

Novelties of solid–liquid phase transfer catalysed synthesis of *p*-toluenesulfonyl fluoride from *p*-toluenesulfonyl chloride

Ganapati D. Yadav*, Priyanvada M. Paranjape

Department of Chemical Engineering, University Institute of Chemical Technology,
University of Mumbai, Matunga, Mumbai 400019, India

Received 5 September 2004; received in revised form 12 October 2004; accepted 13 October 2004
Available online 2 February 2005

Abstract

Organic sulfonyl fluorides are of interest owing to their insecticidal, germicidal and enzyme inhibitory properties. In the current work, synthesis of *p*-toluenesulfonyl fluoride was accomplished by reacting *p*-toluenesulfonyl chloride with solid potassium fluoride using PEG-400 as a catalyst under solid–liquid phase transfer catalysis (S–L PTC) at 30 °C. *p*-Toluenesulfonyl fluoride is used as peroxygen bleach activator. It also finds use in the treatment of Alzheimer's disease. The mechanism is based on homogeneous solubilization of solid. PEG forms a complex with metal cation which associates with the nucleophile and it participates in SN₂ type reactions. The reaction is intrinsically kinetically controlled. A complete theoretical analysis is done to determine both the rate constant and equilibrium constant from the same set of data. The activation energy and Gibbs free energy are also calculated.

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Keywords: Solid–liquid phase transfer catalysis; *p*-Toluenesulfonyl fluoride; KF; PEG-400; Rate constant; Equilibrium constant; Modeling

1. Introduction

Organic sulfonyl fluorides are of interest owing to their insecticidal, germicidal and enzyme inhibitory properties. *p*-Toluenesulfonyl fluoride is used as peroxygen bleach activator. It also finds use in the treatment of Alzheimer's disease. There are several routes for manufacture of organic sulfonyl fluorides, most of which involve halogen exchange (i.e., conversion of the corresponding sulfonyl chloride to the sulfonyl fluoride). Boiling of a sulfonyl chloride with an aqueous solution of potassium fluoride will not work for water sensitive compounds. Other synthesis include: (a) refluxing the corresponding sulfonyl chloride and potassium fluoride in a cosolvent system (e.g., dioxane/water) (70% yield), (b) addition of sodium nitrite to a solution of the corresponding sulfonamide in anhydrous hydrogen fluoride (53–78%) and (c) heating the sulfonyl chloride with sodium fluoride suspended in tetramethylenesulfone, acetonitrile or

dimethylformamide (62–72%) [1]. All of these methods give low yield of the compound. On the other hand, if hydrogen fluoride is used as fluorinating agent, it has been reported that with sulfonyl chlorides, the reaction had to be carried out under pressure and at elevated temperature for a longer period. Due to high reaction temperatures required, substantial amounts of energy must be employed when the processes are carried out on an industrial scale.

We would like to report a very facile and convenient method (which generates a naked fluoride anion) to synthesize *p*-toluenesulfonyl fluoride at room temperature. Further, a general modeling method is devised by which it would be possible to determine the rate constant and also the overall equilibrium constant using the same set of data.

Phase transfer catalysis (PTC) has matured to over 600 industrial processes in a variety of industries such as intermediates, dyestuffs, agrochemicals, perfumes, flavours, pharmaceuticals and polymers [2–4]. A large number of PTC processes use the liquid–liquid (L–L) mode of operation. One of the ways to suppress by-product formation and also intensify the rates of reactions of L–L PTC is through the use of solid–liquid phase transfer catalysis (S–L

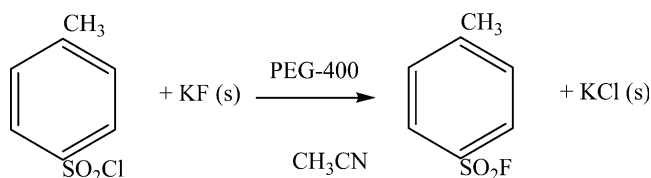
* Corresponding author. Tel.: +91 22 2410 2121; fax: +91 22 2414 5614.

E-mail addresses: gdyadav@yahoo.com, gdyadav@udct.org
(G.D. Yadav).

PTC). The aqueous phase promoted reactions can thus be totally suppressed and better selectivities obtained. While L–L PTC involves heterogeneous reaction between two reagents located in an aqueous, and an organic phase, S–L PTC involves reaction of an anionic reagent in a solid phase (usually a salt) with a reactant located in a continuous organic phase. Yadav and Sharma [5] proposed the first mechanistic and kinetic model of solid–liquid PTC followed by Naik and Doraiswamy [6]. We have carried out the detailed mechanistic and modelling studies for industrially important reactions under S–L PTC conditions [7,8]. The role of small amounts of water, the so-called omega phase, in S–L PTC was analysed in our earlier work [9] including others [2–4] and a rigorous model of S–L PTC with omega phase has been established [9].

