Journal of the Taiwan Institute of Chemical Engineers 57 (2015) 54–61

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

The novel synthetic route of 3,5-dimethyl-1-(3-phenylpropyl)-1H-pyrazole under solid–liquid phase transfer catalysis conditions assisted by an ultrasound application—A study of some kinetic parameters

Maw-Ling Wang [a,*], Manuri Brahmayya [a,**], Yu-Ming Hsieh [b]

[a] Department of Environmental Engineering Safety and Health, Hung Kuang University, Shalu District, Taichung City 43302, Taiwan
[b] Department of Health Nutrition and Biotechnology, Asia-Pacific Institute of Creativity, Toufen, Miaoli 35153, Taiwan

ARTICLE INFO

Article history:
Received 11 July 2014
Revised 11 May 2015
Accepted 24 May 2015
Available online 19 June 2015

Keywords:
Chemical kinetics
Reaction mechanism
Phase transfer catalysis
Ultrasonic irradiation
Water free conditions
Synthesis

ABSTRACT

The kinetic study for synthesis of 3,5-dimethyl-1-(3-phenylpropyl)-1H-pyrazole was studied successfully by reacting the 3,5-dimethyl pyrazole with 1-bromo-3-phenyl propane under phase transfer catalysis and ultrasonic irradiation conditions using aqueous solution of NaOH (5 g or 0.25 g/ml), excess amount of bromobenzene and tetrahexyl ammonium bromide as a phase transfer catalyst. The reaction was carried out at 40 °C under pseudo-first order conditions and was monitored by gas chromatography (GC). Kinetic reaction found to follow 'pseudo first order' rate law. From the experimental data, a rate expression had been developed to explain the kinetic behavior of the reaction from which the apparent rate constant (k_{app}) of the organic phase was attained. The effects of agitation speed, amount of sodium hydroxide, effect of quaternary ammonium salts, amount of catalyst and temperature on the reaction were also studied.

1. Introduction

A necessary, extreme, well known condition of collisions is must for two reactants to be involved in chemical reaction. However, the rate of reaction is incomplete by the contact surface area, rate of mass-transfer, and distribution between two immiscible reactants due to their low solubilities. On improvements of immiscible organic reactants to miscible liquids, there was a conventional method introduced to employ a protic or aprotic solvent in order to develop their communal solubilities [1–3]. Nevertheless, this development is not so significant. In addition, the reaction has to be approved in the extreme operating condition of enhanced temperature to change the reaction trend. The drawback is that the by-products are often accompanied by the production of a desired invention. Besides of this exertion of recovery of the pricey aprotic solvent and of carrying out the reaction in an anhydrous form makes the reaction very hard in an industrial application. The struggle of this chemical reaction of two immiscible reactants, was solved by Jarrouse [4] who found that the bi-phasic reaction is extremely increased by adding a little catalytic quantity of quaternary salt. The quaternary salts were used as booming catalysts for raising the two-phase reaction. This methodology occupies an exclusive nook in organic synthesis [5–15]. The benefit of using PTC can be carried out under fair conditions to get hold of a high reaction rate. The supercilious selectivity of the principal product and high conversion of the reactant were obtained [16,17].

The principle theme of this current work is to study the kinetics of alkylation of aromatic imine in presence of alkaline solution of NaOH/organic solvent underneath the influence of ultrasound assisted phase-transfer catalysis conditions.

Presently, a new analytical course of experimental techniques which are green benevolent methods viz., ultrasound and microwave irradiation have become incredibly smart in promoting various organic reactions [18–21]. The purpose of ultrasound waves in chemistry is an appropriate technique for the facilitation of reactions [22]. Several studies have been carried out and it is well predictable that the usage of ultrasound procedures give high-quality yields, gentle conditions and diminutive reaction times [23]. There was no possibility for the direct interaction between ultrasound and substance, and in such a way it is an indirect phenomenon, so that cavitation must be facilitated to encourage a chemical reaction. Hence, the make use of ultrasound to enhance chemical reactivity [24,25] is now familiar as a feasible environmental safe alternative machinery. Kinetics

* Corresponding author. Tel.: +886 932961999
** Corresponding author. Tel.: +886 974001470
E-mail addresses: chmmlw@sunrise.hk.edu.tw (M.-L. Wang), manurichinna_07@yahoo.co.in (M. Brahmayya).

http://dx.doi.org/10.1016/j.jtice.2015.05.039
1876-1070/

of the reaction in synthesizing 3,5-dimethyl-1-(3-phenylpropyl)-1H-pyrazole, such as agitation speed, amount of catalyst, quaternary ammonium salts, amount of sodium hydroxide and temperature on the conversion were investigated in detail.

2. Experimental

2.1. Materials

All required chemicals (reagents) including solvents benzene, toluene, bromobenzene, cyclohexane, anisole, tetrahexylammonium bromide (THAB), benzyltriethylammonium bromide (BTEAB), tetrabutylammonium bromide (TBAB), tetra butyl ammonium tribromide (TBAI), benzyl triethyl ammonium chloride (BTEAC), tetra ethyl ammonium bromide, strong alkaline (NaOH) and other reagents for clubbing of aromatic imine and alkyl halide were guaranteed grade (GR) chemicals.

