Asian Journal of Green Chemistry 3 (2019) 53-69

Contents lists available at Avicenna Publishing Corporation (APC)

Asian Journal of Green Chemistry

Journal homepage: www.ajgreenchem.com

Original Research Article

Synthesis of spiro [cyclobutane-1,2'-indene]-1',3'-dione under a new multi-site phase-transfer catalyst combined with ultrasonication-a kinetic study

Manickam Sathiyaraj, Perumal Venkatesh*

Department of Chemistry, Pachaiyappa's College Chennai, Tamil Nadu, India - 600 030

ARTICLE INFORMATION

Received: 14 May 2018
Received in revised: 7 June 2018
Accepted: 22 June 2018
Available online: 19 July 2018

DOI: 10.22034/ajgc.2018. 66101

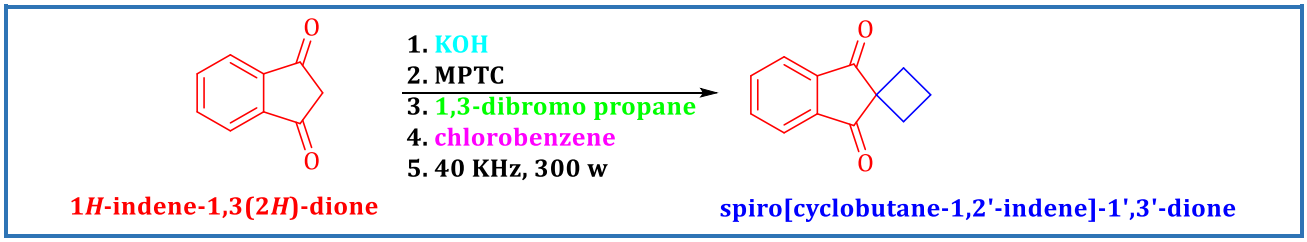
KEYWORDS

Sonocatalysis
Interfacial Reaction
Kinetics
MPTC
1,3-dibromo propane

ABSTRACT

In the present study, kinetics of synthesis of spiro[cyclobutane-1,2'-indene]-1',3'-dione was successfully carried out by spirolation of indene-1,3-dione with 1,3-dibromo propane using aqueous potassium hydroxide and, then, catalyzed by a newly synthesized multi-site phase-transfer catalyst viz., 1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triiu tribromide (MPTC), under ultrasonic (40 kHz, 300 W) assisted organic solvent condition. The pseudo first-order was observed under the ultrasound irradiation (40 kHz, 300 W) in a batch reactor as the overall reaction was greater than the one without the ultrasound.

Graphical Abstract



Corresponding author, email: venkat_28@hotmail.com (P. Venkatesh).
Fax: +9144 26426900.

Introduction

Phase-transfer catalysis (PTC) is an effective tool to synthesize the organic chemicals from two immiscible reactants [1]. As the chemical reactants reside in the immiscible phases, phase-transfer catalysts have the ability to carry one of the reactants as a highly active species for penetrating the interface, into the other phase where the reaction takes place, and to give a high conversion and selectivity for the desired product under mild reaction conditions. The first reaction scheme addressed by Starks in 1971 was for the reaction of aqueous sodium cyanide and organic 1-chlorooctane. In this sense, the cyanide displacement reaction takes place rapidly by adding 1% of the tetrahexylammonium chloride to achieve near 100% of the product yield in 2–3 h, and that is in contrast to his result of observing no reaction after 24 h in the absence of any catalyst [2]. Nowadays, synthetic methods including alkylation, oxidation, reduction, addition, hydrolysis, etherification, chiral reaction, polymerization, and biochemical reactions, are confirmed to have promising results by applying phase-transfer catalysis techniques [2–11].

Currently, ingenious new analytical and experimental techniques which are environmentally benign techniques viz., ultrasound and microwave irradiation have become immensely popular in promoting various organic reactions [12–20]. Ultrasound irradiation which is a transmission of a sound wave through a medium is regarded as a form of energy which enhances the rate of the reaction due to mass transfer and effective mixing [18–25].

In this research study, for the first time, we evaluated the influence of ultrasound in association with a new multi-site phase-transfer catalyst (MPTC) on the synthesis of spiro[cyclobutane-1,2'-indene]-1',3'-dione by spirolation of indene-1,3-dione using 1,3-dibromo propane (DBP) as a limiting agent. Since, the kinetic study of the spirolation of indene-1,3-dione using 1,3-dibromo propane under the controlled MPTC reaction conditions was challenging, we followed the kinetic study of spirolation using 1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triium tribromide (MPTC), as a new phase-transfer catalyst under ultrasonic condition (40 kHz, 300 W). In addition, to the best of our knowledge, there is no literature reporting the spirolation of indene-1,3-dione with 1,3-dibromo propane under MPTC and ultrasonic irradiation condition.

Experimental

Materials and methods

All the reagents; including, indene-1,3-dione (Merk), 1,3-dibromo propane (Alrich), ethylamine (Alrich), paraldehyde (CDH), potassium hydroxide (CDH), toluene (CDH), chlorobenzene (Merk), biphenyl (CDH) and other reagents for synthesis, were guaranteed grade (GR) chemicals and were

used as received without further purification. The FT-IR Spectra were recorded using a Brucker-Tensor 27 FT-IR spectrophometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded by Bruker 300 MHz and 75 MHz spectrometer using TMS as an internal standard and $CDCl_3$ as the solvent. Elemental analysis was performed using a PerkinElmer 240 B elemental analyzer. Gas chromatography was carried out using a GC-Varian, 3700 model.

Ultrasonic process equipment

Ultrasonic energy is transmitted to the process vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor was made of two layers of stainless steel sheet. The sonochemical reactor configuration used in this work was an ultrasonic liquid bath. The internal dimension of the ultrasonic cleaner tank was 48 cm × 28 cm × 20 cm with liquid holding capacity of 5 litres (Ultrasonic water bath, Equitron, Media Instrument Manufacturing Company, Chennai, India-600 004). The reactor has an operating frequency of 28 and 40 kHz with an output of 300 W. Both of the ultrasounds are separately produced through flat transducer mounted at the bottom of the tank. In this ultrasonic instrument, there is a provision for a drain as well as an outlet at the top which provides the facility of the continuous operation of the work. The process vessel was immersed in water. An additional heater equipped with a temperature controller was also used to control the low temperature reactions. When the water level became lower than the outlet, at the 3 cm below the top of the sonicator, the applied frequency was automatically cut off. The reactor was a 250 mL three-necked Pyrex round-bottom flask. This reaction vessel was supported at the center of the ultrasonic cleaning bath at 2 cm above the position of the transducer which is fixed at the bottom of the ultrasonicator in order to get the maximum ultrasonic energy. All the experimental parameters were done at 40 kHz with output power of 300 W [26–30].