2. Results and discussion

The reaction scheme is given by

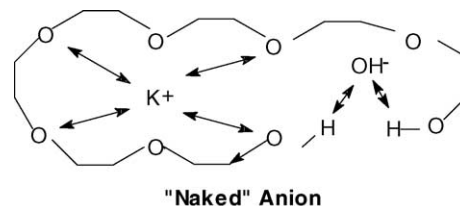


Preliminary experiments established that the reaction was facile at 30 °C. To understand the enhanced rates of reaction under these conditions, it was thought worthwhile to study the mechanism and kinetics of this reaction. Since a typical experiment produced 90% conversion of *p*-toluenesulfonyl chloride, with 100% selectivity to the fluoride, a further insight was obtained by studying the effect of various parameters on the rates of reaction.

2.1. Mechanism and kinetic model

Polyethylene oxide chains form complexes with cations, much like crown ethers, and these complexes cause the anion to be transferred into the organic phase and to be activated [10]. Complexation of solid alkali metal salts by PEG is strongly dependent on both the anion and the cation of the salt [11]. The phase transfer catalytic efficiencies of polyethylene glycols were proven and analyzed [12]. It was observed that best catalytic efficiencies were obtained by using medium chain length PEG ($n = 7-9$).

The first step of the reaction involves the complexation of PEG with metal cation [K^+] (Scheme 1) and forms [$PEG K^+F^-$], which is organophilic and is freely transported to the bulk organic phase. There could be a resistance associated with the transfer of this complex across the liquid film next to solid–liquid interface. The second

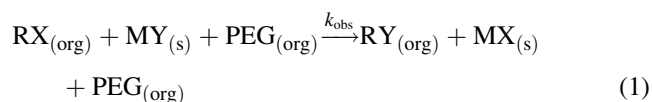


Scheme 1. Complex of PEG with metal cation K^+ .

step involves the reaction of the [$PEG K^+F^-$] with the reactant [RX] located in the organic phase. There are several possibilities by which this reaction can occur. Finally, the third step involves the transport of the co-product anion [X^-], the leaving group to the solid and the transport of another nucleophile [F^-] into the organic phase. In the current case, the S–L PTC mechanistic description is the implication that the reaction takes place in anhydrous condition, since both solid and liquid phases were dry. So the formation of the omega phase was discounted. There are two types of mechanisms for S–L PTC, the homogeneous solubilization mechanism of Yadav and Sharma [5] and heterogeneous solubilization of Naik and Doraiswamy [6]. In the heterogeneous solubilization, the particles are totally insoluble and the catalyst get adsorbed on to the solid whereas in the case of homogeneous solubilization model, the particles are sparingly soluble in the organic phase and the particle solubility is augmented by the phase transfer agent [PEG]. The particle size goes on decreasing with time due to the reaction in the organic phase. Depending on the relative rate of transfer of [$PEG K^+F^-$] in the organic film next to the solid and the reaction of the species, four different regimes can be identified just like the L–L PTC. [13] These are shown in Fig. 1 and the importance of various steps is delineated in the captions.

Preliminary experiments suggested that the homogeneous solubilization model illustrated by the SN_2 type of reaction of the substrate RX with the nucleophile Y of the solid reactant MY .

The overall reaction is:



The solid reactant is in equilibrium with its solution in the organic phase. This is the solubility of KF in the solvent in the presence of the catalyst. It was obtained by taking a large and known amount of KF in the solvent and catalyst and stirring for 1 h and then filtering the solution under vacuum and weighing the dry solids again. It was obtained $2.62 \times 10^{-5} \text{ mol/cm}^3$. In the absence of the catalyst the solubility was less.



This represents saturation solubility of the solid in organic liquid.