2.2. Instrumentation

Fig. 1 shows a schematic diagram of the experimental setup. The ultrasonic machine model L-400 was designed and constructed by a Ko Hsieh Instruments Co. Ltd., Taipei, Taiwan. The instrument was equipped with dual frequencies 28 kHz, 50 kHz respectively and the electric power 300 W. Fig. 1 represents the schematic diagram of experimental set-up, where square shaped water tank of liquid holding capacity (D) (20 l) which contains ultra sound frequency (A), temperature control meter (B), time set (C) respectively. This ultrasound tank has the electric output capacity of 200 W and 300 W and was well connected with external hot water tank (F) which was fitting with temperature control computer for the reading of circulation of hot water to maintain constant temperature in it. In further, this ultrasound machine fixed with mechanical stirrer (H) into the reactor (G, 250 ml pyrex glass flask) about to read revolutions per minute (rpm) in reaction and it was suspended at center of ultrasonic cleaning bath to attain maximum radiation where the round bottom of reactor always suspended into water level. The reactor was further connected with external cooling circulator (E) via cooling condenser. It was also well connected with thermometer or a dropping funnel. D, E, F and H were well connected with local electric supply. The continuous ultrasound radiations [26–29] through water tank (D) will give the high energy water waves for colliding the molecules in the reaction leads to form our expected product. So that we have applied pseudo first order conditions. A gas chromatography Shimadzu (1700) was used for contents monitor.

2.3. Kinetic measurements

The container of reaction mixture was a 250 ml three-necked pyrex flask (reactor), which helps in the purposes of stirring the reaction mixture, with inserting setting of the thermocouple, to take samples and for feeding the feed. A known quantity of NaOH (5 g, 0.25 g/ml) was dissolved in deionized water (20 ml) to prepare a 40 wt.% alkaline solution. Known quantities of 3,5-dimethyl pyrazole, THAB 1.5 mol% and naphthalene (internal standard, 0.35 g) were then dissolved in bromo benzene (40 ml) to make the organic phase liquid. To start up the reaction, the aqueous and organic solutions were mixed in the reactor which was overhanging at the center of the ultrasonic cleaning bath to get the supreme ultrasound energy. The organic-phase sample (0.5 ml) was collected from the reactor at each time interval, was taken into the test tubes containing 3 ml of methanol. These contents had been measured by GC (Shimadzu GC 17A, J&W Scientific Inc., capillary column (db-1 column); 100% poly (dimethylsiloxane) stationary phase; 15 × 0.525 m column dimension; carrier gas, nitrogen (60 ml/min); flame ionization detector; injection temperature, 250 °C).

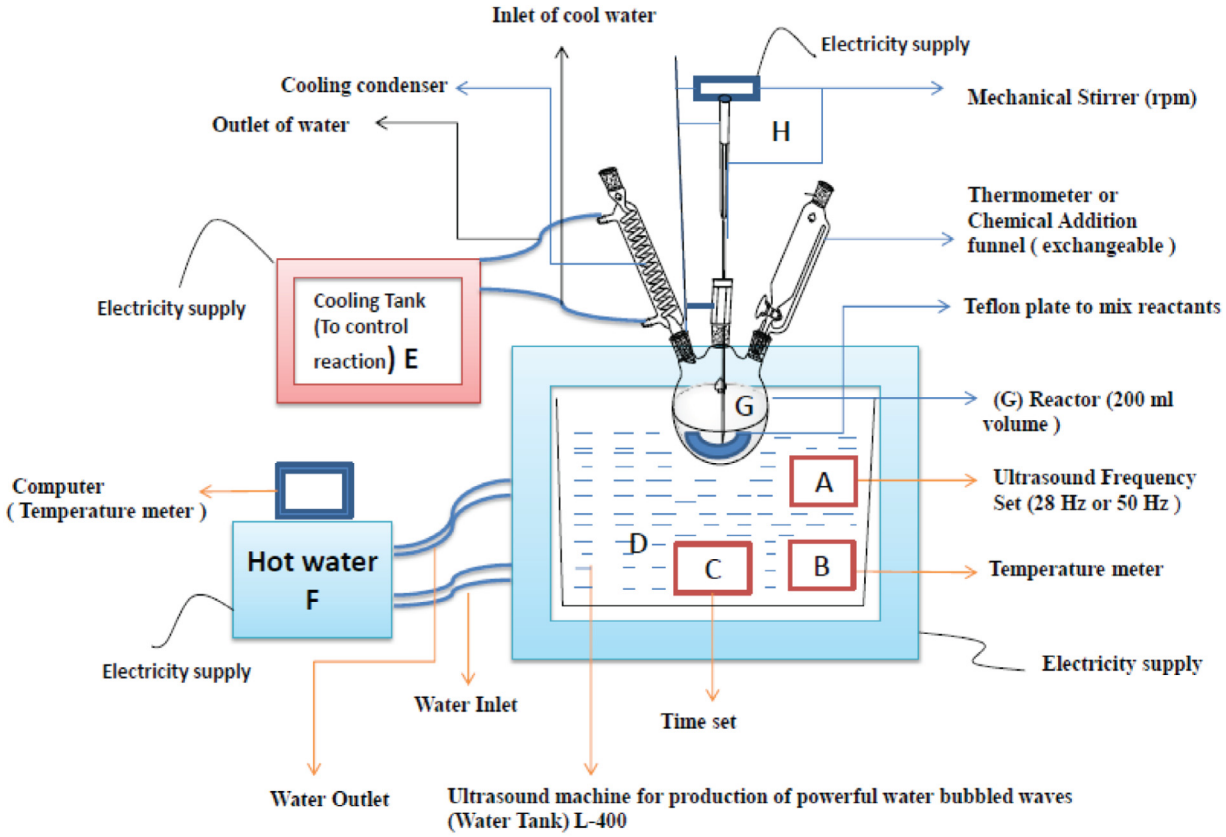

Fig. 1. Schematic diagram of experimental set up.