Synthesis of a new multi-site phase-transfer catalyst

Synthesis of 1,3,5-triethyl-1,3,5-triazinane

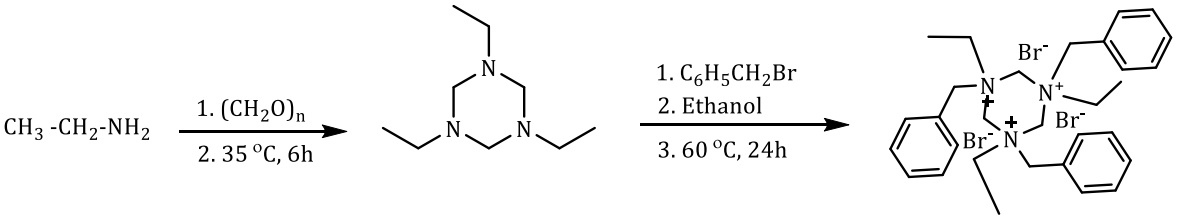
A mixture of 83 g of ethylamine, 40 g of paraldehyde was placed in a 250 mL three necked round bottomed pyrex flask. The reaction was carried out at 35 °C for 6 h and gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum to produce the 1,3,5-triethyl-1,3,5-triazane (Scheme 1). The white liquid was stored in a $CaCl_2$ desiccator. Yield 92%, ^{1}H NMR (300 MH_Z, $CDCl_3$): δ 1.054-1.102 (t, 9H-CH_2-CH_3), 2.449-2.522 (q, 6H-CH_2-CH_3), 3.432 (s, 6H, N-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$): δ 12.62 (CH_2-**C**H_3), 46.50 (CH_2-CH_3), 73.72 (N-CH_2). MS (EI, 70 Ev, %): m/z 171.17; Anal. Calcd.: C, 62.98; H, 12.16; N, 24.23; Found: C, 63.11; H, 12.36; N, 24.53.

Synthesi of 1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triium tribromide (MPTC)

A mixture of 8.7 g (50.7 mmol) of 1,3,5-triethyl-1,3,5-triazane, 25 mL of benzyl bromide, and 75 mL of ethanol was placed in a 250 mL three necked round bottomed pyrex flask. The reaction was carried out at 60 °C for 24 h and, then, was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and onium salt, such as 1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triium tribromide, MPTC, (Scheme 1) was washed with n-hexane (3×20 mL). The white solid MPTC was stored in $CaCl_2$ desiccators. Yield 94%, mp 191 °C, ^{1}H NMR (300 MH_Z, $CDCl_3$): δ 1.403-1.451 (t, 9H-CH_2-CH_3), 2.960-3.02 4 (q, 6H-CH_2-CH_3), 4.140 (s, 6H-Ar-CH_2), 5.203 (s, 6H, N^+-CH_2) 7.345-7.666 (m, 15H, ArH). ^{13}C NMR (75 MH_Z, $CDCl_3$): δ 50.40 (Ar-CH_2), 66.18 (N^+-CH_2), 41.92 (**C**H_2-CH_3), 11.22 (CH_2-CH_3), 128.98, 129.41, 130.51, 131.36 (Ar-C). Anal. Calcd.: C, 65.19; H, 7.28; N, 7.02; Found, C, 65.39; H, 7.68; N, 7.62.

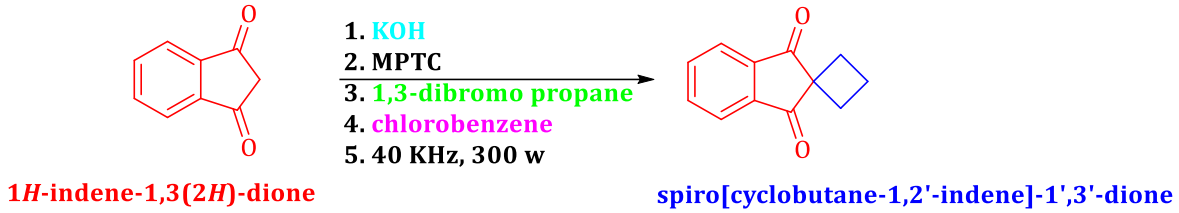
General procedure for the synthesis spiro[cyclobutane-1,2'-indene]-1',3'-dione

To the mixture of KOH (15 g, 0.26 mol) in water (30 mL), with 1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triium tribromide (MPTC), (0.5 g), indene-1,3-dione (1 g, 0.0068 mol) was added under overhead stirring to generate the carbanion. Then, 1,3-dibromo propane (1.64 g, 0.82 mL, 0.0081 mol) in chlorobenzene (30 mL) was added slowly. The reaction mixture was heated up to 45 °C and vigorously stirred for 6 h. The crude product was isolated by simple extraction with diethyl ether (3×25 mL). The organic layer was collected and the solvent was evaporated under the reduced pressure. The crude product was chromatography (SiO_2) employing *n*-hexane/ethyl acetate (9:1) as an eluent to obtain a pure monoderivative (Scheme 2). The identity of the product was confirmed by ^{1}H NMR and ^{13}C NMR spectra. ^{1}H NMR (300 MH_Z, $CDCl_3$): δ 1.928-2.003 (m, 2H, CH), 2.279-2.320 (t, 4H, CH_2), 7.038-7.370 (m, 4H, Ar-CH). ^{13}C NMR (75 MH_Z, $CDCl_3$): δ 16.04 (CH_2), 28.50 (HC), 69.60 (C), 129.64, 133.22, 138.09, (Ar-CH). 193.37 (C=O).