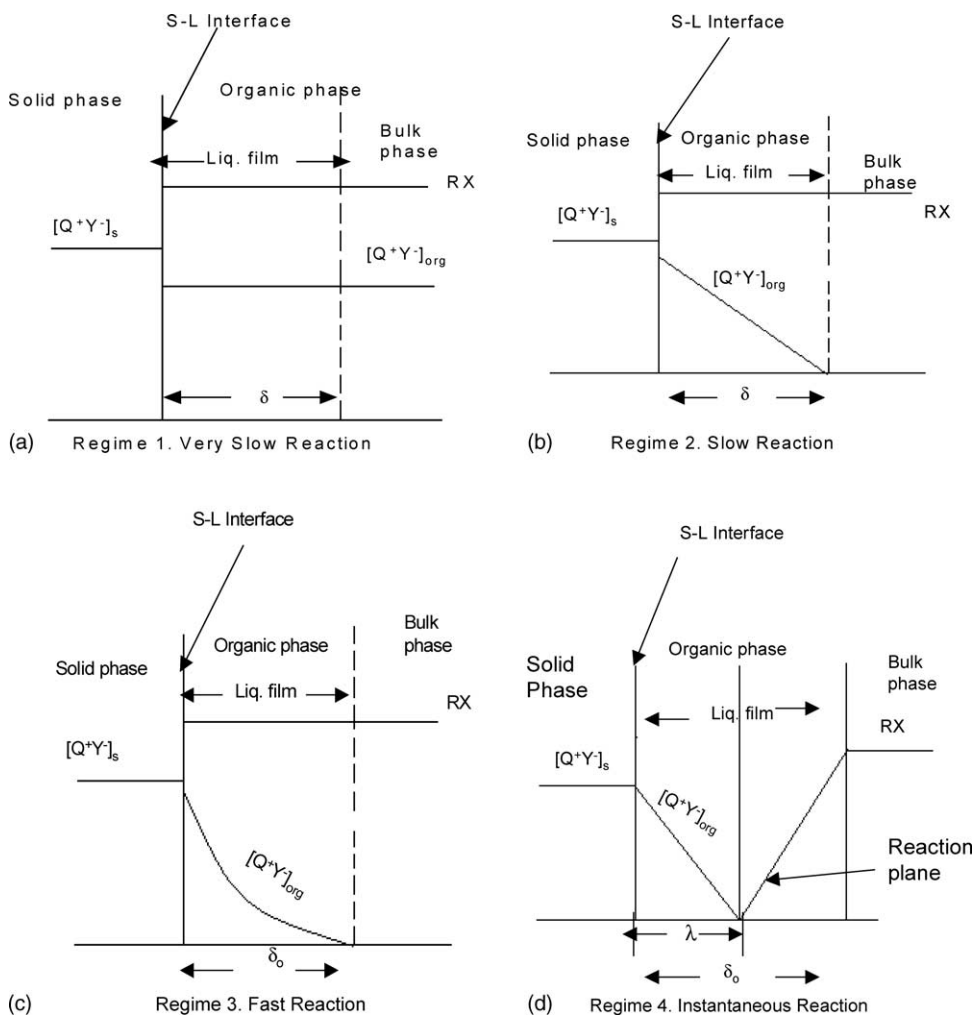
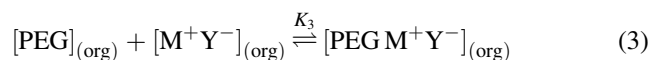
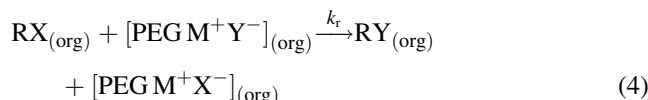


Fig. 1. Typical S–L PTC under homogeneous solubilization. (a) Regime 1: very slow reaction. The reaction occurs in the bulk organic phase as a homogeneous reaction. Mass transfer effects are unimportant. (b) Regime 2: slow reaction. The reaction occurs in the bulk organic phase. No free concentration of ion pairs exists in the bulk organic phase. (c) Regime 3: fast reaction. Diffusion of $[Q^+Y^-]_{org}$ and its reaction with RX are steps in parallel, and the reaction occurs in the organic liquid film next to the S–L interface. (d) Regime 4: instantaneous reaction. The reaction between $[Q^+Y^-]_{org}$ and RX is so fast that they cannot coexist in the organic phase. $[Q^+Y^-]_{org}$ diffuses from the L–L interface, and RX diffuses from the bulk organic phase into the organic liquid film and react at a plane from the interface. No free $[Q^+Y^-]_{org}$ exists beyond distance λ and no free RX exists beyond distance $(\delta_0 - \lambda)$ toward the interface. Note that for simplicity other ion pairs are not shown.

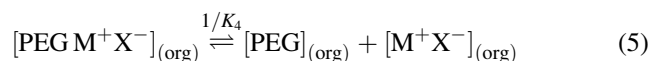
PEG forms the complex with metal cation M^+



The substance RX reacts with the complex $[PEG M^+Y^-]_{(org)}$ according to



where k_r is rate constant.



PEG is thus generated repeatedly to catalyze the reaction.

The equilibrium constant, K_e , which is a sort of a solubility parameter is defined by combining steps (2), (3), (5) and (6) as follows:

$$K_2 = \frac{[M^+Y^-]_{(org)}}{[MY]_s} \quad (7)$$

$$K_3 = \frac{[PEG M^+Y^-]_{(org)}}{[PEG][M^+Y^-]_{(org)}} \quad (8)$$

$$\frac{1}{K_4} = \frac{[PEG][M^+X^-]_{(org)}}{[PEG M^+X^-]_{(org)}} \quad (9)$$

$$K_5 = \frac{[MX]_s}{[M^+X^-]_{(org)}} \quad (10)$$

$$K_e = \frac{K_2 K_3 K_5}{K_4} = \frac{[\text{PEG M}^+ \text{Y}^-]_{(\text{org})} [\text{MX}]_s}{[\text{MY}]_s [\text{PEG M}^+ \text{X}^-]_{(\text{org})}} \quad (11)$$

$$[\text{PEG M}^+ \text{Y}^-]_{(\text{org})} = K_e \frac{[\text{MY}]_s}{[\text{MX}]_s} [\text{PEG M}^+ \text{X}^-]_{(\text{org})} \quad (11)$$

