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Microwave-Irradiated Synthesis of Nitrophen Using PEG 400 as Phase Transfer Catalyst and Solvent

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Abstract:

Nitrophen is a widely used herbicide which is commonly produced by an energy intensive process using high temperature and pressure. In the current work, nitrophen is synthesized by using PEG-400 as a phase transfer catalyst in a solid−liquid (S-L) system from potassium 2,4-nitrophenolate and *p*-nitrochlorobenzene using xylene as a solvent under microwave irradiation. It gives 100% selectivity to nitrophen. The use of PEG-400 as a solvent was also examined both under microwaves and conventional heating at 120 °C. The synergism of microwave activation and S-L PTC using PEG 400 as a catalyst and solvent results in enhancements in the rate of reaction and selectivity of nitrophen. The proposed method for the synthesis of nitrofen reduces the total reaction time and also allows easy separation of the product. The kinetics and mechanism of S-L PTC and the homogeneous reaction were also established with PEG 400.

Introduction

Nitrophen is a widely known selective pre-emergence and early postemergence herbicide.[1] The most commonly used method for the synthesis of nitrofen is the base-catalyzed condensation of 2,4-dichlorophenol with *p*-nitrochlorobenzene (*p*-NCB).[2] This process is energy intensive, being carried out at high temperature and pressure, and it requires long reaction times. Several patents have been published on this process.[3−11] Nitrophen was synthesized by reacting 1-chloro-4-nitrobenzene with 30% molar excess of equimolar phenol and NaOH under microwave irradiation at 160 °C to get 63% yield within 5 min, whereas conventional heating gave only 8% yield.[12] The various methods reported in the literature for the synthesis of nitrophen are energy intensive and use much higher temperatures and pressure conditions. Thus, there is still scope to develop energy-efficient, economical processes. For this reason, the current work was undertaken.

Microwave heating is a clean, selective, and efficient methodology to carry out organic reactions with substantial improvements in terms of reaction conditions, simplicity in operating procedures, yields, and selectivity.[13−18] Microwaves are advantageous because of instantaneous "in core" heating of materials, in a homogeneous and selective manner, even with poor heat conduction properties without inertia since only the product is heated. Phase transfer catalysis (PTC) is practised in many industries, including fine chemicals, agrochemicals, specialty chemicals, pharmaceuticals, perfumes, flavors, dyes, and polymers, and is extended to pollution and environmental control processes.[19−22] The advantages of PTC for industrial-scale processing are listed in several books and reviews.[23−28]

In recent years, PTC reactions catalyzed by polyethylene glycol (PEG) and their many derivatives have become popular and are used in several commercial processes to replace expensive and environmentally harmful PTCs.[29−37] PEGs are soluble, recoverable, thermally stable, and inexpensive phase transfer catalysts. Lower-molecular weight liquid PEGs can be used as solvents with or without addition of water. PEGs are attractive green reaction media because of characteristics such as low-toxicity, low volatility, biodegradability, relatively low cost, and ease of separability.[38−42] PEGs are stable at high temperatures up to 150−200 °C and show higher stability in

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acidic and basic conditions vis-à-vis quaternary onium salts. Well-known applications of PEGs in organic syntheses include Williamson ether synthesis, substitution reactions, and oxidation and reduction reactions. PEG has been modified with some typical catalysts such as crown ethers, ammonium salts, cryptands, and polypodands to enhance phase transfer in two-phase reactions. PEG and its aqueous solutions are alternative solvents to ionic liquids, supercritical carbon dioxide, and micellar systems.[43] The role of microwave irradiation in PTC has been studied by our group for liquid−liquid, (L-L), solid−liquid (S-L), and liquid−liquid−liquid (L-L-L) PTC.[44−47]

There is no published information on the use of phase transfer catalysis (PTC) and microwave irradiation for the synthesis of nitrophen. The various methods reported in the literature for the synthesis of nitrophen are energy intensive and use much higher temperatures and pressure, resulting in byproduct formation, and these reactions need to be replaced. An attempt has been made in this work to synthesize nitrofen by a S-L PTC reaction with potassium 2,4-dichlorophenolate and *p*-NCB by using PEG-400 as a catalyst under microwave irradiation. In addition, the role of PEG as a green solvent in this reaction is explored. We delineate a protocol to extract both rate constant and ion-exchange equilibrium constant from the same set of data which will be useful for reactor design and scale-up. The current work specifically explores PEG 400 as a catalyst as well as solvent-cum catalyst for the synthesis of nitrophen under microwave irradiation. This is a novel method since it requires less energy, the rates are intensified by orders of magnitude, and the selectivity to nitrophen is 100%.

2. Experimental Section

2.1. Materials. All chemicals and solvents used in this study were commercially available and used without further purification. *p*-Nitrochlorobenzene (*p*-NCB), and 2,4-dichloro phenol were procured from M/s E. Merck India Ltd., Mumbai. India. Potassium hydroxide, *n*-decane, polyethylene glycol (PEG 400), ethylene dichloride (EDC), mixed xylene, and diethyl ether were purchased from M/s S.D. Fine Chemicals, Mumbai.