1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triium bromide

Scheme 1. (Preparation of MPTC) 1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triium tribromide (MPTC)



Scheme 2. Preparation of spiro [cyclobutane-1,2'-indene]-1',3'-dione

Sonicated kinetics of the formation of spiro[cyclobutane-1,2'-indene]-1',3'-dione

The reactor was a 250 mL three-necked pyrex flask, serving the purposes of agitating the solution, inserting the thermometer, taking samples and feeding the feed. 15 g of KOH was dissolved in 30 mL deionized water in order to prepare a aqueous alkaline solution. Known quantities of MPTC (0.5 g), indene-1,3-dione (1 g, 0.0068 mol) and biphenyl (Internal standard, 0.2 g) were added to the reactor. The reaction vessel (The reactor) was supported at the center of the ultrasonicator to get the maximum ultrasonic energy. To form the organic phase, after stirring at 600 rpm for ten minutes at 45 °C, 1,3-dibromo propane (1.64 g, 0.0081 mol, 0.82 mL) in 30 mL of chlorobenzene (Solvent) was added. To start the reaction, the aqueous and organic solutions were mixed in the flask. The organic phase sample (0.2 mL) was withdrawn from the reactor at each time interval and was put into the glass vials containing 2 mL of chlorobenzene. The contents of the reaction mixtures were analyzed by GC. The analyzing conditions are as follows: GC-Varian 3700 model, column, 30 m ×0.525 mm i.d. capillary column containing 100% poly (Dimethyl siloxanen); injection temperature, 250 °C; FID detector (300 °C). Yields were determined from standard curve and using biphenyl as internal standard (IS).

Reaction mechanism and kinetic model

For synthesizing spiro[cyclobutane-1,2'-indene]-1',3'-dione compound, the overall reaction of indene-1,3-dione and 1,3-dibromo propane (DBP) was catalyzed by a new phase-transfer catalyst, viz., 1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triium tribromide (MPTC), (Q^+Br^-) in the aqueous alkaline (KOH) bi-phase medium as is illustrated in (Scheme 2). The reaction was carried out under MPTC assisted ultrasonic irradiation condition. In the current investigation the kinetics was followed in the presence of an excess amount of indene-1,3-dione and by fixing 1,3-dibromo propane as the limiting agent. The main reason for investigating this reaction is the effect of low frequency ultrasound irradiation (40 kHz, 300 W) along with agitation speed (600 rpm) to find out the change of k_{app} value of this system.

Results and discussion

Definition

The conversion (X) of 1,3-dibromo propane(DBP) is defined as follows:

$$X=1-\{[DBP]_0 /[DBP]_{.o,i}\} \quad (1)$$

Where $[DBP]_o$ and $[DBP]_{o,i}$ represent the concentration of 1,3-dibromo propane at time (t) t = 0 and t>0, respectively.

Rate expression

The rate expression for this reaction may be expressed as:

$$-r_{DBP}=k_{app}[DBP]_o \quad (2)$$

Where k_{app} is the apparent reaction rate constant. This reaction is carried out in a batch reactor, so the diminution rate of DBP with time (t) can be expressed as:

$$-d[DBP]_0/dt=-r_{DBP}=k_{app}[DBP]_o \quad (3)$$

on integrating the Eq. (3) yields:

$$-\ln\{[DBP]_0/[DBP]_{.o,i}\}=-\ln(1-X)=k_{app} \quad (4)$$

Using Eq. (4), we can get the k_{app} value experimentally by plotting –ln(1-X) against time, (t). This pseudo first-order equation was used to calculate the k_{app} value for the present study.

The reaction was conducted in a 250 mL three-necked pyrex round-bottom flask which permits agitating the solution, inserting the water condenser to recover organic reactant and taking samples and feeding the reactants. This reaction vessel was suspended at the centre of the sonicator. A known quantity of chlorobenzene (30 mL, solvent), potassium hydroxide (0.26 mol) and 0.2 g biphenyl IS, (Internal standard) was introduced into the reactor. Then, 1 g (0.0068 mol), of indene-1,3-dione and 0.82 Ml (0.0081 mol) of 1,3-dibromide propane, 0.5 g of the newly synthesized MPTC (With respect to 1,3-dibromide propane, limiting reagent) were introduced to the reactor to start the reaction. The reaction mixture was stirred at 600 rpm along with sonication (40 kHz, 300 W). The phase separation was almost immediate on arresting the stirring process. Samples were collected from the organic layer of the mixture (by stopping the stirring for 20–30 s (Each time) at regular time intervals. A pinch of anhydrous $CaCl_2$ was placed in the sample vials to

absorb any moisture present in the organic layer. Each run consisted of six samples taken over the period ranging from 5 to 30 min. The kinetics was followed by estimating the amount of 1,3-dibromo propane (Limiting reagent) that disappeared using a gas Chromatography (GC-Varian 3700 model). The analyzing conditions were as follows; Column, 30 m × 0.525 mm i.d. capillary column containing 100% poly (Dimethyl siloxanen); injection temperature, 250 °C; FID detector (300 °C). Yields were determined from standard curve using biphenyl as an internal standard.

Combined effect of ultrasound and stirring on reaction rate

To ascertain the influence of agitation speed on the rate of spirolation of indene-1,3-dione, the speed of agitation was varied in the range of 100–1000 rpm along with ultrasound irradiation (40 kHz, 300 W) using the newly prepared 1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triium tribromide (MPTC) as the phase-transfer catalyst. The results showed that the rate of the reaction increases linearly as the agitation speed increases from 100 to 600 rpm (Figure 1). However, by increasing the agitation seed from 600 to 1000 rpm, no significant improvement in the reaction rate constant was observed. This is due to the fact that the interfacial area per unit volume of dispersion increased linearly with increasing the stirring speed up to 600 rpm, while there was no significant increase in the interfacial area per unit volume of dispersion with the corresponding increase in the speed. Thus, increasing the stirring speed changed the particle size of the dispersed phase. Therefore, the agitation speed was set at 600 rpm for studying the reaction phenomena from which the resistance of mass transfer stays at a constant value [28–30]. The k_{app} values are evaluated from the linear plot of –ln(1-X) versus time. The results indicate that the mechanical effects brought up by the use of ultrasounds are responsible for the enhancement of the kinetics by harsh mixing, enhancement of mass transfer and so on. Moreover, when the same reaction was carried out in the absence of ultrasound, k_{app} value (k_{app} = 5.22×10^{3}, min^{-1}, silent condition) was observed at almost four folds lesser than the one in the presence of ultrasonication (k_{app} = 23.82×10^{3}, min^{-1}, 40 kHz, 300 W).

