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Flash C-H Chlorination of Ethylene Carbonate Using a New Photoflow Setup

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Abstract

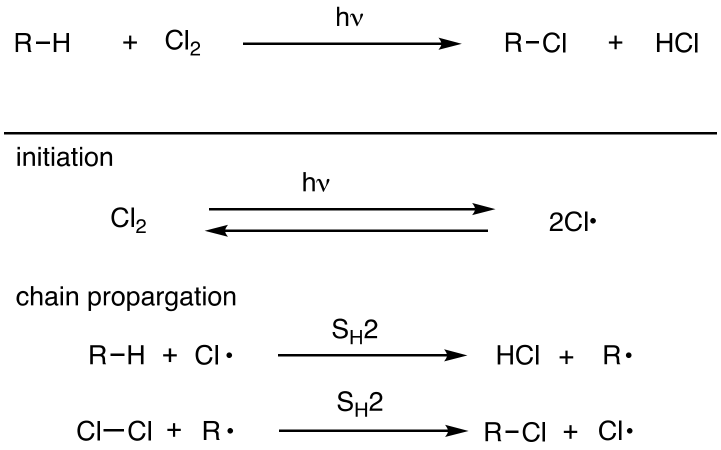
We report flash C-H chlorination of ethylene carbonate, which gives chloroethylene carbonate, a precursor to ethylene carbonate. A novel photoflow setup designed for a gas-liquid biphasic reaction turned out to be useful for the direct use of chlorine gas in flow. The setup employed sloped channels so as to make the liquid phase thinner, ensuring high surface to volume ratio. When ethylene carbonate was introduced to the reactor, the residence time was measured to be 15 or 30 sec, depending on the slope of the reactor to be 15 or 5 °C, respectively. Such short time exposition sufficed the photo C-H chlorination. The partial irradiation of the flow channels sufficed for the C-H chlorination, which is consistent with the requirement of photoirradiation for the purpose of radical initiation. We also found that the contaminated water negatively influenced the performance of C-H chlorination. The 100% selectivity for single chlorination required the low conversion of ethylene carbonate such as 9%, which was controlled by limited introduction of chlorine gas. At a higher conversion of ethylene carbonate such as 63%, the selectivity for mono-chlorinated ethylene carbonate over di-chlorinated ethylene carbonate was 86%. We found that the contaminated water negatively influenced the performance of the C-H chlorination.

Keywords

ethylene carbonate; chlorine gas; C-H chlorination; photo flow reactor; vinylidene carbonate.

Introduction

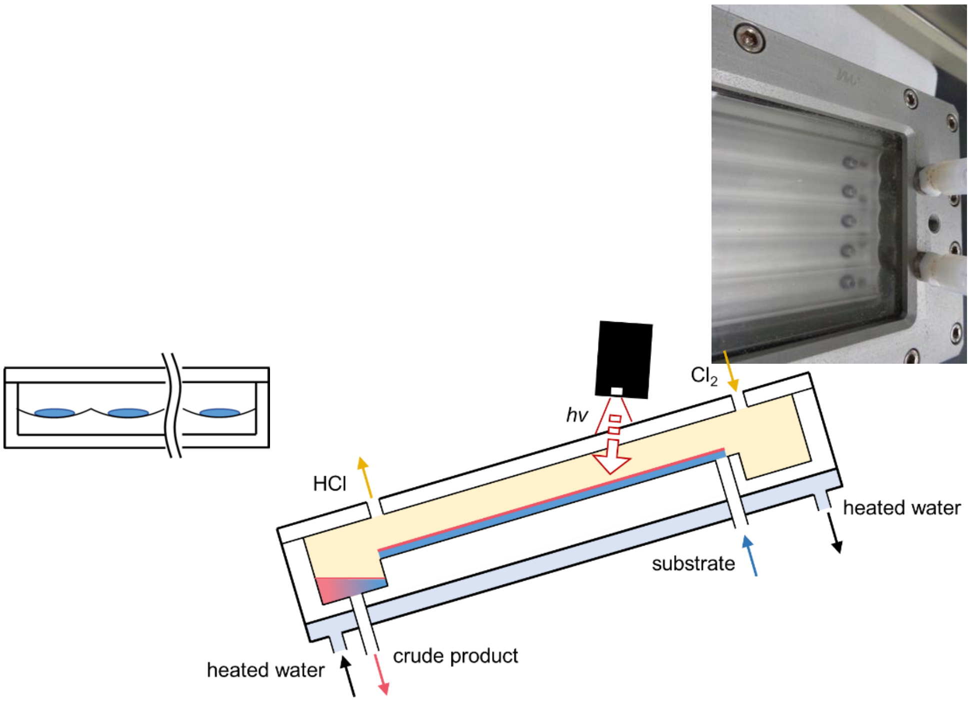
C-H chlorination by molecular chlorine is a highly exothermic reaction that proceeds via a radical chain mechanism as illustrated in Scheme 1.[1-6] Photoirradiation is used for radical initiation by causing homolysis of Cl-Cl bond to generate chlorine radicals. Then S_H2 reaction by chlorine radicals at C-H bonds generates alkyl radicals and HCl. The second S_H2 reaction by alkyl radicals and molecular chlorine then occurs to give C-H chlorinated product and chlorine radical, sustaining the radical chain. Chlorine gas is a cheap feedstock since it is formed as a byproduct of the electrolysis of NaCl to produce NaOH in the industrial process.[7] We felt that C-H chlorination would be updated by using scalable flash chemistry.[8]