The rate of reaction of Eq. (4) is given by

$$\frac{-d[\text{RX}]_{(\text{org})}}{dt} = k_r [\text{RX}]_{(\text{org})} [\text{PEG M}^+ \text{Y}^-]_{(\text{org})} \quad (12)$$

$$\frac{-d[\text{RX}]_{(\text{org})}}{dt} = k_r K_e \frac{[\text{MY}]_s}{[\text{MX}]_s} [\text{RX}]_{(\text{org})} [\text{PEG M}^+ \text{X}^-]_{(\text{org})} \quad (13)$$

But

$$\begin{aligned} Q_0 &= [\text{PEG M}^+ \text{Y}^-]_{(\text{org})} + [\text{PEG M}^+ \text{X}^-]_{(\text{org})} \\ &= \text{Total concentration of catalyst in organic phase} \end{aligned} \quad (14)$$

$$[\text{PEG M}^+ \text{X}^-]_{(\text{org})} = [Q_0 - [\text{PEG M}^+ \text{Y}^-]_{(\text{org})}] \quad (15)$$

$$\begin{aligned} [\text{PEG M}^+ \text{Y}^-]_{(\text{org})} &= K_e \frac{[\text{MY}]_s}{[\text{MX}]_s} Q_0 \\ &\quad - [\text{PEG M}^+ \text{Y}^-]_{(\text{org})} \end{aligned} \quad (16)$$

$$[\text{PEG M}^+ \text{Y}^-]_{(\text{org})} = [Q_0 - [\text{PEG M}^+ \text{Y}^-]_{(\text{org})}] R \quad (17)$$

$$[\text{PEG M}^+ \text{Y}^-]_{(\text{org})} = \frac{Q_0 R}{1 + R} \quad (18)$$

$$R = K_e \frac{[\text{MY}]_s}{[\text{MX}]_s} \quad (19)$$

The fractional conversion of RX at time t is defined by:

$$X_A = \frac{N_{\text{RX}0} - N_{\text{RX}}}{N_{\text{RX}0}} \quad (20)$$

where $N_{\text{RX}0}$ are the initial moles of RX at time $t = 0$.

Let $M = \frac{N_{\text{MY}0}}{N_{\text{RX}0}}$ = initial molar ratio of solid reactant (MY) to organic substrate (RX) (21)

By substituting these terms in Eq. (13), the following is obtained:

$$\left(\frac{1+R}{R} \right) \frac{dX_A}{1-X_A} = k_r Q_0 t \quad (21)$$

Substituting for R , $[\text{MX}]_s$ and $[\text{MY}]_s$ in terms of X_A and M , and then separation of variable in Eq. (21) leads to:

$$\int_0^{X_A} \left[\frac{X_A + K_e M - K_e X_A}{K_e (M - X_A)(1 - X_A)} \right] dX_A = k_r Q_0 t \quad (22)$$

This integral is solved by the method of partial fractions to get the following:

$$\begin{aligned} \left(\frac{M}{M-1} \right) \ln \left(\frac{M-X_A}{M} \right) - \left(\frac{1-K_e+K_e M}{M-1} \right) \\ \ln(1-X_A) = k_r Q_0 t, \quad \text{for } M \neq 1 \end{aligned} \quad (23)$$

Eq. (12) can be further manipulated to the following to extract both K_e and k_r :

$$\begin{aligned} \left[\frac{\ln \left(\frac{M-X_A}{M} \right)}{\ln(1-X_A)} \right] - \left[\frac{1-K_e+K_e M}{M} \right] \\ = \left[\frac{(M-1)k_r Q_0}{M} \right] \frac{t}{\ln(1-X_A)} \end{aligned} \quad (24)$$

A plot of $\left[\frac{\ln \left(\frac{M-X_A}{M} \right)}{\ln(1-X_A)} \right]$ versus $\frac{t}{\ln(1-X_A)}$ should give

$$\begin{aligned} \text{slope} &= \left[\frac{(M-1)k_r Q_0}{M} \right] \text{ and intercept} \\ &= \left[\frac{(M-1)K_e + 1}{M} \right] \end{aligned} \quad (25)$$

Thus, both K_e and k_r can be obtained from the slope and intercept from the knowledge of M and Q_0 . Further for equimolar quantities of substrate and nucleophile, the following form of the integrated equation results:

$$\begin{aligned} \left(\frac{X_A}{1-X_A} \right) + (1-K_e) \ln(1-X_A) = k_r Q_0 t, \\ \text{for } M = 1 \end{aligned} \quad (26)$$

Eq. (15) can also be manipulated to the following:

$$\left(\frac{X_A}{1-X_A} \right) = k_r Q_0 \frac{t}{(1-X_A)} + (K_e - 1) \quad (27)$$

A plot of $\left[\frac{\left(\frac{X_A}{1-X_A} \right)}{\ln(1-X_A)} \right]$ versus $\frac{t}{\ln(1-X_A)}$ will give a straight line

with slope equal to $k_r Q_0$ and intercept equal to $(K_e - 1)$. The validation of the above model was verified by conducting several experiments.