2.2. Experimental Procedure. The experimental studies were carried out in a commercial microwave monomode reactor assembly [Discover, CEM-SP1245 model, CEM Corporation, U.S.A.] with focused waves operating at 2.45 GHz and a provision of magnetic and mechanical stirring. The temperature was maintained constant at a chosen value by modulation of the emitted power. Magnetic stirring all along the irradiation provided a good homogeneity (power and temperature) and a data treatment which was followed by a computer. All reactions were performed in closed single-neck round-bottom flask. CEM-SP1245 model gives a facility to choose between the modes of operation such as constant temperature mode and constant power mode. We had chosen a constant temperature mode for all the reactions.

In order to compare microwave irradiation with conventional heating the reactions were performed under similar sets of experimental conditions. When using a thermostatic oil bath, the temperature was measured with a quick digital thermometer introduced into the reaction mixture. It was thought desirable to make potassium 2,4-dichlorophenolate in bulk to get uniformity in the concentration of the same in all consecutive reactions. 2,4-Dichlorophenol and potassium hydroxide in a mole ratio of 1:1.2 were refluxed at 110 °C in 10 cm^3 of toluene and water, respectively, for 3 h. The water present in the reaction (i.e. added and formed in the reaction) was removed from the reaction by Dean−Stark apparatus. The reaction mass was allowed to cool and was washed with ethylene dichloride (EDC) several times. The unreacted 2,4-dichlorophenol was dissolved in EDC, and the obtained potassium 2,4-dichlorophenolate was dried under nitrogen atmosphere.

Using PEG 400 as a phase transfer catalyst, a typical reaction mixture consisted of 0.126 mol *p*-NCB and 0.1 mol solid potassium 2,4-dichlorophenolate with 0.02 mol PEG 400 in 25 cm^3 of mixed xylene as a solvent at 120 °C. With PEG 400 as a solvent, a typical reaction mixture consisted of 0.005 mol of *p*-NCB and 0.01 mol potassium 2,4-dichlorophenolate in 25 cm^3 of PEG 400 at 120 °C. Samples were withdrawn periodically and analyzed according to the methods described below.

2.3. Method of Analysis. Analysis was performed on GC (Chemito Gas Chromatograph, model 8510) by using a 4 m × 3.8 mm stainless steel column packed with 10% SE 30 on Chromosorb WHP, coupled with a flame ionization detector. The injector and detector temperatures were kept at 300 °C. The oven temperature was programmed from 130 °C (1 min) up to 295 °C with a ramp rate of 20 °C min^{-1}. Nitrogen gas was used as a carrier gas at 30 mL min^{-1}. Synthetic mixtures were used to calibrate the chromatograms and quantify the data.

2.3.1. Product Confirmation. Upon completion of reaction, the reaction mass was washed with water to remove unreacted potassium 2,4-dichlorophenolate, and it was distilled under reduced pressure to separate the product, which was analyzed by GC−MS for characterisation. Both analyses showed that nitrophen was the sole product.

2.3.2. Separation of Reactant and Product from PEG 400 for Analysis. The reaction samples were withdrawn at regular time intervals to determine concentration/time profiles. However, the samples needed to be separated from PEG 400 before analysis by the method described below.

Diethyl ether was added to the samples in an equal volume, and to this mixture was added about 100 times excess water

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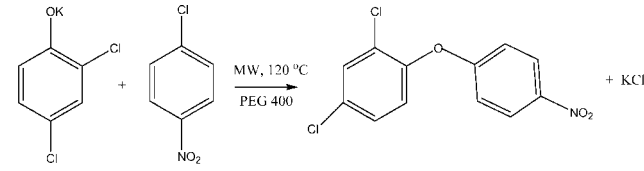
Scheme 1



Potassium 2,4-dichloro-phenolate | p-Nitrochloro-benzene | Nitrophen

and shaken well. Two layers were clearly visible, an organic layer containing *p*-NCB and nitrofen (extracted in the ether layer) and a polymeric layer containing PEG 400 and unreacted potassium phenoxide dissolved in water.

2.4. Reaction Scheme. The overall reaction is shown in Scheme 1. It was observed that there was no formation of any byproduct at any conversion levels in S-L PTC.

3. Results and Discussion

The synthesis of nitrophen was studied in two different ways under microwave irradiation.

(a) Using PEG 400 as a catalyst under S-L PTC.

(b) Using PEG 400 as a solvent.

3.1. Kinetics and Mechanism. The overall reaction is:

$$[RX]_{org} + [MY]_s \xrightarrow[[PEG]_{org}]{k_r} [RY]_{org} + [MX]_s \quad (1)$$

The mechanism of reactions of S_N2 type using PEG as a catalyst and/or catalyst cum-solvent is depicted as follows:

3.1.1. Reaction Mechanism and Model Used for Microwave Irradiated Synthesis of Nitrophen Using PEG 400 As a Catalyst under S-L PTC. For S-L PTC reaction in the presence of microwaves as well as conventional heating, the following model is developed. When PEG was used as a catalyst, the following catalyst/complex formation reactions takes place in the liquid phase.

$$[PEG] + [M^+Y^-] \overset{K_Y}{\rightleftharpoons} [PEG\ M^+Y^-] \quad (2)$$

$$[PEG\ M^+X^-] \overset{1/K_X}{\rightleftharpoons} [PEG] + [M^+X^-] \quad (3)$$

$$K_Y = \frac{[PEG\ M^+Y^-]}{[PEG][M^+Y^-]} \quad (4)$$

$$K_X = \frac{[PEG\ M^+X^-]}{[PEG][M^+X^-]} \quad (5)$$

At a given time, PEG is distributed among various complexes.