Scheme 1. Radical Chain Mechanism for Photo-Induced C-H Chlorination

Flow C-H chlorination using a compact flow reactor is highly desirable in terms of the efficiency and the safety in handling a highly toxic chlorine gas. In 2002, Jähnisch and co-workers reported the first microflow chlorination of 2,4-diisocyanate-1-methylbenzene, which used an IMM's falling film reactor.[9] While the flow rate employed was quite slow (0.12 mL/min of toluene), the residence time was less than 14 seconds. More recent studies on flow C-H chlorination focused on the use of Cl_2 gas in situ generated by photolysis sulfuryl chloride[10] or acid treatment of NaOCl.[11,12] We thought that if rationally designed scalable photoflow setups are available, flow C-H chlorination using chlorine gas would be able to focus on production. In this study, we tested a novel photoflow setup consisting of quartz-made straight-line reactors, which are provided from MiChS LX-1 (Figure 1(a)) and a high-power LED (MiChS LED-s, 365 nm) (Figure 1(b)). Each channel track has a 2 mm depth and 557 mm length, while the width varies from 6 or 13 mm depending on the number of channels 7 or 5, respectively. The flow photoreactor is embedded into an aluminum frame equipped with a heat carrier channel. The design concepts including angle settings to ensure thin liquid layer are summarized in Figure 1.

(a) Photoflow Reactor, MiChS LX-1



Concepts

- quartz-glass made
- slope setting for thin liquid phase
- minimum use of chlorine gas
- gas outlet for hydrogen chloride
- partial photoirradiation
- heat control function in the aluminum frame

