loss of active sites both during the reaction and during drying in the hydroxide form at 60°C.

A similar decrease in the activities of the recovered catalysts was reported by Balakrishnan and Ford (1983) and Balakrishnan *et al* (1990) for the reaction of benzylcyanide with 1-bromobutane catalysed by 50% aqueous NaOH and polystyrene-bound trimethylbenzylammonium chloride and polystyrenebound triethylbenzylammonium chloride.

4. Mechanism

The generation and reaction of carbene with styrene may be represented as follows:



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