$[PEG]_0 =$

initial concentration of PEG the reaction mass, mol/cm^3 (6)

$$[PEG]_0 = [PEG] + [PEG\ M^+X^-] + [PEG\ M^+Y^-] \quad (7)$$

By using eqs 4 and 5, the concentration of free PEG is obtained as follows:

$$[PEG] = \frac{[PEG]_0}{1 + K_Y[MY] + K_X[MX]} \quad (8)$$

The substrate RX reacts with the complex [PEG M^+Y^-]according to the following:

$$RX + [PEG\ M^+Y^-] \underset{k_r'}{\overset{k_r}{\rightleftharpoons}} RY + [PEG\ M^+X^-] \quad (9)$$

The net rate of reaction of RX is given by:

$$-\frac{d[RX]}{dt} = k_r[RX][PEG\ M^+Y^-] - k_r'[RY][PEG\ M^+Y^-] \quad (10)$$

By substituting for [PEG M^+Y^-] and [PEG M^+X^-], the following is obtained:

$$\therefore -\frac{d[RX]}{dt} = \frac{k_r[RX][PEG]_0}{(1 + K_Y[MY] + K_X[MX])} - \frac{k_r'[RY]K_X[MX][PEG]_0}{(1 + K_Y[MY] + K_X[MX])}$$

$$= \frac{k_r[PEG]_0}{(1 + K_Y[MY] + K_X[MX])}\left\{[RX] - \frac{[RY]K_X[MX]}{K_r}\right\} \quad (11)$$

where K_r = reaction equilibrium constant

$$K_r = \frac{[RY][PEG\ MX]}{[PEG\ MY]} = \frac{K_Y[RY][MX]}{K_X[RX][MY]} \quad (12)$$

Thus, the final equation is

$$-\frac{d[RX]}{dt} = \frac{k_r[PEG]_0}{(1 + K_Y[MY] + K_X[MX])}\left\{[RX] - \frac{K_X}{K_r}[RY][MX]\right\} \quad (13)$$

when K_r is very high, the reaction becomes irreversible, and thus,

$$-\frac{d[RX]}{dt} = \frac{k_r[PEG]_0[RX]}{(1 + K_Y[MY] + K_X[MX])} \quad (14)$$

[MY] and [MX] can be related to the fractional conversion, X_{RX}

$$X_{RX} = \frac{[RX]_0 - [RX]}{[RX]_0} \quad (15)$$

where $[RX]_0$ = initial concentration of RX, mol/cm^3

$$[MY] = [RX]_0(M_R - X_{RX}) \quad (16)$$

where

$$M_R = \frac{[MY]_0}{[RX]_0} = \text{initial molar ratio of reactants} \quad (17)$$

Similarly,

$$[MX] = [RX]_0 X_{RX} \quad (18)$$

Substituting eqs 17 and 18 in eq 14,

$$-\frac{d[RX]}{dt} = [X]_0 \frac{dX_{RX}}{dt} = \frac{k_r[RX]_0(1 - X_{RX})[PEG]_0}{1 + K_Y([RX]_0(M_R - X_{RX})) + K_X X_{RX}[RX]_0} \quad (19)$$

Thus,

$$\frac{dX_{RX}}{dt} = \frac{k_r(1 - X_{RX})[PEG]_0}{1 + K_Y([RX]_0\{M_R - X_{RX}\}) + K_X X_{RX}[RX]_0} \quad (20)$$

The solution of eq 20 is given in the Appendix and is as follows:

$$-\ln(1 - X_{RX}) + ([RX]_0 K_Y\{(1 - M_R)\ln(1 - X_{RX}) + X_{RX}\}) + ([RX]_0 K_X\{-\ln(1 - X_{RX}) - X_{RX}\}) = k_r[PEG]_0 t \quad (27)$$

where

$$k_1 = k_r[PEG]_0 \quad (28)$$

A plot of the left-hand side of eq 27 vs t will give a straight line passing through the origin with a slope of k_1 at a fixed concentration of PEG. However, it is necessary to either determine K_X and K_Y independently or use a nonlinear regression analysis to fit the equation.

3.1.2. Reaction Mechanism and Model Used for Synthesis of Nitrophen Using PEG 400 As Solvent (Homogeneous Reaction). Since the catalyst is used as solvent also, this can be treated as a typical second-order reaction. Then, eq 9 can be written as:

$$-\frac{d[RX]}{dt} = k_H[RX][M^+Y^-] \quad (29)$$

In terms of fractional conversion of limiting reactant RX, eq 29 becomes

$$-\frac{d[RX]}{dt} = k_H[RX]_0(1 - X_{RX})(M_R - X_{RX}) \quad (30)$$

Separation of variables and integration leads to the following:

$$\ln\left[\frac{(M_R - X_{RX})}{(1 - X_{RX})}\right] = M_R[RX]_0 k_H t = k_{app} t \quad (31)$$

where

$$k_{app} = M_R[RX]_0 k_H t$$

Equation 31 can be further manipulated to extract both k_{app} and k_H.

A plot of $[\ln((M_R - X_{RX}))/((1 - X_{RX}))]$ versus t gives a straight line passing through origin and thus, k_H can be found from the slope.