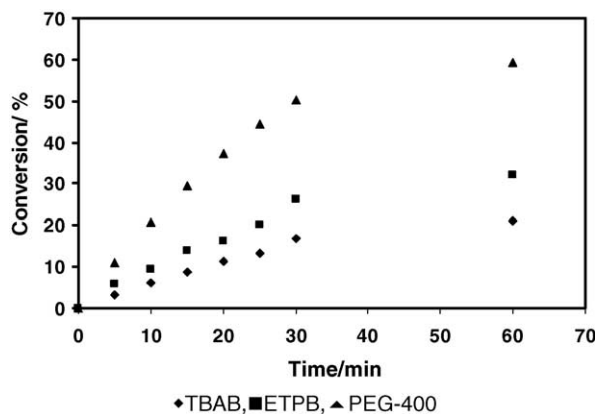


Fig. 2. Effect of different catalysts. *p*-Toluenesulfonyl chloride, 0.02 mol; KF, 0.04 mol; speed, 1500 rpm; acetonitrile, 46 ml; temperature, 30 °C, time, 90 min.

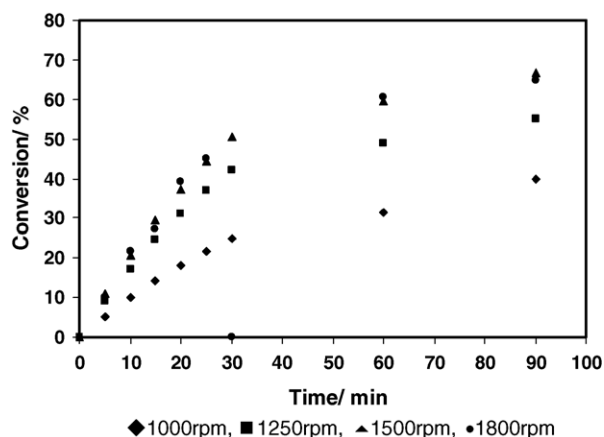


Fig. 3. Effect of speed of agitation. *p*-Toluenesulfonyl chloride, 0.02 mol; KF, 0.04 mol; PEG-400, 0.8 g; acetonitrile, 46 ml; temperature, 30 °C; time, 90 min.

2.2. Effect of various catalysts

Different catalysts such as tetrabutyl ammonium bromide (TBAB), ethyl triphenyl phosphonium bromide (ETPB) and PEG-400 were selected for the reaction under otherwise similar concentration of catalyst at 30 °C and 1500 rpm (Fig. 2). Out of these PEG-400 gave maximum rates of reaction and conversion. It was conjectured that the ineffectiveness of the quaternary salt in the overall reaction process was due to the absence of chelating heteroatom which can favour the process of removing ion pair from solid matrix. Apart from high reactivity of PEG-400 as compared to others it is very cheap (Rs. 160 kg⁻¹). Thus, further experiments were conducted with PEG-400. The selectivity to the product *p*-toluenesulfonyl fluoride was 100%.

2.3. Effect of speed of agitation

The reaction was carried out at four different speeds of agitation (Fig. 3) with PEG-400 as catalyst. There was a significant increase in the conversion from 1000 to 1500 rpm. But it was almost constant at 1500 and 1800 rpm. All

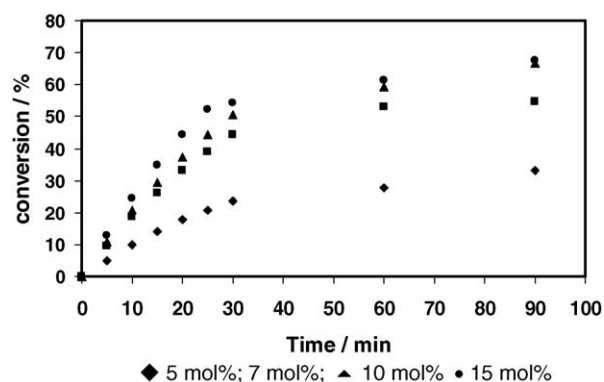


Fig. 4. Effect of catalyst loading. *p*-Toluenesulfonyl chloride, 0.02 mol; KF, 0.04 mol; speed, 1500 rpm; acetonitrile, 46 ml; temperature, 30 °C; time, 90 min.

