

## 마이크로파 하에서 아온성 액체 촉매를 이용한 프로필렌 카보네이트와 메탄올의 에스테르 교환 반응

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### Transesterification of Propylene Carbonate with Methanol Using Ionic Liquid Catalyst under Microwave Irradiation

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#### Introduction

Microwaves gained considerable interest for driving chemical reactions during the past few years and found successful in the selective preparation of chemicals of interest [1]. Dimethyl carbonate (DMC) finds quite diversified application in the chemical industry [2,3,4]. Due to its very high oxygen content, good blending octane, freedom from phase separation, low toxicity and rapid biodegradability, DMC established its usage as a possible gasoline-blending component. In addition to these, it meets the property for solvents, reagents (for alkylation or acylations reactions) and the component of special materials. Along with high heat efficiency, microwave irradiation can accelerate the reaction and decrease the run time resulting in fewer by-products than by conventional heating. In this work we were successful in preparing dimethyl carbonate and propylene glycol from propylene carbonate and methanol using environmentally friendly ionic liquids [5,6,7] as catalysts.

#### Experimental

Synthesis of DMC performed under microwave irradiation was carried out in a Pyrex glass reactor. Propylene carbonate, methanol and IL catalyst were added to the reactor at a mole ratio of 1:8:2. The microwave oven containing a source with continuously adjustable power from 0 to 1000 W operating at a frequency of 2450 MHz was utilized for the experiment. The reactor was irradiated for the required time at a given power and the irradiation was stopped in between to avoid explosion due to the formation of high pressure. After the required time of irradiation, the reactor was allowed to cool to room temperature. From the GC (Agilent Tech. Inc. 6890N, HP-5, 30 m X 0.320 mm, 0.25 micron, 60 to 325/350 °C) data, conversion and selectivity were calculated. For comparison, the same reaction was performed in an autoclave with an inner volume of 50 mL without microwave heating.

#### Result and Discussion

Several types of quaternary ammonium salts were screened as a catalyst for the transesterification of propylene carbonate with methanol under microwave irradiation. The reaction results obtained are listed in Tables 1-5. The reaction rate usually depends greatly on the structure of the cation as well as the nucleophilicity of the anion. The effect of anions on the synthesis of DMC has been studied using

quaternary ammonium salts containing different halide ions (Table 1). The activity of the catalyst followed the order TBAI > TBAB > TBAC > TBAH. TBAI showed higher activity than TBAB and TBAC because of the difference in the nucleophilicity of the halide ions, which has the order  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ , proving the activity of the catalyst for the reaction.

Table 1. Effect of anions on DMC synthesis

No	Catalyst	Amount of catalyst (mmol)	MW power (W)	Time (min)	PC Conversion (mol%)	Selectivity (mol%)	
						DMC	PG
1	TBAC	2	100	10	31.7	29.2	2.6
2	TBAB	2	100	10	32.1	35.6	10.3
3	TBAI	2	100	10	51.1	50.1	45.2
4	TBAH	2	100	10	21.4	3.1	3.9

Table 2 showed the effect of cation on the reaction. The conversion of propylene carbonate increased as the alkyl group increased from TPAC < TBAC ≤ THAC. The effective activity of the tetra alkyl ammonium salt comes from the bulkiness of the tetrahedral ammonium ion, which forces the halide ion away from the cation easier, resulting less electrostatic interaction between anion and cation and consequently making the anion more nucleophilic. But effect of cation for more bulky quaternary salts showed controversial result than conventional route. This may be due to effect of microwaves, which changed the order in a different manner.

Table 2. Effect of different alkyl substituents on DMC synthesis

No	Catalyst	Amount of catalyst (mmol)	MW power (W)	Time (min)	PC Conversion (mol%)	Selectivity (mol%)	
						DMC	PG
1	TPAC	2	100	10	28.9	1.1	2.9
2	TBAC	2	100	10	31.7	29.2	2.6
3	THAC	2	100	10	31.8	1.5	2.6
4	TOAC	2	100	10	25.7	-	6.9
5	TDAC	2	100	10	27.8	-	2.9

The effect of microwave power on the reaction were studied and tabulated in Table 3. The microwave power ranging from 100 to 500 W in the presence of TBAB was studied. 100 W microwave powers with 10 minutes irradiation were found to give higher conversion. But 500 W microwave powers were proved to be the optimum condition for the reaction, thereby reducing reaction time from 10 to 2 minutes.

Comparative study was performed for the microwave reaction with conventional method. In the presence of microwaves, the reaction time showed an abrupt reduction with no  $\text{CO}_2$  pressure. The

microwave irradiation was managed to give preferable propylene carbonate conversion at a faster rate without any pressure effect (Table 4).

Table 3. Effect of MW power on DMC synthesis

No	Catalyst	Amount of catalyst (mmol)	MW power (W)	Time (min)	PC Conversion (mol%)	Selectivity (mol%)	
						DMC	PG
1	TBAC	2	100	10	31.7	29.2	2.6
2	TBAC	2	200	5	28.0	20.8	2.9
3	TBAC	2	300	5	26.9	26.9	3.0
4	TBAC	2	400	2	21.2	50.9	3.8
5	TBAC	2	500	2	24.9	69.5	23.2

Table 4. Comparison of microwave heating with conventional heating.

Catalyst	Mode of Heating	Pressure of CO <sub>2</sub> (psi)	Time (min)	PC conversion (mol %)	Selectivity (mol %)	
					DMC	PG
TBAC	CH	250	360	55.2	65.7	78.3
TBAC	MW	-	10	31.7	29.2	2.6

Table 5 explains the influence of different type of ionic liquids on the transesterification reaction. The activity decreases in the order quaternary ammonium > imidazolium > pyridinium. The order can be explain on the basis of bulkiness of catalyst. Quaternary ammonium catalysts are more bulky than the other two, hence showed more activity.

Table 5. Effect of different type of ionic liquids on DMC synthesis

No	Catalyst	Amount of catalyst (mmol)	MW power (W)	Time (min)	PC Conversion (mol%)	Selectivity (mol%)	
						DMC	PG
1	EMImCl	2	100	10	24.2	6.8	3.4
2	TBAC	2	100	10	31.7	29.2	2.6
3	EPCl	2	100	10	22.4	4.6	7.5

## Conclusion

Comparing to imidazolium and pyridinium type ionic liquid catalysts, quaternary ammonium catalyst showed good catalytic activity towards the synthesis of dimethyl carbonate from propylene carbonate and methanol under microwave irradiation. The reaction rate depends greatly on the structure of the cation as well as the nucleophilicity of the anion. Higher propylene carbonate conversion was

observed for catalysts having cations with long chain or bulky substituent and anions with low electro negativity values. High microwave power is found to be favorable for dimethyl carbonate selectivity but conversion of propylene carbonate showed an opposite trend. Microwaves are proved to be active for imidazolium and pyridinium type ionic liquids catalyzed DMC synthesis, even though they showed lower activity than quaternary ammonium salts. In order to find out the effectiveness of microwave heating for the reaction, a comparative study had been performed. The results were considered to be approvable since the conventional heating method needed high pressure of CO<sub>2</sub> (250 psi) and longer reaction time (6 h) to get high conversion (55.2 %) whereas microwave heating required no CO<sub>2</sub> pressure and lesser reaction time (10 min) to achieve sufficient conversion (31.7%). The conversion and selectivity can be improved by changing the reaction conditions.

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