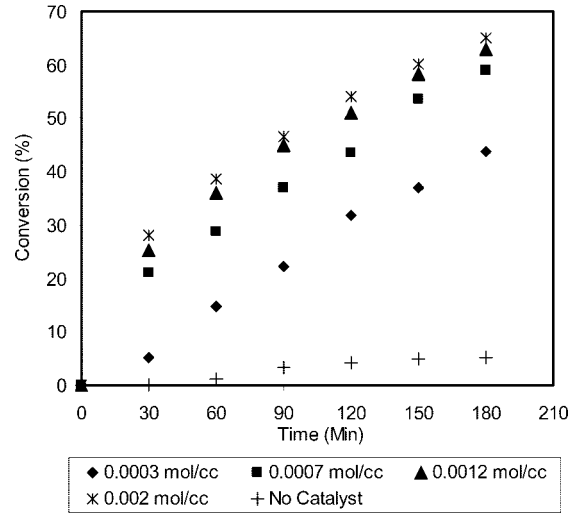


Figure 1. **Effect of PEG 400 loading on conversion of *p*-NCB under S-L PTC (potassium 2,4-dichlorophenolate 0.1 mol, *p*-NCB 0.126 mol, 0.02 mol of PEG 400, 25 cm^3 mixed xylene, temperature 120 °C).**

3.2. PEG-400 as a Catalyst for S-L PTC. *3.2.1. Effect of Catalyst Concentration.* The conversion of the limiting reactant was found to be independent of speed of agitation in the range of 800−1200 rpm at 120 °C and therefore was not controlled by external solid−liquid mass transfer resistance. For the sake of brevity, these data are not shown. The effect of PEG-400 concentration on the initial rate of reaction was studied from 3 × 10^{-4} to 2 × 10^{-3} mol/cm^3 (Figure 1). The initial rate of reaction was found to increase with increasing concentration of the catalyst. This behavior is typical of PTC reactions. All further experiments were done at a catalyst concentration of 2 × 10^{-3} mol/cm^3.

3.2.2. Effect of Mole Ratio. Mole ratio of *p*-NCB to potassium 2,4-dichlorophenolate was varied from 1:0.5 to 1:1 (Figure 2). The conversion increases with concentration of potassium 2,4-dichlorophenolate under otherwise similar conditions. The initial reaction rate increased with an increase in

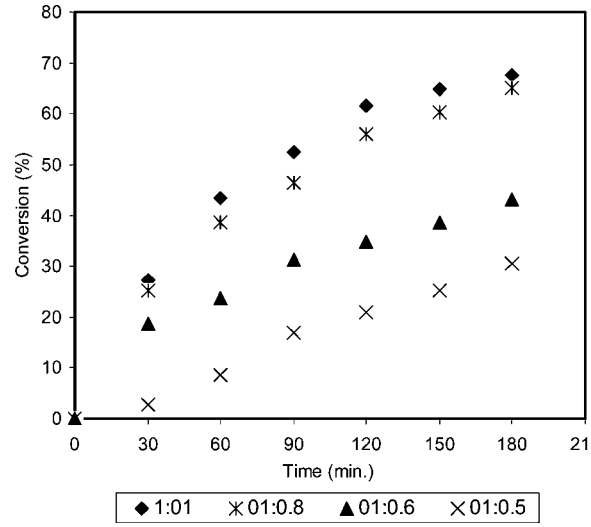


Figure 2. **Effect of *p*-NCB to potassium 2,4-dichlorophenolate mole ratio on conversion of *p*-NCB using PEG 400 as a catalyst under S-L PTC (potassium 2,4-dichlorophenolate 0.01 mol, *p*-NCB 0.126 mol, 0.02 mol of PEG 400, 25 cm^3 mixed xylene, temperature 120 °C).**

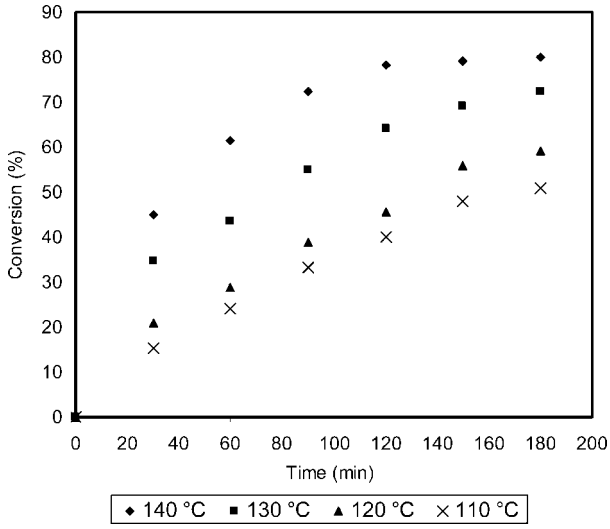


Figure 3. **Effect of temperature on conversion of *p*-NCB using PEG 400 as a catalyst under S-L PTC (potassium 2,4-dichlorophenolate 0.01 mol, *p*-NCB 0.126 mol, 0.02 mol of PEG 400, 25 cm^3 mixed xylene).**