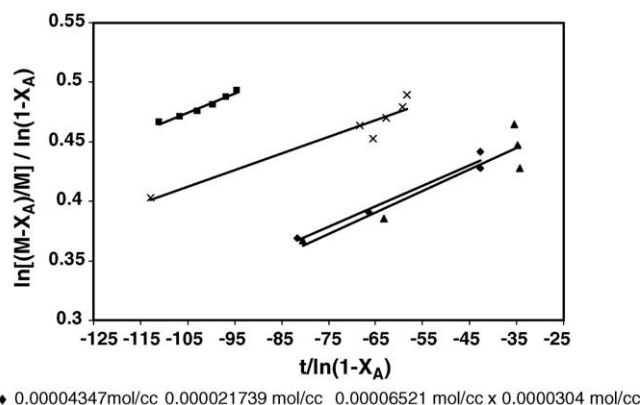


Fig. 5. Determination of k_t and K_e values. *p*-Toluenesulfonyl chloride, 0.02 mol; KF, 0.04 mol; speed, 1500 rpm; acetonitrile, 46 ml; temperature, 30 °C; time, 90 min; k_t , 77.1 cm³ mol⁻¹ min⁻¹; K_e , 0.11.

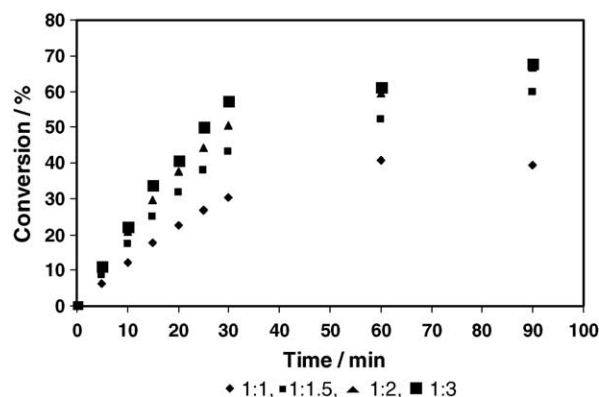


Fig. 6. Effect of mole ratio of *p*-toluenesulfonyl chloride to KF. *p*-Toluenesulfonyl chloride, 0.02 mol; PEG-, 0.8 g; speed, 1500 rpm; acetonitrile, 46 ml; temperature, 30 °C; time, 90 min.

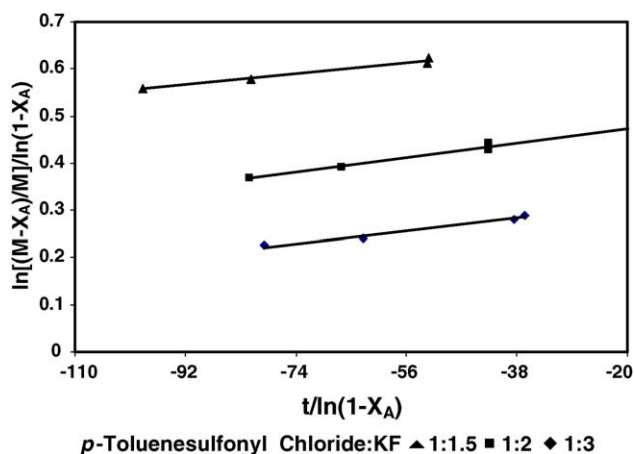


Fig. 7. Validation of the model. *p*-Toluenesulfonyl chloride, 0.02 mol; PEG-, 0.8 g; speed, 1500 rpm; Acetonitrile, 46 ml; Temperature, 30 °C; Time, 90 min.

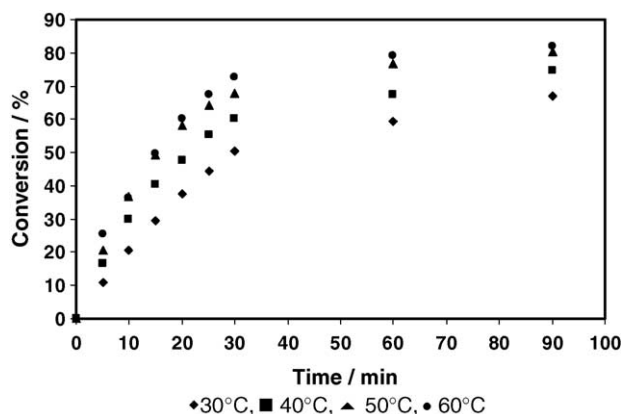


Fig. 8. Effect of temperature. *p*-Toluenesulfonyl chloride, 0.02 mol; KF, 0.04 mol; PEG-400, 0.8 g; speed, 1500 rpm; Acetonitrile, 46 ml; Time, 90 min.

subsequent reactions were carried out with 1500 rpm while assessing the effect of other variables on the rate of reaction.