Effect of MPTC

The experiments were conducted by varying the amounts of the newly prepared MPTC as the other experimental parameters were kept constant. The influence of the amount of MPTC on the spirolation of indene-1,3-dione has been studied by varying amounts of MPTC from 0.1 g to 0.9 g under ultrasound irradiation (40 kHz, 300 W). Apparent rate constants were evaluated from the plot of –ln(1-X) versus time, which follow pseudo first-order kinetics. As shown in (Figure 2), the rate of the reaction increased with increasing in the amount of MPTC along with ultrasound

irradiation (40 kHz, 300 W). The k_{app} values are linearly dependent on the amount of phase-transfer catalyst. The increase in the k_{app} value which is attributed to the positive effect of ultrasound might be enlarged along with stirring speed (600 rpm).

Effect of varying 1,3-dibromo propane concentration

To investigate the influence of 1,3-dibromo propane (DBP) on the kinetics of spirolation synthesis of 1,3-indanedione under ultrasonic irradiation condition (40 kHz, 300 W), the amount of DBP was varied from 0.25 to 1.25 mL. In the presence and absence of the ultrasound, the results are shown in (Table 1). The data clearly indicate that the k_{app} value increases with increasing the amount of 1,3-dibromo propane. As the 1,3-dibromo propane concentration increased, the probability of finding the substrate with active-site of the catalyst is enhanced and thereby the rate of the reaction can be increased [31, 32]. The results also indicate an additional increase when the reaction was carried out under ultrasound condition at 40 kHz, 300 W [28–31]. This is more likely due to reducing the surface area between the aqueous and organic phases, which results in having more reactants collide with each other simultaneously producing higher k_{app} value.

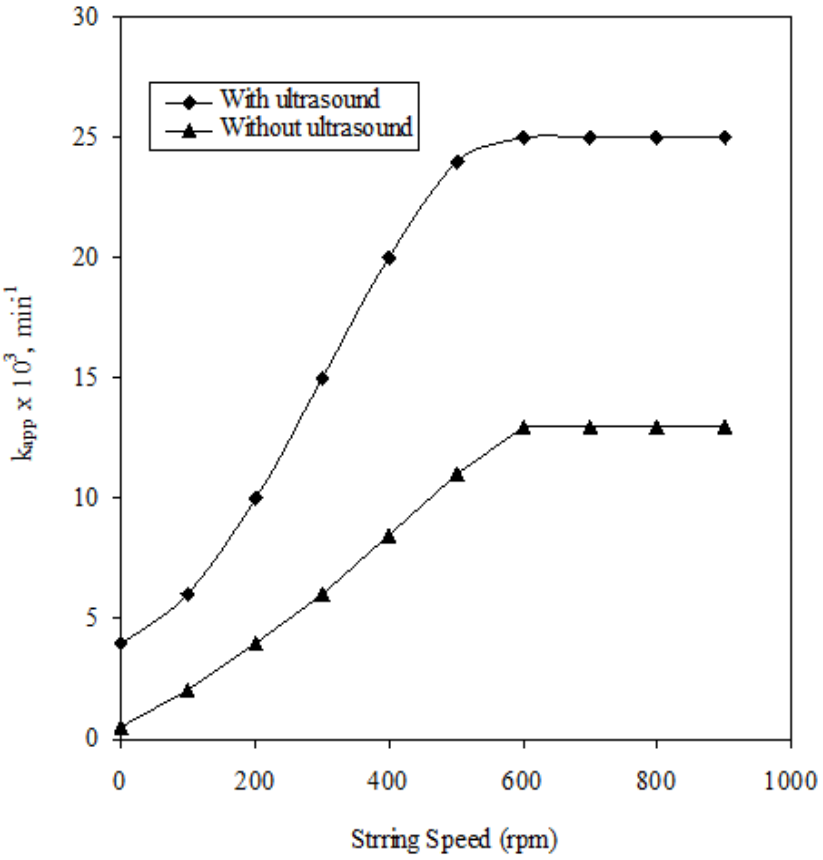


Figure 1. Effect of stirring speed [Plot of the apparent rate constant versus various stirring speeds; spirolation of indene-1,3-dione under ultrasonic condition: 15 g of KOH, 30 mL of H_2O, 1g of indene-1.3-dione 0.82 mL of 1,3-dibromo propane, 0.2 g of internal standard (biphenyl), 0.5 g of MPTC, 30 mL of chlorobenzene, 45 °C; ultrasound conditions (40 kHz, 300 W)]

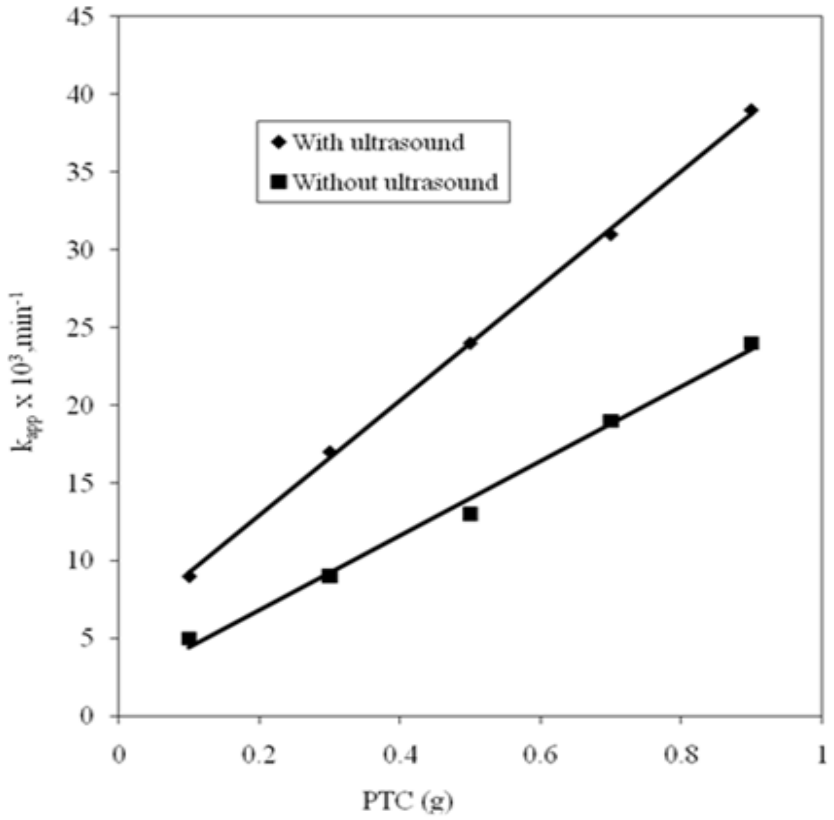


Figure 2. Effect of MPTC [Effect of the amount of PTC on the apparent rate constant: spirolation of indene-1,3-dione under ultrasonic condition: 15 g of KOH, 30 mL of H_2O, 1 g of indene-1.3-dione, 0.82 mL of 1,3-dibromo propane, 0.2 g of internal standard (biphenyl), 30 mL of chlorobenzene, 600 rpm, 45 °C; ultrasound conditions (40 kHz, 300 W)]