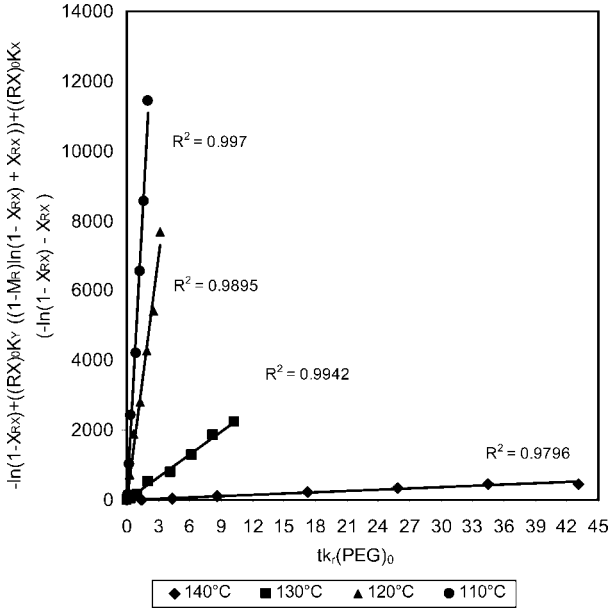


Figure 4. **Validity of kinetic model at various temperatures using PEG 400 as a catalyst under S-L PTC in microwave irradiation (potassium 2,4-dichlorophenolate 0.1 mol, *p*-NCB 0.126 mol, 0.02 mol of PEG 400, 25 cm^3 mixed xylene).**

concentration of potassium 2,4-dichlorophenolate because the organic phase was almost saturated with [PEG M^+Y^-]. The highest reaction rate was observed for a mole ratio of 1:1. As there was no significant increase in reaction rate with increase in mole ratio of 1:0.8, it was selected for further studies.

3.2.3. Effect of Temperature. The effect of temperature on the rate of the reaction was studied at different temperatures from 100 to 140 °C using microwave heating mode. The reaction is facile at higher temperatures (Figure 3). The rate of reaction increased substantially with an increase in temperature.

3.2.4. Validation of Model. In order to validate the model, eq 27 was used to fit the observed data at different temperatures (Figure 4). The best-fit values of K_X and K_Y were obtained by nonlinear regression using Polymath 5.1. The slopes were used to calculate k_r (Table 1). The K_Y values increase marginally

Table 1. **K_Y, K_X, and k_r values obtained by nonlinear regression analysis: PEG 400 as a catalyst and xylene as a solvent in S-L PTC under microwave irradiation**

	temperature, °C			
	110	120	130	140
K_Y, cm^3/mol	1.93	2.66	2.75	2.80
K_X, cm^3/mol	9.27	9.74	38.03	111.31
k_r, cm^3/(mol·s)	3.67	5.52	18.35	76.70

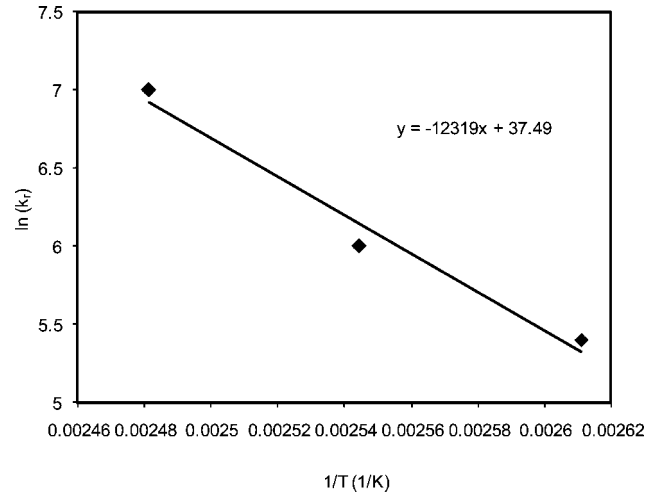


Figure 5. **Arrhenius plot for reaction of *p*-NCB with potassium 2,4-dichlorophenolate using PEG 400 as a catalyst under S-L PTC in microwave irradiation (potassium 2,4-dichlorophenolate 0.01 mol, *p*-NCB 0.126 mol, 0.02 mol of PEG 400, 25 cm^3 mixed xylene).**

with temperature, whereas K_X values increase substantially with temperature which is expected if eqs 2−4 are examined. Potassium 2,4-dichlorophenolate salt (K_Y) solubility does not increase substantially with temperature, whereas the KCl solubility increases. The increase in the value of the rate constant (k_r) with temperature is correct according to the Arrhenius equation, since the apparent energy of activation is high.

These values were then used to generate simulated conversion values. Equation 26 was integrated numerically using Euler's method and a step size of integration of 0.5. Limits imposed on the integration were times varying from 0 to 180 min, with initial conversion X_{RX} as zero. Simulated values of conversion so obtained were compared with experimental values, and their respective times were also compared.

The Arrhenius plots are shown in Figure 5 to get the activation energy value as 24.48 kcal/mol for S-L PTC under microwave irradiation.

3.3. Homogeneous Reaction Using PEG 400 As a Catalyst-Cum Solvent. *3.3.1. Effect of Mole Ratio.* Potassium 2,4-dichlorophenolate loading was varied from a mole ratio of 1:1 to 1:2.5 times the limiting reactant (*p*-NCB) under otherwise similar conditions, where the organic phase volume was kept constant. Figure 6 shows that the reaction was independent of the loading of the solid beyond mole ratio 1:2. The rate was dependent on the loading of the solid potassium 2,4-dichlorophenolate up to twice the limiting reactant.