The observed initial rate of reaction for a typical experiment was equal to $1.6667 \times 10^{-7} \text{ mol cm}^{-3} \text{ s}^{-1}$ whereas the rate of mass transfer was estimated from the knowledge of solid–liquid mass transfer coefficient ($k_{\text{SL-A}}$), particle surface area ($a_{\text{P}} = 611.20 \text{ cm}^{-1}$) and the solubility of potassium fluoride in acetonitrile was measured as $2.62 \times 10^{-5} \text{ mol/cm}^3$. The solid–liquid mass transfer coefficient ($k_{\text{SL-A}} = 0.199 \text{ cm/s}$) which was found from Sherwood number ($k_{\text{SL-A}} d_{\text{P}}/D_{\text{A}} = 2$). A limiting value of Sherwood number was taken as 2 since the particles were very fine. The Wilke–Chang equation was used to calculate the bulk diffusivity. The mass transfer rate was equal to $3.201 \times 10^{-3} \text{ mol cm}^{-3} \text{ s}^{-1}$ which is 1.996×10^4 times greater than the rate of reaction. Thus, the observed reaction rate was much smaller than the mass transfer rate. Therefore, there was no mass transfer resistance associated with the reaction and the reaction would be kinetically controlled.

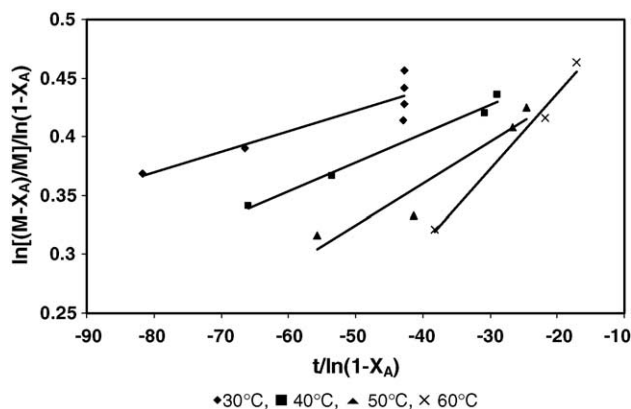


Fig. 9. Validation of model at different temperatures. *p*-Toluenesulfonyl chloride, 0.02 mol; KF, 0.04 mol; PEG-400, 0.8 g; speed, 1500 rpm; Acetonitrile, 46 ml; Time, 90 min. $k_{\text{r}} = 78.34 \text{ cm}^3 \text{ mol}^{-1} \text{ min}^{-1}$, $K_{\text{e}} = 0.019$ at 30 °C; $k_{\text{r}} = 115.2 \text{ cm}^3 \text{ mol}^{-1} \text{ min}^{-1}$, $K_{\text{e}} = 0.0018$ at 40 °C; $k_{\text{r}} = 165.09 \text{ cm}^3 \text{ mol}^{-1} \text{ min}^{-1}$, $K_{\text{e}} = 0.0044$ at 50 °C; $k_{\text{r}} = 299.03 \text{ cm}^3 \text{ mol}^{-1} \text{ min}^{-1}$, $K_{\text{e}} = 0.1324$ at 60 °C.

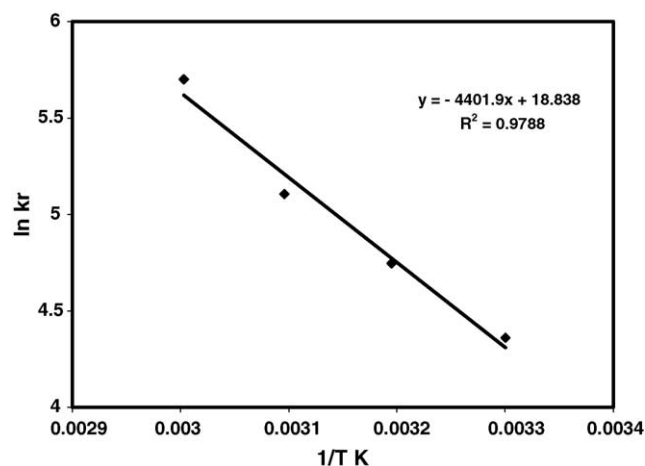


Fig. 10. Arrhenius plot for activation energy.

2.4. Effect of catalyst loading

The concentration of the catalyst was varied from 2.1739×10^{-5} to $6.521 \times 10^{-5} \text{ mol/cm}^3 \text{ org}$ (Fig. 4). It was observed that as the concentration was increased, the conversion increased, but above a concentration of $4.3447 \times 10^{-5} \text{ mol/cm}^3 \text{ org}$, there was no further increase in the conversion. The validity of Eq. (13) was tested. Appropriate plots were made for $M = 2$ as shown in Fig. 5. There is an excellent fit for different values of catalyst concentration. The average values of k_{r} and K_{e} were obtained as $77.1 \text{ cm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ and 0.11, respectively.