Table 1. Effect of amount of 1,3-dibromo propane[a]

1,3-dibromo propane (DBP), mL	$k_{app} \times 10^3$, min^{-1} (With ultrasound, 40 kHz, 300 W)	$k_{app} \times 10^3$, min^{-1} (Without ultrasound)
0.25	16.91	7.01
0.50	21.82	9.02
0.75	23.82	11.33
1.00	26.42	12.14
1.25	27.82	13.97

[a] Effect of amount of 1,3-dibromo propane (DBP) on the rate of spirolation of indene-1,3-dione under ultrasonic condition: 15 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 1 g of indene-1,3-dione, 0.5 g of MPTC, 30 mL of chlorobenzene, 600 rpm, 45 °C; ultrasound conditions (40 kHz, 300 W)

Effect of temperature

The effect of temperature on the reaction between 1,3-indanedione and 1,3-dibromo propane was studied under similar conditions. The temperature was varied from 30 to 55 °C. The kinetic profile of the reaction is obtained by plotting the pseudo first-order relation i.e. –ln(1-X) versus time. It is obvious that the reactivity is increased with an increase in the temperature along with ultrasonic effect [33]. The reason is that the number of reactant molecules possess higher activation energy at a higher temperature and thus the ultrasonic wave easily passes through the reactor [34]. The other point is that the collision of the reactants at higher temperature is also increased. Hence, the apparent rate constant is increased at higher temperature. Therefore, the apparent rate constants are increased with an increase in the temperature along with ultrasonic condition viz., 40 kHz, 300 W. Arrhenius plots were made in (Figure 3) of –ln k_{app} against 1/T to get the activation energy of 49.46 kJ. mol^{-1}.

From the literature survey, the dehydrobromination of (2-bromoethyl) benzene was catalyzed by tetraoctylammonium bromide (TOAB) and, then, an extraction mechanism was proposed [32–35] due to lower Ea value (< 43 $kJ.mol^{-1}$). In general, higher activation energy (more than 43 $kJ.mol^{-1}$) suggests an interfacial mechanism. The activation energy for the heterogeneous ethylation of phenylacetonitrile was reported to be 53.64 $kJ.mol^{-1}$ and for this reason an interfacial mechanism was proposed [32–36]. Further, in the *N*-alkylation of pyrrolidine-2-one, the E_a (51.35 $kJ.mol^{-1}$) was reported by Sasson and Bilman [37], and for this reaction they proposed an interfacial mechanism. They concluded that the deprotonation of the substrate takes place at the interphase and consequently the organic anion is extracted and reacts in the bulk or the organic phase. The rate-determining step in the process is the anion exchange at the interphase. In our study, the observed Ea value is 48.36 kJ. mol^{-1}. Hence, we proposed an interfacial mechanism for our present study [32–39].

Effect of ultrasonic power

Ultrasonic irradiation is defined as acoustic waves with frequencies in the 20 kHz -100 MHz range [28–40]. They create cavities locally generating high temperature and pressures or strong electric fields [40–42]. Ultrasound is known to accelerate diverse types of organic reactions as it is established in many organic reactions, which are otherwise slow due to poor mass transfers and are accelerated by sonication due to cavitation [43, 44]. It has been reported that a combination of MPTC and ultrasound is often better than either of the two techniques alone [28–31, 45–47]. Such a transfer of species across the interface and ultrasound merely facilitates this transfer, possibly by increasing the interfacial area across which this transfer occurs.

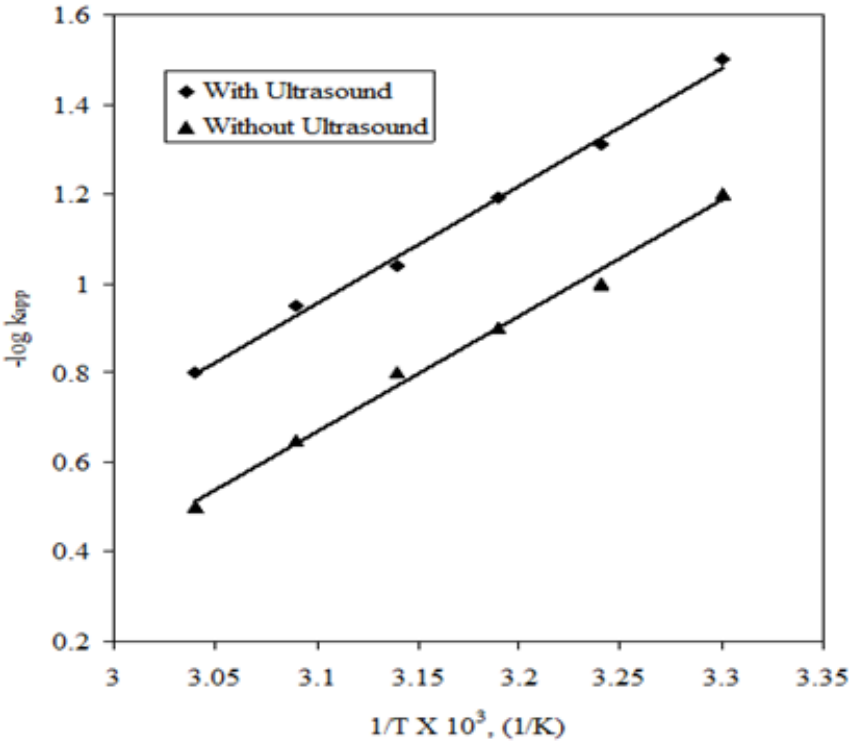


Figure 3. Arrhenius plot [Arrhenius plot; spirolation of indene-1,3-dione under ultrasonic condition: 1 g of KOH, 30 mL of H_2O, 1 g of indene-1.3-dione, 0.82 mL of 1,3-dibromo propane, 0.2 g of internal standard (biphenyl), 0.5 g of MPTC, 30 mL of chlorobenzene, 600 rpm, ultrasound conditions (40 kHz, 300 W)]