3.3.2. Effect of Temperature. The effect of temperature on the rate of the reaction was studied from 100 to 150 °C using both microwave irradiation and conventional heating. The conversion of *p*-NCB was increased with an increase in the

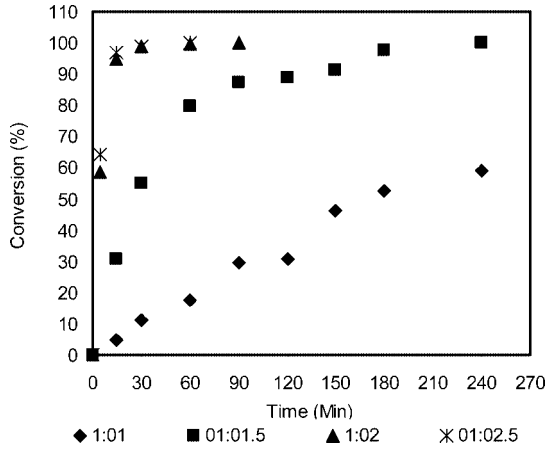


Figure 6. **Effect of mole ratio on conversion of *p*-NCB using PEG 400 as a solvent in microwave reactor (*p*-NCB/potassium 2,4-dichlorophenolate, 1:2; PEG 400 made up to 25 cm^3; temperature 150 °C).**

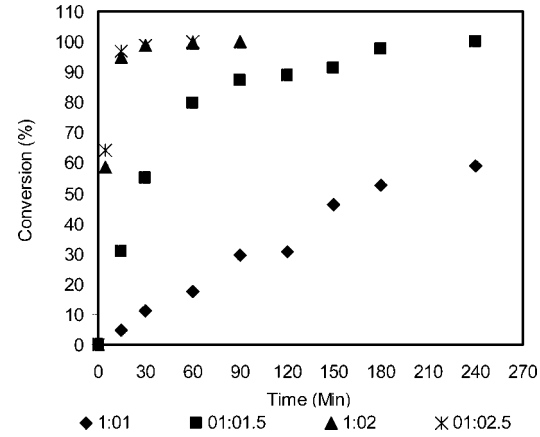


Figure 7. **Effect of temperature on conversion of *p*-NCB using PEG 400 as a solvent in microwave reactor) *p*-NCB 0.01 mol, potassium 2,4-dichlorophenolate 0.02 mol, PEG 400 made up to 25 cm^3, temperature 150 °C).**

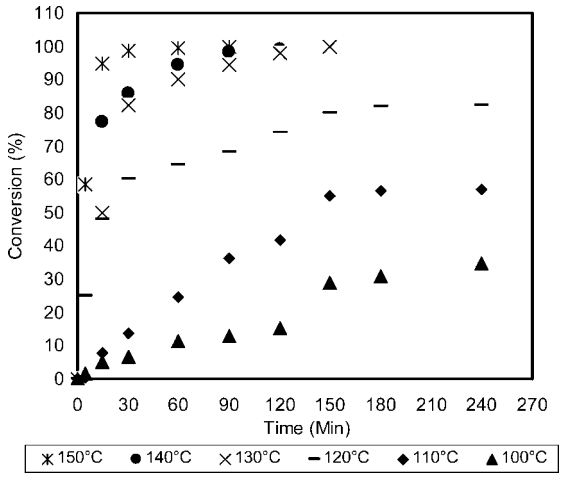


Figure 8. **Effect of temperature on conversion of *p*-NCB using PEG 400 as a solvent in conventional heating (*p*-NCB 0.01 mol, potassium 2,4-dichlorophenolate 0.02 mol, PEG 400 made up to 25 cm^3, *T* 150 °C).**

reaction temperature in both microwave irradiation (Figure 7) and conventional heating (Figure 8). The rate constants under microwave irradiation are very high in comparison with those under conventional heating when PEG-400 is used as a solvent-

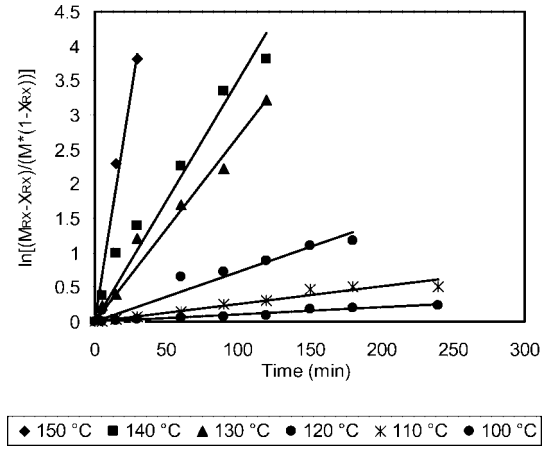


Figure 9. **Validity of kinetic model at various temperatures using PEG 400 as a solvent in microwave irradiation.**

Table 2. **Reaction rate constants obtained by nonlinear regression analysis for the synthesis of nitrophen in a microwave irradiation and conventional heating with PEG-400 as a solvent-cum-catalyst**

	temperature,°C					
	100	110	120	130	140	150
$k_{H\text{-}MW} \times 10^6$, cm^3/(mol·s)	0.83	2.08	6.00	21.67	29.17	83.33
$k_{H\text{-}CH} \times 10^6$, cm^3/(mol·s)	–	0.33	1.00	2.08	5.50	8.67