(b) MiChS LED-s

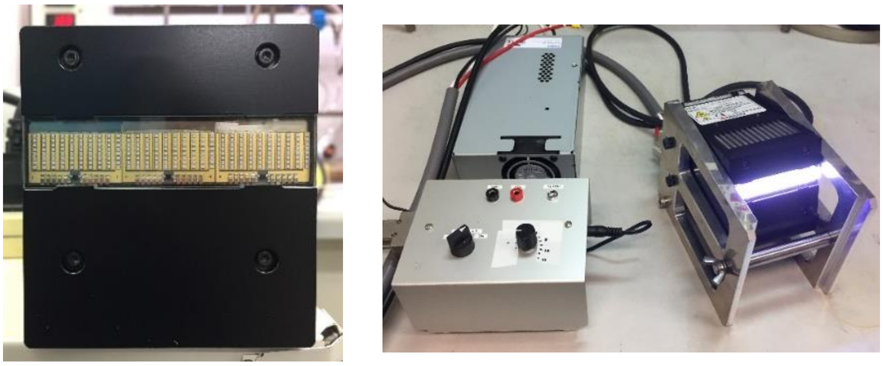
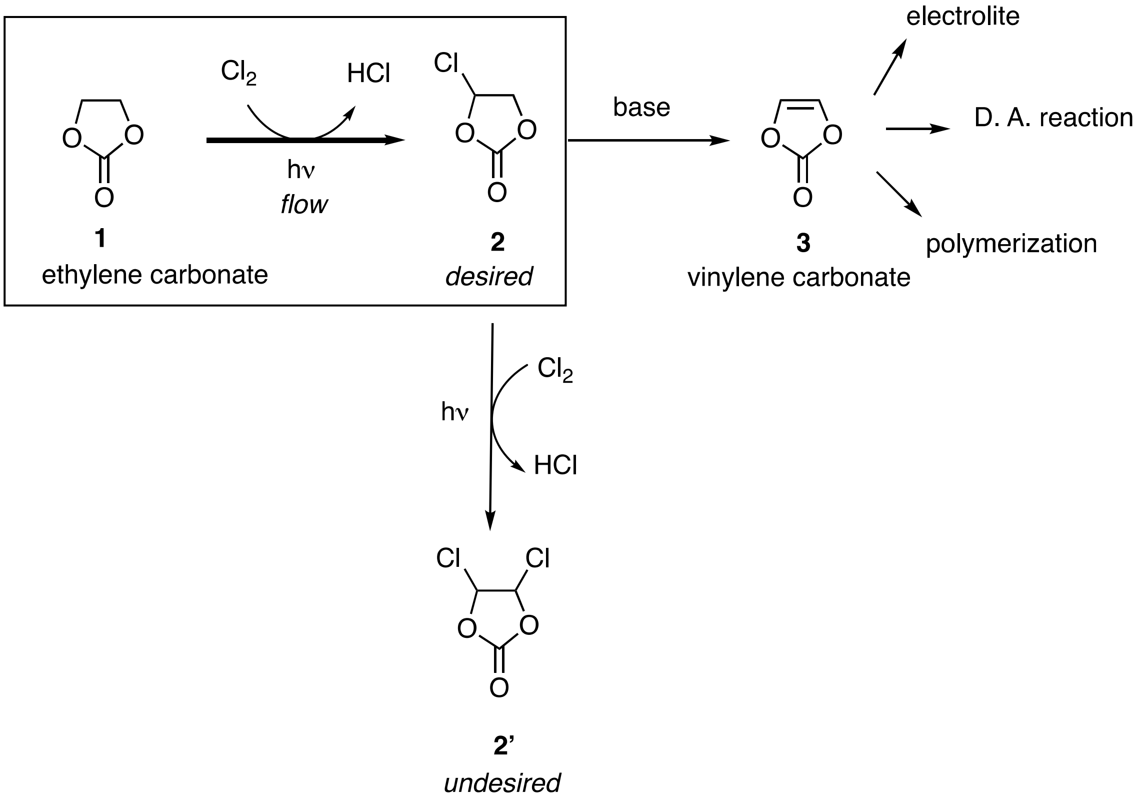


Figure 1 Components for Photoflow Setup: (a) MiChS LX-1, (b) MiChS LED-s (365 nm, 60-600 W):

We chose C-H chlorination of ethylene carbonate (**1**) as a model reaction (Scheme 2). Chlorinated ethylene carbonate (**2**) is a precursor to vinylene carbonate, which is used as an electrolyte additive for Li-ion batteries.[13-19] Vinylene carbonate also serves as a useful synthetic building block for Diels-Alder reaction[20-24] and polymerization.[25-29]



Scheme 2. Model Reaction: Photoflow C-H Chlorination of Ethylene Carbonate (1) to Chloroethylene Carbonate (2)

Results and Discussion

Using a PTFE tube, we connected the photoflow setup with a chlorine gas cylinder through a floating gas level meter (Figure 2). Since melting points of ethylene carbonate (**1**) are 34-37°C, we preheated the container of **1** using an oil bath at 70 °C and pumped it to the photoreactor. In the reactor, hot water (80°C) was circulated through a hole channel manufactured in an aluminum-made frame to keep the contacted glass reactor warm. The LED lamp was placed on the upper side of the reactor with a 20° angle to the reactor surface. Exiting gases (HCl and unreacted Cl_2) were trapped by an aqueous NaOH solution (1.7 M). Reactors are set with a slope of 15° or 5° to make the substrate layer thin to cause rapid gas/liquid biphasic reaction. The residence time was estimated to be 15 and 30 seconds, respectively. In general, we used ethylene carbonate (**1**) with the grade containing less than 0.03% of water. Results are summarized in Table 1.