Table 2. Effect of ultrasonic frequency[a]

Ultrasonic frequency (kHz, 300 W)	$k_{app} \times 10^3$, min^{-1}
0	5.22
28	15.85
40	23.82

[a] Influence of ultrasonic frequencies on the rate of spirolation of indene-1,3-dione under ultrasonic condition: 15 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 1 g of indene-1,3-dione, 0.82 mL of 1,3-dibromo propane, 0.5 g of MPTC, 30 mL of chlorobenzene, 600 rpm, 45 °C

In the present study two different ulltrasonic frequencies i.e. 28 kHz and 40 kHz were used for the spirolation of indene-1,3-dione with the same output power of 300 W, under similar conditions using MPTC as the catalyst. The pseudo first-order kinetic profile of the reaction is obtained by plotting –ln(1-X) against time. In our experimental condition at 30 min, without ultrasonic irradiation (Silent condition), the k_{app} values can be as 5.22×10^{-3}, min^{-1} but in the presence of ultrasonic irradiation the k_{app} values are 15.85×10^{-3}, min^{-1} and 23.82×10^{-3}, min^{-1} for 28 kHz (300 W)

and 40 kHz (300 W), respectively (Table 2). The applied ultrasonic frequency induces various degrees of "cavity factor". The cavity factor is otherwise called cavitational effect. It is the propagation of ultrasound through a liquid solution in the reactor inducing both physical and chemical processes by acoustic cavitation: the formation, growth and adiabatically implosive collapse of bubbles in the liquid solution. The final collapse of the bubbles produces extremely high temperatures (> 5000 °C) and pressures (> 100 Mpa), which accelerated the reaction.

At lower frequencies (under 100 kHz) the formation of bubble has more time to grow and therefore the cavitational collapse is more violent. Consequently, studies would look for mass transfer improvement generally for the lower frequency range. At higher frequencies more bubbles are produced which collapse, producing more products [28]. *Mason* et al. demonstrated the inverse dependence of mechanical and chemical effects on frequency in their treatment of polyphenylene ether [48]. Additionally, increased sonochemical activity at high frequencies was shown in a comparative study by *Entezari* and *Kruus* [49]. Hence at higher frequencies, a higher reaction rates are observed [50]. The exact maximum frequency for cavitation to occur is also dependent on the geometry, temperature, ambient pressure, viscosity and the gas composition of the reactor solution. Moreover, there is general agreement for chemical processes which are maximised at high frequencies and mechanical effects which are maximised at low frequencies. It is worth mentioning that the literature produced conflicting results as can be observed [51–53]. However, in our experimental condition (Table 2), the overall k_{app} was increased by increasing the ultrasonic frequency in the order of silent condition (without ultrasonication) < 28 kHz (300 W) < 40 kHz (300 W).

Effect of organic solvents

In this work, the influence of various organic solvents on the rate of spirolation of indene-1,3-dione was followed under other standard reaction conditions. Five organic solvents employed in this study are toluene, anisole, cyclohexane, chlorobenzene, and n-hexane. From the pseudo first-order plot of –ln(1-X) against time, the k_{app} values are shown in Table 3. From the Table 3, chlorobenzene possesses a higher k_{app} value among the five organic solvents, due to its higher dielectric constant. In another view, the ultrasonic irradiation can enhance the rate in the presence of more polar solvents due to passing higher ultrasonic waves to the reactor as it makes fruitful collision between the reactants, and hence we get higher k_{app} value for chlorobenzene solvent of this system and also this statement is not always true [43].

Effect of varying potassium hydroxide concentrations

In the MPTC/OH^- catalyzed reaction, the reaction rate is known to be greatly affected by a concentration of the alkaline compound. The rate of spirolation of indene-1,3-dione strongly depends on the strength of the potassium hydroxide. The pseudo first-order kinetic experiments were carried out, employing 20 to 40 g of KOH under similar reaction conditions. The kinetic profile of the reaction is obtained by –ln(1-X) against time. The k_{app} values tremendously increased with increase in basicity of hydroxide ion (Table 4).

Table 3. Effect of organic solvents[a]

Solvents	Dielectric constant	$k_{app} \times 10^3$, min^{-1}(With ultrasound 40 kHz, 300 W)	$k_{app} \times 10^3$, min^{-1} (Without ultrasound 40 kHz, 300 W)
Cyclohexane	2.02	10.02	4.98
n-hexane	2.28	11.24	5.92
Toluene	2.31	18.92	7.82
Anisole	4.30	21.61	10.21
Chlorobenzene	5.60	23.82	11.43

[a] Influence of organic solvents on the rate of spirolation of indene-1,3-dione under ultrasonic condition: 15 g of KOH, 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 1 g of indene-1,3-dione, 0.82 mL of 1,3-dibromo propane, 0.5 g of MPTC, 600 rpm, 45 °C; ultrasound conditions (40 kHz, 300 W)

Table 4. Effect of potassium hydroxide[a]

Amount of KOH(g)	$k_{app} \times 10^3$, min^{-1} (With ultrasound, 40 kHz, 300 W)	$k_{app} \times 10^3$, min^{-1} (Without ultrasound)
20	14.22	7.82
25	18.93	9.91
30	23.82	11.21
35	31.84	15.34
40	40.34	19.44