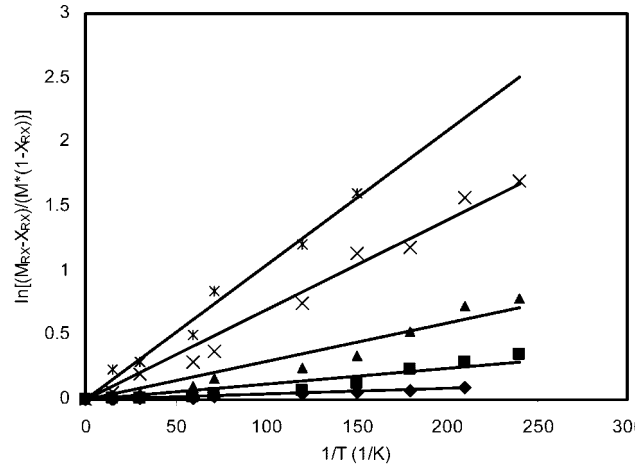


Figure 10. **Validity of kinetic model at various temperatures using PEG 400 as a solvent in conventional heating (*p*-NCB 0.01 mol, potassium 2,4-dichlorophenolate 0.02 mol, PEG 400 made up to 25 cm^3).**

cum catalyst (Table 2). The model is validated for both microwave irradiation (Figure 9) and conventional heating (Figure 10). The Arrhenius plots were made for both microwave irradiation (Figure 11) and conventional heating (Figure 12). The activation energy was calculated as 27.47 kcal/mol for microwave irradiation and 26.54 kcal/mol for conventional heating. The values of activation energy are close, which would suggest an increase in the rate constant. In microwave kinetics, the overall order of reaction does not change nor does the order in individual reactants and catalyst concentration. Thus, the reaction rate is enhanced due to increased rate constant. The rate constant can be written in the usual Arrhenius equation with activation energy and pre-exponential factor k_0. The

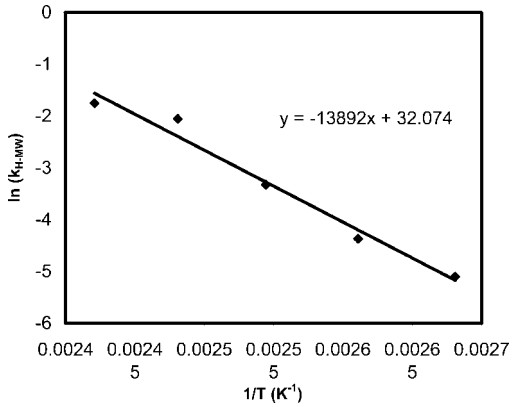


Figure 11. **Arrhenius plot for reaction of *p*-NCB with potassium 2,4-dichlorophenolate using PEG 400 as a solvent under microwave irradiation (*p*-NCB 0.01 mol, potassium 2,4-dichlorophenolate 0.02 mol, PEG 400 made up to 25 cm^3).**

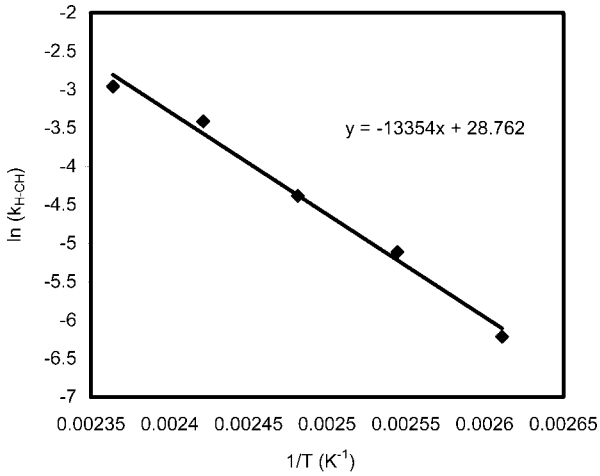


Figure 12. **Arrhenius plot of reaction of *p*-NCB with potassium 2,4-dichlorophenolate using PEG 400 as a solvent in conventional heating (*p*-NCB 0.01 mol, potassium 2,4-dichlorophenolate 0.02 mol, PEG 400 made up to 25 cm^3).**

activation energy values are practically the same in both types of heating, so that the only parameter that can change is k_0. There has been some speculation that microwaves affect the orientation of molecular collisions and the activation energy, but there is no evidence that supports either of these ideas. Microwaves do not influence the orientation of those collisions nor does the activation energy. Activation energies remain constant for each particular reaction. However, microwave energy will affect the temperature parameter in this equation. An increase in temperature causes molecules to move about more rapidly, which leads to a greater number of more energetic collisions. This occurs much faster with microwave energy, due to the high instantaneous heating of the substance(s) above the normal bulk temperature, and is the primary factor for the observed rate enhancements.[46,47]

3. Conclusion

A synergistic combination of S-L PTC and low-energy microwave irradiation with PEG 400 as catalyst was employed in the synthesis of nitrophen. It leads to 100% selectivity with rate enhancement. A kinetic model was developed to describe the overall reaction system. The current work demonstrates that a low input of microwave energy leads to remarkable enhancement in rates. The use of PEG 400 as a solvent was also studied. The enhancement in rates of reaction in the synthesis of nitrophen under microwave irradiation vis-à-vis conventional heating was significant. The advantages of this environmentally benign and safe protocol include a simple reaction setup, application of commercially available reagents and catalysts, high product yields, and short reaction times.

