

AlCl₃-catalysed dimerization of 1,3-cyclopentadiene in the chloroaluminate room temperature ionic liquid

Anil Kumar*, Sanjay S. Pawar

Physical Chemistry Division, National Chemical Laboratory, Pashan Road, Pune 411008, India

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Abstract

The dimerization of 1,3-cyclopentadiene has been studied in the chloroaluminate ionic liquids. The rate of dimerization of cyclopentadiene is higher in the 1-ethyl-3-methyl-1H-imidazolium chloride (EMIC)-containing chloroaluminate than in the *N*-1-butylpyridinium chloride (BPC)-containing chloroaluminate. Acceleration of the dimerization process is noted take place with increasing AlCl₃ contents in both BPC and EMIC and is attributed to the Lewis acid catalysis. The temperature-dependent studies indicate that high temperature induces the dimerization. Quantitative information on the extent of dimerization of 1,3-cyclopentadiene in some Diels–Alder reactions has been offered in this work.

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Keywords: Dimerization; 1,3-Cyclopentadiene; Dicyclopentadiene; Rates; Diels–Alder reaction; Temperature effect

1. Introduction

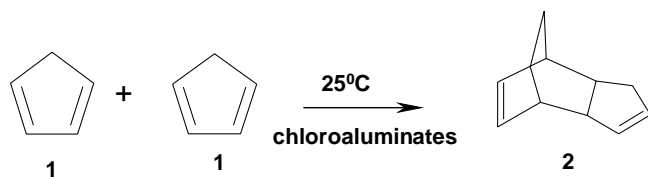
1,3-Cyclopentadiene **1** (Scheme 1) is a key diene employed in Diels–Alder reactions. There exists a large number of reactions in which 1,3-cyclopentadiene is used both for the synthetic work and deciphering the mechanistic aspects of cycloaddition. 1,3-Cyclopentadiene has strong tendency to dimerize in order to give dicyclopentadiene **2** (Scheme 1) during the course of reaction.

This dimerization in conventional organic solvents has been studied extensively and understood with regard to its dependence on solubility parameters, viscosities, etc. of solvents [1–5]. Due to dimerization, less concentration of reactive 1,3-cyclopentadiene becomes available for its reaction with a dienophile. This is true in several sluggish Diels–Alder reactions, where completion of reaction may take several hours. It is therefore, essential to obtain accurate kinetic data of the dimerization of 1,3-cyclopentadiene, as it participates in the reaction and not dicyclopentadiene. Very recently, several reports have become available describing the use of room temperature ionic liquids in view

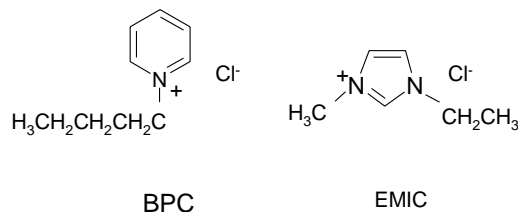
of the urgent need of replacing volatile organic solvents by environmental-benign reaction media in the wake of Green Chemistry [6–12]. The preference of room temperature ionic liquids over conventional organic solvents in organic synthesis is established and is described in several reports [6–12]. In view of growing use of ionic liquids in the synthetic chemistry and also because of importance of 1,3-cyclopentadiene in Diels–Alder reactions, it is essential that one obtain quantitative information on its dimerization in ionic liquid. It may be noted that availability of such data in the area of ionic liquids can help in exploring the use of ionic liquids in various reactions. Such studies will help in rate manipulation of organic reactions by appropriate mixing of ionic liquids. In view of growing use of ionic liquids in the synthetic chemistry and also because of importance of cyclopentadiene in Diels–Alder chemistry, it is essential that one obtains quantitative information on its dimerization in ionic liquid.

The chloroaluminates are important room temperature ionic liquids that have been observed to exhibit the Lewis acid catalysis [13]. They are emerging as viable replacements for carrying out organic reactions [9]. The chloroaluminates (Scheme 2) are the ambient temperature ionic liquids with composition as AlCl₃:MCl, where MCl is either *N*-1-butylpyridinium chloride (BPC) or 1-ethyl-3-methyl-1H-imidazolium chloride (EMIC). The main advantage of

* Corresponding author. Tel.: +91-20-5893044; fax: +91-20-5893044.
E-mail address: akumar@ems.ncl.res.in (A. Kumar).