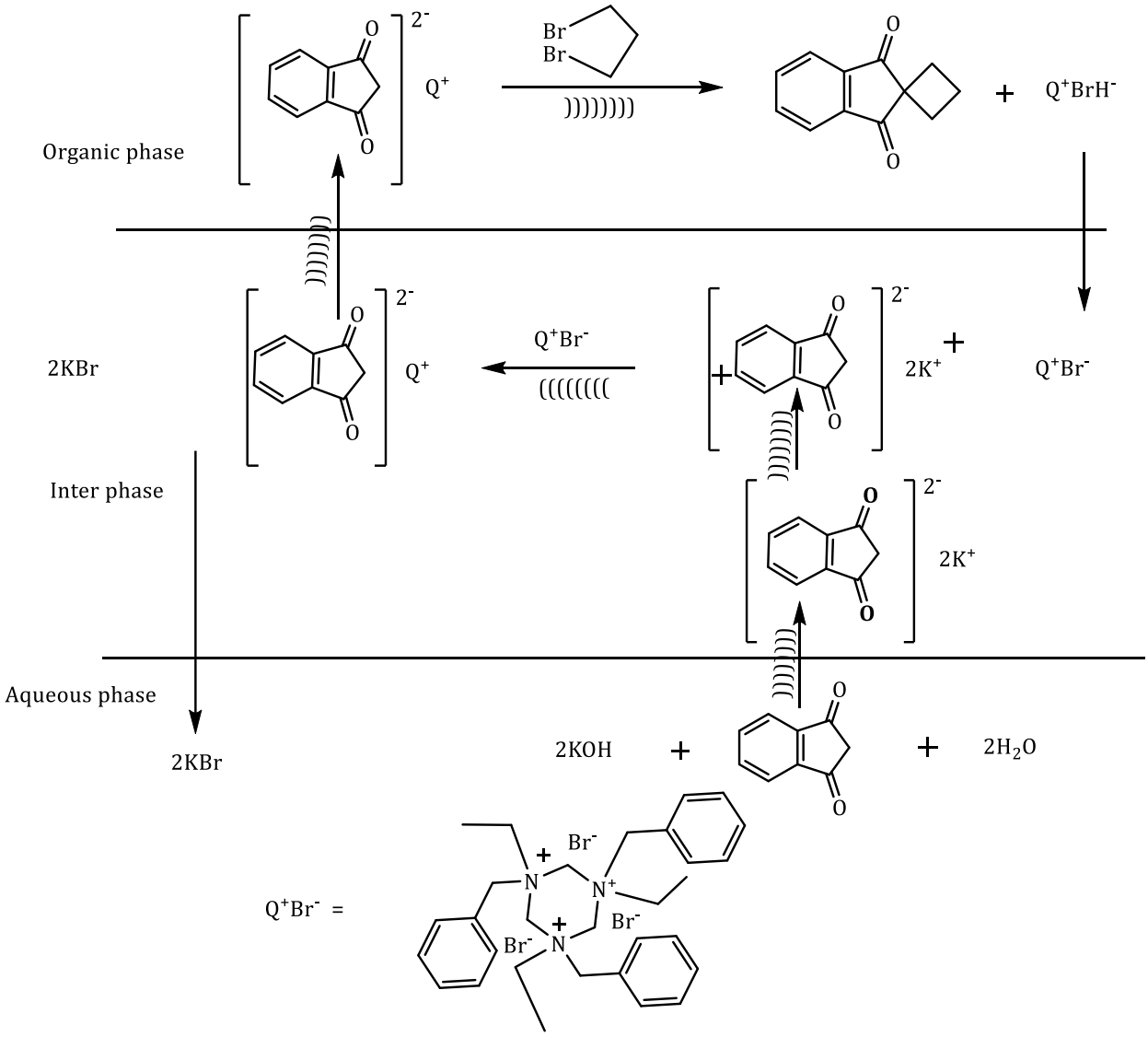
[a] Influence of alkalinity on k_{app} in the spirolation of indene-1,3-dione under ultrasonic condition: 30 mL of H_2O, 0.2 g of internal standard (biphenyl), 1 g of indene-1,3-dione, 0.82 mL of 1,3-dibromo propane, 0.5 g of MPTC, 30 mL of chlorobenzene, 600 rpm, 45 °C; ultrasound conditions (40 kHz, 300 W)

It suggests that the hydroxide ions are less solvated by water molecules at higher concentration of KOH as the activity of the hydroxide ion increases. In the kinetic study of C–alkylation of benzyl cyanide with n-bromopropane under PTC condition [33–35] the observed rate constant tremendously increased with an increase in basicity of hydroxide ion. In the present case,

extraction of indene-1,3-dione is more effective when the reaction is carried out in the presence of ultrasound irradiation along with higher concentration of potassium hydroxide.

Mechanism

The experimental result from the present kinetic study indicates that the dependencies of the kinetic data on the entire stirring speed, concentration of the catalyst, aqueous potassium hydroxide and temperature and higher E_a value are indicatives of an interfacial mechanism. Hence, we proposed an interfacial mechanism for the current study (Scheme 3).



1,3,5-tribenzyl-1,3,5-triethyl-1,3,5-triazinane-1,3,5-triium tribromide (MPTC)

Scheme 3. Reaction mechanism

Initially, the hydroxide ion deprotonates indene-1,3-dione at the interface, forming an ion-pair (InC^-K^+). Upon addition of the catalyst, Q^+X^-, ion exchange takes place at the interface (InC^-Q^+) and the new formed ion pair InC^-Q^+ which is more organophilicity easily migrates into the organic phase. This ion-pair reacts with the propargylating agent (DBP) in the organic phase resulting the formation of the required propargylated product i.e., spiro[cyclobutane-1,2'-indene]-1',3'-dione.

Conclusion

In the present study, the reaction was controlled to study the kinetic aspects of the formation of the spiro[cyclobutane-1,2'-indene]-1',3'-dione from indene-1,3-dione and 1,3-dibromo propane under ultrasonic-phase-transfer catalyst condition. The apparent reaction rates were observed to obey the pseudo-first order kinetics, performing the reaction in ultrasonic condition resulted in shorter reaction time, selectivity, high yield, etc. The reaction mechanism and the apparent rate constants were obtained from the experimental results, the apparent rate constants are found to be directly dependent on each kinetic variable, viz., [MPTC], [KOH], ultrasonic frequency, stirring speed, organic solvent and temperature. The Energy of activation was calculated from the Arrhenius plot. Based on the experimental evidence, an interfacial mechanism has been proposed. Combination of ultrasound and MPTC resulted in a better efficacy as compared to the individual operations.