Acknowledgment

G.D.Y. received support of the Darbari Seth Professor Endowment for a personal Chair, and B.G.M. gratefully thanks University Grants Commission for SRF. This paper is dedicated to the memory of the late Dr Chris Schmidt, with whom G.D.Y. had interacted on several occasions.

Appendix

The rate equation in terms of fractional conversion is as follows:

$$\frac{dX_{RX}}{dt} = \frac{k_r(1 - X_{RX})[PEG]_0}{1 + K_Y([RX]_0\{M_R - X_{RX}\}) + K_X X_{RX}[RX]_0} \quad (20a)$$

On separation of variables and integration of eq 20,

$$\int_0^{X_{RX}} \left[\frac{1 + K_Y([RX]_0\{M_R - X_{RX}\}) + K_X X_{RX}[RX]_0}{(1 - X_{RX})}\right] dX_{RX} = k_r[PEG]_0 \int_0^t dt \quad (21)$$

On separation of each term:

$$\int_0^{X_{RX}} \left[\frac{dX_{RX}}{(1 - X_{RX})}\right] + [RX]_0 K_Y \int_0^{X_{RX}} \left[\frac{(M_R - X_{RX})}{(1 - X_{RX})}\right] dX_{RX} + [RX]_0 K_X \int_0^{X_{RX}} \left[\frac{X_{RX}}{(1 - X_{RX})}\right] dX_{RX} = k_r[PEG]_0 t \quad (22)$$

Solving each integral separately,

Term 1:

$$\int_0^{X_{RX}} \left[\frac{dX_{RX}}{(1 - X_{RX})}\right] = [-\ln(1 - X_{RX})]_0^{X_{RX}} = -\ln(1 - X_{RX}) \quad (23)$$

Term 2:

$$[RX]_0 K_Y \int_0^{X_{RX}} \left[\frac{(M_R - X_{RX})}{(1 - X_{RX})}\right]$$

$$= [RX]_0 K_Y \left(\int_0^{X_{RX}} \left[\frac{(M_R - X_{RX})}{(1 - X_{RX})}\right] dX_{RX} + [RX]_0 K_X \int_0^{X_{RX}} \left[\frac{(X_{RX})}{(1 - X_{RX})}\right] dX_{RX} \right)$$

$$= [RX]_0 K_Y (M_R [-\ln(1 - X_{RX})]_0^{X_{RX}} - [-\ln(1 - X_{RX}) - (1 - X_{RX})]_0^{X_{RX}})$$

$$= [RX]_0 K_Y \{-M_R \ln(1 - X_{RX}) + X_{RX} + \ln(1 - X_{RX})\}$$

$$= [RX]_0 K_Y \{(1 - M_R) \ln(1 - X_{RX}) + X_{RX}\} \quad (24)$$

Term 3:

$$[RX]_0 K_X \int_0^{X_{RX}} \left[\frac{X_{RX}}{(1 - X_{RX})}\right] dX_{RX}$$

$$= [RX]_0 K_X \{-\ln(1 - X_{RX}) - X_{RX})\} \quad (26)$$

Thus, the final solution of eq 22 is:

$$-\ln(1 - X_{RX}) + ([RX]_0 K_Y \{(1 - M_R) \ln(1 - X_{RX}) + X_{RX}\}) + ([RX]_0 K_X \{-\ln(1 - X_{RX}) - X_{RX})\}) = k_r [PEG]_0 t \quad (27a)$$

When $-t = 0$, the left-hand side (LHS) of eq 27 is equal to zero, which also shows the internal consistency of the solution.

NOMENCLATURE

k_1	$k_r[PEG]_0$, pseudo-first-order constant for solid−liquid PTC reaction, s^{-1}
k_{app}	$M_R[RX]_0 k_H$, apparent rate constant for homogeneous reaction, s^{-1}
k_H	Second-order rate constant for homogeneous reaction, $cm^3/mol \cdot s$
k_r	Second-order rate constant for solid−liquid PTC reaction, $cm^3/mol \cdot s$
K_r	Reaction equilibrium constant, dimensionless
K_X	([PEG M^+Y^-])/([PEG] [M^+X^-]), cm^3/mol
K_Y	([PEG M^+Y^-])/([PEG] [M^+Y^-]), cm^3/mol
M_R	$([MY]_0)/([RX]_0)$, dimensionless
$[MX]_s$	Salt of leaving group in solid phase
$[MY]_s$	Salt of nucleophile group in solid phase
$[PEG]_0$	Initial concentration of PEG in the reaction mass, mol/cm^3
[PEG M^+X^-]	PEG and leaving group complex salt
[PEG M^+Y^-]	PEG and nucleophile complex salt
$[RX]_{org}$	Concentration of RX in organic phase, mol/cm^3
$[RX]_0$	Initial concentration of RX, mol/cm^3
$[RY]_{org}$	Concentration of RY in organic phase, mol/cm^3
t	Time, min
X_{RX}	Fractional conversion of RX

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