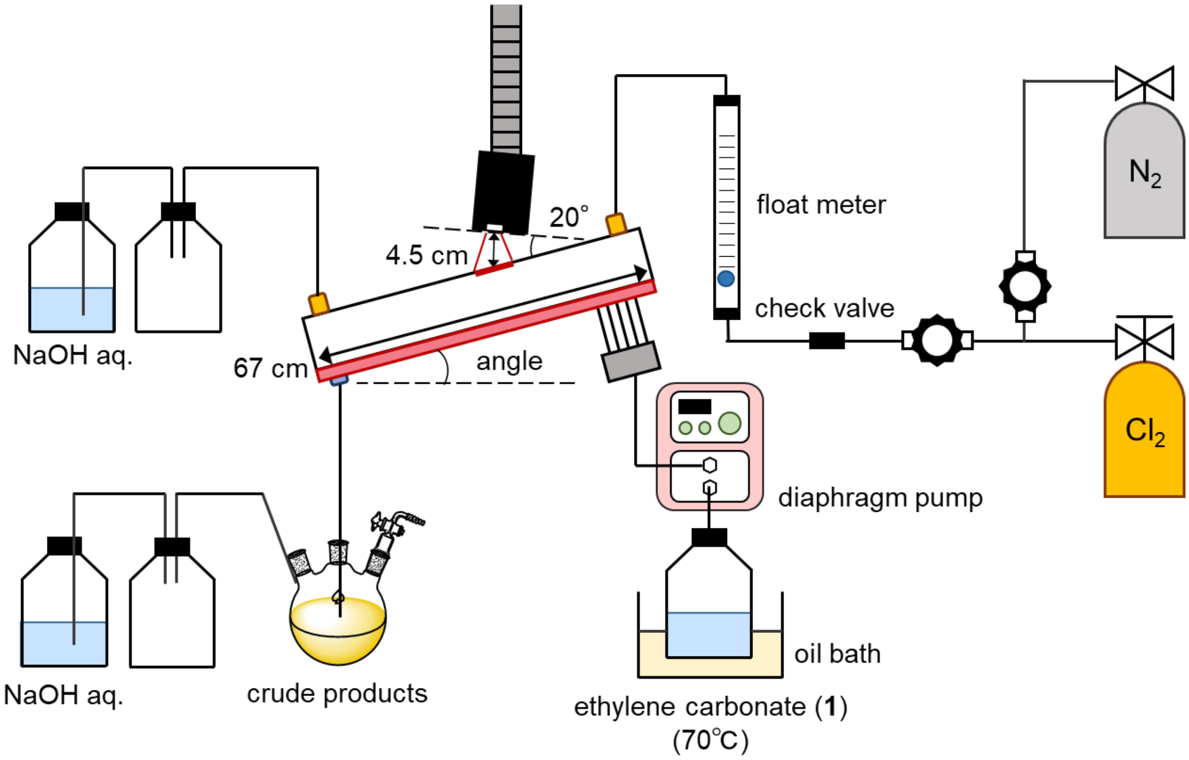


Figure 2. Photoflow Setup for C-H Chlorination of Ethylene Carbonate (1)

When the reaction of ethylene carbonate (**1**) (flow rate: 74.9 mmol/min, containing 0.03% of H_2O) with 0.17 equiv of Cl_2 gas (flow rate: 12.5 mmol/min) was carried out under irradiation from UV-LED (240 W) with a 15° reactor angle, the desired chloroethylene carbonate (**2**) was formed in 100% selectivity by GC with 9 % conversion of **1** (Table 1, entry 1). When 0.23 equivalent of Cl_2 was used, the selectivity became 96% with 13% conversion of **1**, in which a small amount of undesired 1,2-dichlroethylene carbonate (**2'**) was detected by GC (Table 1, entry 2). When 0.45 equivalent of Cl_2 was used, the conversion of **1** increased to 22% and the selectivity of **2** became 89% (Table 1, entry 3). The reaction of **1** with one equivalent of Cl_2 gave **2** and **2'** in a ratio of 89:11 with 41% conversion of **1** (Table 1, entry 4). When the reaction mixture was circulated twice, we observed a higher conversion of **1** (88%) and a 73:27 mixture of **2** and **2'** (Table 1, entry 5). Then we limited the feeding of **1** (flow rate: 46.4 mmol/min) in order to have more conversion, which worked well. The reaction of **1** with 0.81 equivalent of Cl_2 resulted in 63% conversion of **1** and an 86:14 ratio of **2** and **2'** (Table 1, entry 6). When a lower feeding of **1** (29.6 mmol/min) and an excess amount of Cl_2 (3.09 equiv) were used, higher conversion of **1** (77%) was attained with the selectivity of 83 : 17 (Table 1, entry 7). The irradiation at 600 W gave an almost similar result (Table 1, entries 8 and 9), which suggested that 240 W sufficed the reaction. Indeed When the reaction was carried out with a shallow reactor angle such as 5°, conversion of **1** was increased from 51 to 63%（Table 1, entries 8 and 10）. This is due to the extended residence time from 15 to 30 sec.