Scheme 1. Dimerization of cyclopentadiene.



Scheme 2. Chloroaluminate ionic liquid.

using the chloroaluminates lies in the fact that their nature can be easily altered from basic (EMIC or BPC in excess) to acidic (AlCl_3 in excess) by manipulating its composition. Proton in the room temperature chloroaluminates function like Bronsted superacids with Hammett acidity functions, H_0 ranging from -12.6 (1.04:1.0 mol ratio AlCl_3 –EMIC) to -18 (2:1 mol ratio AlCl_3 –EMIC) [14,15]. Higher concentration of AlCl_3 in chloroaluminates impart Lewis acid catalysis to the ionic liquid. In this work, we present the kinetic data of dimerization of 1,3-cyclopentadiene to dicyclopentadiene in the chloroaluminate ionic liquids. No studies on the dimerization of 1,3-cyclopentadiene in ionic liquids have been reported so far.

2. Experimental

2.1. Preparation of chloroaluminate

The chloroaluminates were prepared following the procedures described in the literature [16–19]. For a typical batch of BPC, pyridine (0.30 mol) and *n*-butyl chloride (0.28 mol) were refluxed in dark for about 72 h. After reflux, the mixture was cooled and solid was obtained after separating it from liquid by filtration. The solid was washed with ethyl acetate and recrystallized with 1:1 ethyl acetate/acetonitrile. After repeated filtration and washing with ethyl acetate the solid was transferred in a RB flask. The solid was dried over 70°C for about 24 h under high vacuum. The solid was transferred to the dry box where it was stored in dark glass bottles. The chloroaluminate was prepared by mixing appropriate amount of AlCl_3 by weight with BPC while stirring under nitrogen atmosphere. The material obtained was a clear colorless liquid. A similar procedure was used to prepared EMIC-based chloroaluminate. Sufficient care was taken to handle the moisture-related problems of chloroaluminates [1,9]. The percent compositions are given in (w/w).

2.2. Chemicals

1,3-Cyclopentadiene was freshly cracked from its dimer just prior its use and stored over ice. Methyl acrylate and methyl methacrylate were distilled before their use. Methyl *trans*-crotonate was prepared by heating freshly recrystallized *trans*-crotonic acid with methanol and sulfuric acid for 18 h. The detailed method is described elsewhere [20].

2.3. Dimerization kinetics

Approximately 0.1 ml (~ 0.08 g) of freshly cracked and chilled 1,3-cyclopentadiene was added to ~ 16 ml of chloroaluminate. The reaction flasks were fitted with screw-cap tops with a view to prevent the loss due to evaporation and also to take care of hygroscopic problems. The reaction flasks placed in a thermostat bath with its temperature controlled to $\pm 0.05^\circ\text{C}$ were magnetically stirred for 300 h or times mentioned in the study. Aliquots of 1 ml were removed and diluted to a volume of 20 ml with HPLC grade *n*-hexane.

Temperature dependence of the rate of dimerization was estimated by Arrhenius equation: $\log k_2 = \log A - (E_a/2.30RT)$, where a plot of $\log k_2$ versus $1/T$ gave a straight line, the value of activation energy E_a was calculated from its slope and $\log A$ is intercept of the equation.

2.4. Diels–Alder reactions

A 0.6 ml each of 1,3-cyclopentadiene (7.28 mmol) and methyl acrylate (6.64 mmol) was taken for the reaction of 1,3-cyclopentadiene with methyl acrylate, while 1.5 ml each were taken for the reaction of 1,3-cyclopentadiene (18.20 mmol) with methyl methacrylate (9.65 mmol). In the case of the reaction involving methyl *trans*-crotonate, 1 ml each of 1,3-cyclopentadiene (12.13 mmol) and methyl *trans*-crotonate (9.43 mmol) were taken. In a typical run, freshly cracked cold 1,3-cyclopentadiene was added to 5 ml of chloroaluminate. Then a dienophile was added to another 5 ml of chloroaluminate. Both these solutions were mixed and magnetically stirred at $25 \pm 0.05^\circ\text{C}$ up to times reported. The reaction was quenched by adding chilled water and CH_2Cl_2 was employed for extraction of organics for usual workup as described elsewhere [21].