2.5. Effect of mole ratio

Mole ratio of *p*-toluenesulfonyl chloride to potassium fluoride (KF) was varied from 1:1 to 1:3. (Fig. 6) The catalyst loading was kept at $4.3447 \times 10^{-5} \text{ mol/cm}^3 \text{ org}$. The reaction rate was found to increase at the mole ratio of *p*-toluenesulfonyl chloride to KF from 1:1 to 1:1.5. It was observed that there is insignificant increase in the conversion at mole ratio of 1:2–1:3. This is because of the saturation of the binding sites available in PEG. So further addition of potassium fluoride does not help in enhancement of the rate of reaction. The average values of k_{r} and K_{e} were obtained as $73.216 \text{ cm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ and 0.0257, respectively. There is an excellent fit of the proposed model with the experimental data. (Fig. 7)

2.6. Effect of temperature

The effect of temperature was studied under otherwise similar reaction conditions from 30 to 60 °C (Fig. 8). It was found that the conversion increased substantially with increase in temperature. However, there was a marginal increase in conversion at 60 °C over than that at 50 °C. The same theory was again validated at all temperatures (Fig. 9). Thus, Arrhenius plot was made and the activation energy calculated as 36.59 kJ/mol (Fig. 10), which suggested that

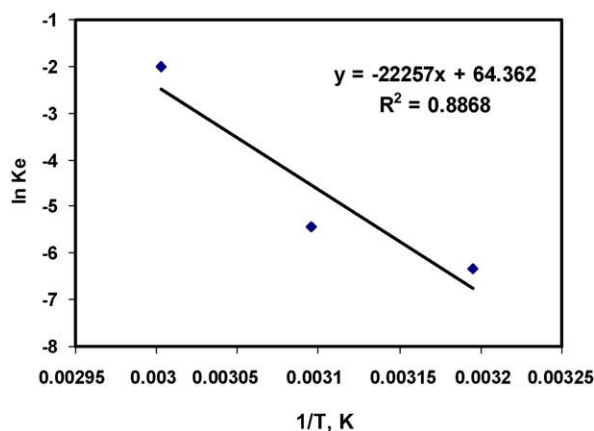


Fig. 11. Gibbs free energy plot.

the reaction was kinetically controlled. K_e is a sort of combination of solubility and distribution constant of ion pairs. The Gibbs free energy value was calculated as 185.01 kJ/mol, which shows that the equilibrium exchange of ions and solubility are thermodynamically feasible (Fig. 11).

3. Conclusion

p-Toluenesulfonyl fluoride is used as peroxygen bleach activator. It also finds use in the treatment of Alzheimer's disease. The synthesis of this compound was undertaken by using a variety of catalysts amongst which PEG-400 was found to be the best catalyst. A complete theoretical analysis of the process was carried out to explain the observed rate data. Both equilibrium constant and rate constant could be calculated from the same set of data. The apparent activation energy is 36.59 kJ/mol.

4. Experimental details

4.1. Experimental procedure

The reaction was studied in 5 cm i.d. fully baffled mechanically agitated glass reactor of 100 cm³ total capacity which was equipped with a six-blade pitched turbine impeller (1 cm diameter). The impeller was located at a distance of 2 cm from the bottom. This arrangement ensured excellent solid–liquid mixing for high mass transfer rates. The assembly was kept in a water bath to maintain the desired temperature and mechanically stirred at a known speed with an electric motor.

Typically the reaction was carried out as follows: initially potassium fluoride (0.04 mol) along with PEG-400 (0.002 mol) and diphenyl ether (0.004 mol, used as an internal standard) in 25 ml acetonitrile was stirred at 30 °C for 1 h. This procedure allowed the salts to be continually solubilized and precipitated until a constant particle size was

achieved. (Without employing these procedures reproducible data were difficult to achieve.)

After stirring for an hour, *p*-toluenesulfonyl chloride (0.02 mol) dissolved in 21 ml of acetonitrile was added and the mixture was stirred. A zero time sample was collected and sampling was done periodically to get concentration–time profiles of reactants and products.

4.2. Chemicals and catalysts

p-Toluenesulfonyl chloride, acetonitrile, diphenyl ether, all of A.R. grade, were procured from M/s E. Merck Ltd., Mumbai. Potassium fluoride, (Anhydrous L.R. grade) was purchased by M/s s.d. Fine Chemicals, Mumbai. PEG-400, was obtained from S-D Fine Chemicals, Mumbai. All other PTCs were gift samples from M/s Dishman Pharmaceuticals and Chemicals Ltd. Ahmedabad, India.

4.3. Analysis

Analysis was performed on GC (Chemito Gas Chromatograph, model 8610) by using a 2 m × 3.175 mm stainless steel column packed with 10% OV-17 on Chromosorb WHP, coupled with a flame ionization detector. Synthetic mixtures of the reactant and internal standard were used to calibrate the chromatograms and quantify the data. The product was confirmed by GC–MS.

Acknowledgement

G.D. Yadav acknowledges Darbari Seth Endowment for supporting the Chair. Priyanvada Paranjape acknowledges UGC, New Delhi for an award of JRF, which enabled this work to be carried out.

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