Acknowledgments

The authors would like to thank, The Pachaiyappa's Trust and Pachaiyappa's College, Chennai, Tamil Nadu, India-600 030 and University of Madras, Chennai, Tamil Nadu, India-600 005 for their grant permission to do this research work.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1]**.** Yadav G.D. *Top Catal.*, 2004, **29**:145
[2]. Starks C.M., Liotta C.L., Halpern M. *Chapman & Hall*., 1994
[3]. Dehmlow E.V., Dehmlow S.S. *VCH*., 1993
[4.] Sasson Y., Neumann R., *Blackie academic*., 1997
[5]. Weber W.P., Gokel G.W., *Springer – Verlag*., 1977

[6]. Amiri K., Rostami A., Rostami A. *New J.Chem.,* 2016, **40**:7522

[7]. Yang Z., Zeng H., Zhou H., Ji H. *Tetrahedron*, 2012, **68**:5912

[8]. Banerjee B. *Ultrason. Sonochem*., 2017, **35**:14

[9]. Banerjee B. *J. Serb. Chem. Soc*., 2017, **82**:755

[10]. Yang H.M., Chu W.M. *Ultrason. Sonochem*., 2014**, 21:**400

[11]. Anandan S., Asiri A.M., Ashokkumar M. *Ultrason. Sonochem*., 2014, **21**:923

[12]. Lee L.W., Yang H.M. *Ind. Eng. Chem. Res*., 2014, **53**:12257

[13]. Abimannan P., Rajendran V. *Current Catalysis*, 2016, **5**:44

[14]. Zhao P., Wang J., Chen G., Zhou Y., Huang J. *Catal. Sci. Technol.,* 2013, **3**:1394

[15]. Mason T.J., Peters D. *Ellis Horwood*., 2002

[16]. Luche J.L. *Plenum Press*., 1998

[17]. Dubey S.M., Gogate P.R. *Ind. Eng. Chem. Res*., 2014, **53**:7979

[18]. Selvaraj V., Rajendran V. *Ultrason. Sonochem*., 2014, **21**:619

[19]. Soltani Rad M.V. *Ultrason. Sonochem*., 2017, **34**:872

[20]. Safaei-Ghomi J., Tavazoa M., Mahdavinia G.H. *Ultrason. Sonochem*., 2018, **40**:237

[21]. Wang M.L., Brahmayya M., Hsieh Y.M. *J. Taiwan. Inst. Chem. Eng*., 2015, **57**:61

[22]. Toma M., Fukutomi S., Asakura Y., Koda S. *Ultrason. Sonochem*., 2011, **18**:197

[23]. Patil R., Bhoir P., Deshpande P., Wattamwar T., Shirude M., Chaskar P. *Ultrason Sonochem*., 2013, **20**:1327

[24]. Piiskop S., Salmar S., Tuulmets A., Kuznetsov A., Jarv J. *Ultrason. Sonochem*., 2013, **20**:1414

[25]. Akhbari K., Morsali A., Retailleau P., *Ultrason. Sonochem*., 2013, **20**:1428

[26]. Murugan E., Tamizharasu G. *J. Mol. Catal. A: Chem*., 2012, **363**:89

[27]. Wang J., Zong Y., Fu R., Niu Y., Yue G., Quan Z., Wang X., Pan Y. *Ultrason Sonochem*., 2014, **21**:29

[28]. Bussemaker M.J., Zhang D. *Ultrason. Sonochem*., 2013, **21**:436

[29]. Niemczewski B. *Ultrason. Sonochem*., 2014, **21**:354

[30]. Yang H.M., Lin D.W. *Cataly. Commun*., 2011, **14**:101

[31]. Wang M.L., Rajendran V. *Ultrason. Sonochem*., 2007, **14**:368

[32]. Murugesan V., Umapathi M.J. *Ind. J. Ind.Chem*., 2016, **7**:441

[33]. Abimannan P., Selvaraj V., Rajendran V. *Ultrason. Sonochem*., 2015, **23**:164

[34]. Murugesan V., Marimuthu E., Yoganand K.S., Umapathy M.J. *Ind.J. Ind. Chem*., 2017, **8**:241

[35]. Halpern M., Sasson Y., Rabinovitz M. *J. Org. Chem*., 1984, **49**:2011

[36]. Rajendran V., Wang M.L. *J. Mol. Catal. A: Chem*., 2008, **288**:23

[37]. Sasson Y., Bilman N. *J. Chem. Soc. Perkin. Trans*., 1989, **2**:2029

[38]. Wang M.L., Lee Z.F. *J. Mol. Catal. A: Chem*., 2006, **264**:119

[39]. Bhatkhande B.S., Adhikari M.V., Samant S.D. *Ultrason. Sonochem*., 2002, **9**:31

[40]. Mason T.J., Lorimer J.P. *Wiley-VCH*., 2002

[41]. Margulis M.A. *High. Energ. Chem*., 2004, **38**:135

[42]. Ambulgekar G.V., Bhanage B.M., Samant S.D. *Tetrahedron. Lett*., 2005, **46**:2483

[43]. Davidson R.S., Safdar A., Spencer J.D., Robinson B. *Ultrasonics*, 1987, **25**:35

[44]. Lepoint T., Mullie F. *Ultrason. Sonochem*., 1994, **1**:S13

[45]. Mahamuni N.N., Gogate P.R., Pandit A.B. *Ind. Eng. Chem. Res*., 2006, **45**:98

[46]. Wang M.L., Rajendran V. *J. Mol. Catal. A: Chem*., 2007, **273**:5

[47]. Yang H.M., Peng G.Y. *Ultrason. Sonochem*., 2010, **17**:239

[48]. Masson T.J., Cobley A.J., Graves J.E., Morgan D. *Ultrason. Sonochem*., 2011, **18**:226

[49]. Liju W., Ablajan K., Jun F. *Ultrason. Sonochem*., 2015, **22**:118

[50]. Kanthale P., Ashokumar M., Grieser F. *Ultrason. Sonochem*., 2008, **15**:143

[51]. Hatanaka S.I., Mitome H., Yausui K., Hayashi S. *Ultrasonics*., 2006, **44**:e435

[52]. De La Rochebrochar S., Suptil J., Blais J.F., Naffrechoux E. *Ultrason. Sonochem.,* 2012, **19**:280

[53]. Koda S., Kimura T., Kondo T., Mitome H. *Ultrason. Sonochem*., 2003, **10**:149

How to cite this manuscript: Manickam Sathiyaraj, Perumal Venkatesh*. Synthesis of spiro [cyclobutane-1,2'-indene]-1',3'-dione under a new multi-site phase-transfer catalyst combined with ultrasonication - a kinetic study. *Asian Journal of Green Chemistry*, 3 (1) 2019, 53-69. DOI: 10.22034/ajgc.2018. 66101