The concentration of 1,3-cyclopentadiene was estimated by injecting the mixture to GC on the basis of the response factors of 1,3-cyclopentadiene monomer and dicyclopentadiene dimer. Both the monomer and dimer were also characterized by ^1H NMR with monomer peak around 6.4 and that of dimer between 5.4 and 5.9 as described elsewhere [5]. An attempt was also made to estimate the concentration of 1,3-cyclopentadiene by UV-Vis spectrophotometry ($\lambda=241$ nm, $\epsilon = 3390$), but the technique worked out to be less accurate. Each measurement was repeated thrice and average value was treated as a final value. The cycloadducts were identified using standard literature data [20].

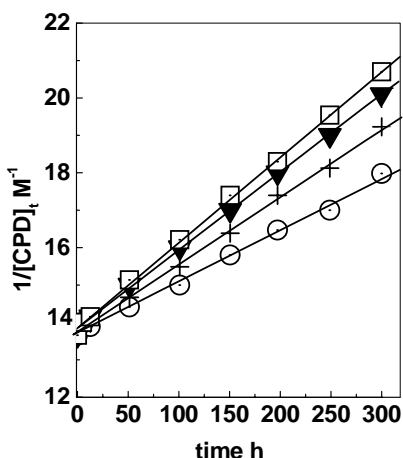


Fig. 1. $1/[\text{CPD}]_t$ vs. time (up to 300 h) for the dimerization of 1,3-cyclopentadiene in BPC-containing chloroaluminates with: (○) 45%; (+) 50%; (▼) 55%; and (□) 60% AlCl_3 .

Entire procedure of kinetics was carried out in nitrogen environment.

3. Results and discussion

We studied the dimerization of 1,3-cyclopentadiene in BPC and EMIC with varying AlCl_3 contents. Our experiments were carried up to 300 h in BPC and EMIC-containing different compositions of AlCl_3 . The dimerization of 1,3-cyclopentadiene under specific conditions is a second order reaction, the rate of which can be determined by:

$$\frac{1}{[\text{CPD}]_t} - \frac{1}{[\text{CPD}]_0} = 2k_2t \quad (1)$$

where $[\text{CPD}]_0$ and $[\text{CPD}]_t$ are the concentrations of 1,3-cyclopentadiene at time, $t = 0$ and after a specified time, t ; k_2 is the second order rate constant.

In Fig. 1 are shown the kinetic plots of the dimerization of 1,3-cyclopentadiene as a function of AlCl_3 content in the BPC-containing chloroaluminate, while Fig. 2 depicts these plots for the EMIC-containing chloroaluminate.

In both the cases, the rate of dimerization of 1,3-cyclopentadiene increases with the increase in the AlCl_3 content (Table 1). First, the dimerization of 1,3-cyclopentadiene is higher in the EMIC-containing chloroaluminate than in

Table 1

The second order rate constants, k_2 for the dimerization of 1,3-cyclopentadiene at 25 °C in chloroaluminates^a

AlCl_3 (%)	k_2 ($\text{M}^{-1} \text{s}^{-1}$) ($\times 10^6$)	
	BPC	EMIC
45	1.90 ± 0.01	2.72 ± 0.02
50	2.50 ± 0.02	3.52 ± 0.03
55	2.90 ± 0.02	4.18 ± 0.04
60	3.18 ± 0.03	4.52 ± 0.03

^a Each k_2 value is an average of triplicate readings, $k_2 = 2.21 \times 10^{-6} \text{M}^{-1} \text{s}^{-1}$ AlCl_3 without any ionic liquid.

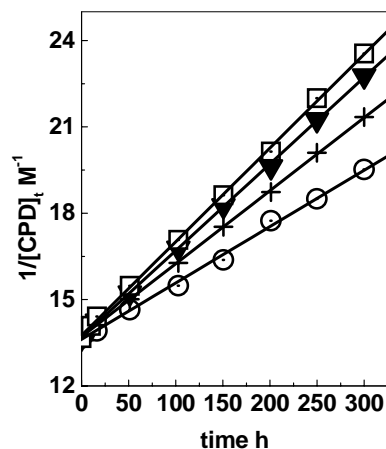


Fig. 2. $1/[\text{CPD}]_t$ vs. time (up to 300 h) for the dimerization of cyclopentadiene in EMIC-containing chloroaluminates with: (○) 45%; (+) 50%; (▼) 55%; and (□) 60% AlCl_3 .

BPC one at all the compositions of AlCl_3 . For example, an increase by $\sim 43\%$ in the k_2 value is noted from BPC to EMIC at a constant composition of 45% AlCl_3 . Let us compare our results of dimerization in chloroaluminates with that in some organic solvents. 1,3-Cyclopentadiene is dimerized in *n*-octane with $k_2 = 0.76 \times 10^{-6} \text{M}^{-1} \text{s}^{-1}$ and in *n*-tetradecane with $k_2 = 1.26 \times 10^{-6} \text{M}^{-1} \text{s}^{-1}$ at 25 °C [4]. These experiments did not report emergence of any cloudiness during the dimerization. The rates for the dimerization process in *n*-octane and *n*-tetradecane at 30 °C under certain experimental conditions (having cloudiness in the solution) have been reported to be about 1.6×10^{-6} and $2.65 \times 10^{-6} \text{M}^{-1} \text{s}^{-1}$, respectively [5]. The rate of dimerization in the BPC-containing chloroaluminate with 60% AlCl_3 becomes four times higher than in *n*-octane, while a six-fold increase is seen in EMIC-containing chloroaluminate with 60% AlCl_3 . These higher rates of dimerization in chloroaluminates can be ascribed to the Lewis acid catalysis by AlCl_3 . As one can see from Fig. 3, the rates of

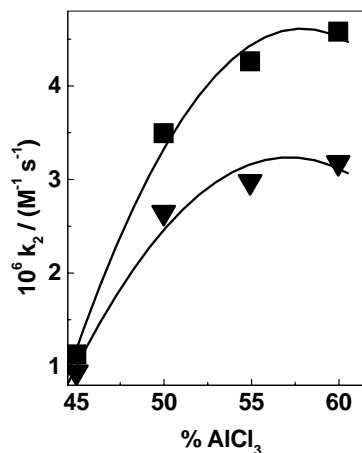


Fig. 3. Rate constant, k_2 as a function of the AlCl_3 content for the dimerization of 1,3-cyclopentadiene in chloroaluminates: (■) EMIC and (▼) BPC.

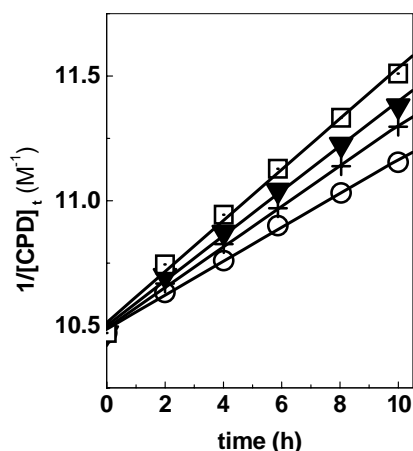


Fig. 4. $1/[\text{CPDI}]_t$ vs. time (up to 10 h) for the dimerization of cyclopentadiene in BPC-containing chloroaluminates with: (○) 45%; (+) 50%; (▼) 55%; and (□) 60% AlCl_3 .

dimerization of 1,3-cyclopentadiene increase with the AlCl_3 contents in both BPC- and EMIC-chloroaluminates. The chloroaluminates with 45% AlCl_3 are basic in nature and hence result into lower k_2 values. With increasing AlCl_3 , the Lewis acid catalysis enhances the dimerization process.

The reaction carried out in AlCl_3 alone offered a rate constant, $k_2 = 2.21 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, which agrees with that obtained in 60% AlCl_3 in EMIC showing the effective role of AlCl_3 in the dimerization process.

Several Diels–Alder reactions involving 1,3-cyclopentadiene, as a diene do not require as many as 300 h. We therefore accurately studied the dimerization process over 10 h. We carried this study only in 45 and 60% of AlCl_3 both in the BPC- and EMIC-chloroaluminates (Fig. 4). The rate of dimerization of 1,3-cyclopentadiene increases from $0.94 \pm 0.02 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ in 45% AlCl_3 to $1.25 \pm 0.03 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ in 60% AlCl_3 (BPC-chloroaluminate), which amounts to be an increase by about 33%. In EMIC-containing chloroaluminates, the rise in k_2 value from 45 to 60% AlCl_3 content is about 42% going from $1.13 \pm 0.03 \times 10^{-6}$ to $1.60 \pm 0.04 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ at 45 and 60%, respectively.

Table 3

The second order rate constants, k_2 for the dimerization of 1,3-cyclopentadiene during its reactions with different dienophiles at 25°C ^a

Dienophile	k_2 ($\text{M}^{-1} \text{ s}^{-1}$) ($\times 10^6$)			
	BPC		EMIC	
	45% AlCl_3	60% AlCl_3	45% AlCl_3	60% AlCl_3
Methyl acrylate ^b	0.28 ± 0.01	0.90 ± 0.02	0.35 ± 0.03	1.08 ± 0.03
Methyl methacrylate ^c	0.65 ± 0.04	1.91 ± 0.04	1.17 ± 0.05	3.44 ± 0.04
Methyl <i>trans</i> -crotonate ^d	0.79 ± 0.03	2.32 ± 0.05	1.71 ± 0.05	5.15 ± 0.06

The reaction carried out in AlCl_3 alone offered a rate constant, rate constant $k_2 = 2.21 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ in AlCl_3 alone without any ionic liquid.

^a Each rate constant value is an average of triplicate readings.

^b Neat reaction (in 11 h) $k_2 = 0.19 \pm 0.01 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, in water $k_2 = 0.35 \pm 0.01 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$.

^c In water $k_2 = 1.08 \pm 0.02 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$.

^d In water $k_2 = 1.69 \pm 0.01 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$.

Table 2

The second order rate constants for the dimerization of 1,3-cyclopentadiene in chloroaluminates at different temperatures^a

AlCl_3 (%)	k_2 ($\text{M}^{-1} \text{ s}^{-1}$) ($\times 10^6$)		
	30°C	35°C	40°C
45% in BP	2.05 ± 0.03	2.16 ± 0.04	2.27 ± 0.03
60% in BPC	3.27 ± 0.04	3.60 ± 0.02	3.82 ± 0.05
45% in EMIC	2.99 ± 0.03	3.27 ± 0.03	3.47 ± 0.01
60% in EMIC	4.68 ± 0.01	4.98 ± 0.05	5.28 ± 0.05

^a Each k_2 value is an average of triplicate readings.

We extended this study to account for the temperature dependence of dimerization. The measurements were made in 45 and 60% AlCl_3 contents in BPC and EMIC at 30, 35 and 40°C in addition to the above reported at 25°C (Table 2). We noted about 15–27% increase in the rate of dimerization from 25 to 40°C indicating higher temperature favors the process of dimerization in chloroaluminates. The energies of activation for the process of dimerization of 1,3-cyclopentadiene in BPC are in the range of $8\text{--}10 \text{ kJ mol}^{-1}$, while for EMIC this range is between 7 and 11 kJ mol^{-1} .

We then examined the above effect in three different model and well-studied Diels–Alder reactions involving 1,3-cyclopentadiene as a common diene and methyl acrylate, methyl methacrylate and methyl *trans*-crotonate (Table 3). Under the given reaction conditions, the reactions with methyl acrylate, methyl acrylate and methyl *trans*-crotonate (as dienophiles) reached their completion in 5, 9 and 24 h, respectively. Each reaction was monitored for the dimerization in the BPC and EMIC-containing chloroaluminates with 45 and 60% AlCl_3 to yield the reaction rates. The controlled reactions were carried in water, as the neat reactions for methyl methacrylate and methyl *trans*-crotonate did not result into sufficient yields for the purpose of analysis, though the neat reaction of 1,3-cyclopentadiene with methyl acrylate offered sufficient product in 11 h for accurate analysis.

On the other hand, the formation of dicyclopentadiene increased for the reactions of 1,3-cyclopentadiene with methyl

methacrylate and methyl *trans*-crotonate with the increase in the AlCl_3 compositions in both BPC and EMIC. The dimerization process in the 60% AlCl_3 -containing BPC or EMIC increased by about 200% as compared to in the 45% AlCl_3 -chloroaluminate again showing the effect of Lewis acid. For the reaction of 1,3-cyclopentadiene with methyl methacrylate in the 60% AlCl_3 BPC-chloroaluminate, however, the dimerization of 1,3-cyclopentadiene shows about 1.8-fold increase as compared to in water. Similarly, a three-fold increase in dimerization takes place in the 60% AlCl_3 -EMIC as compared to in water alone.

In summary, we have demonstrated the kinetics of dimerization of 1,3-cyclopentadiene in the chloroaluminate ionic liquids as influenced by the Lewis acid effect caused by AlCl_3 . How 1,3-cyclopentadiene is dimerized during simple Diels–Alder reactions has been demonstrated in this study. It is hoped that these studies will be helpful in understanding kinetics of the cyclopentadiene involving reactions in a more accurate way.

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