Table 1. Photo Flow C-H Chlorination of Ethylene Carbonate 1 to 2[a]

entry	angle (°)	flow rate		UV-LED (W)	conversion (%)[b]	selectivity (%)[b]	
		1[a] (mmol/min)	Cl_2 (mmol/min) (equiv)			**2**	**2'**
1	15	74.9	12.5 (0.17)	240	9	100	0
2	15	74.9	17.4 (0.23)	240	13	96	4
3	15	74.9	33.9 (0.45)	240	22	91	9
4	15	74.9	75.9 (1.01)	240	41	89	11
5[c]	15	74.9	75.9 + 75.9 (2.02)	240	88	73	27
6	15	46.4	91.5 (1.97)	240	63	86	14
7	15	29.6	91.5 (3.09)	240	77	83	17
8	15	117.6	146.5 (1.25)	240	51	77	23
9	15	117.6	143.7 (1.22)	600	49	77	23
10	5	117.6	146.5 (1.25)	240	63	78	22

[a] Reactions were conducted by using LX-1 with a reactor angle of 15° or 5° (entry10). Photoirradiation was carried out by using by LED-s (365 nm, at the power of 240 or 600 V(entry 9). Ethylene carbonate (**1**) contains 0.03% of H_2O. [b] Determined by GC analysis. [c] Reaction mixture was circulated twice.

We then investigated the effects of contaminated water, since Cl_2 gas is known to react with H_2O under irradiation conditions.[30] The results are summarized in Table 2. The flow rate of **1** and the equivalent of chlorine to **1** were set to be 187 mmol/min and 0.60-0.69, respectively. The reactor angle and the light power were set to be 15° and 240 W, respectively. The chlorination reaction using an ordinary grade of the substrate **1** containing 0.03% of water gave a 95/5 ratio of **2** and **2'** with 27% conversion of **1** (Table 2, entry 1). In contrast when we used **1** containing 0.15% of water, the conversion decreased to 12 % (Table 2, entry 2). With 0.76% of water, the conversion decreased further to 9% (Table 2, entry 3). These results suggest that the reaction has to be carried out carefully under dry conditions.

Table 2. Effect of Contaminated Water[a]

entry	water contamination	flow rate		conversion (%)[b]	selectivity (%)[b]	
		1[a] (mmol/min)	Cl_2 (mmol/min) (equiv)		**2**	**2'**
1	0.03%	187.0	126.8 (0.68)	27	95	5
2	0.15%	187.0	112.7 (0.60)	12	93	7
3	0.76%	187.0	118.3 (0.63)	9	100	0

[a] Reactions were conducted by using LX-1 with a rector angle of 15° using LED-s (240 V). [b] Estimated by GC.

Conclusion

In this work, we reported that a novel photoflow setup designed for a gas-liquid biphasic reaction turned out to be useful for the C-H chlorination using chlorine gas in flow. Two decades after the first report on the microflow chlorination of a toluene derivative by Jähnisch and co-workers, we propose a new photoflow setup for C-H chlorination using chlorine gas, applicable to scalable flow C-H chlorination. In our test reaction using C-H chlorination of ethylene carbonate (**1**), chloroethylene carbonate (**2**) was obtained in good to excellent selectivity by tuning the flow rates of **1** and chlorine gas. Partial irradiation of the flow channel is sufficient for the C-H chlorination, consistent with the requirement for light irradiation for the radical initiation step. If we apply the conditions to give 80% selectivity with 60% conversion with 30 sec residence time, around 15 kilograms of chloroethylene carbonate (**2**) can be synthesized per day, which suggests the high potential of the present photoflow setup. We also demonstrated that the contaminated water in ethylene carbonate (**1**) influenced negatively and the system should be kept dry for continuous production. We are now investigating some other photo gas-liquid flow reactions, which will be reported in due course.

Experimental

Photoflow setup consisting of flow photoreactor LX-1 and a UV-LED-s was supplied from MiChS Inc., Ltd. (http://www.michs.jp). The angle of photoflow reactor was set to be 15 or 5° and the heated water at 80°C was circulated in a channel of aluminum-made frame to avoid solidification of ethylene carbonate (**1**), whose melting point is 34-37℃. The UV-LED (365 nm) was set with an angle of 20° to the reactor surface so as to make light reach to the end of the reactor. Ethylene carbonate (**1**) preheated to 70 ℃ was fed into each channel of the flow photoreactor by using a diaphragm pump. At the same time, chlorine gas was fed into the reactor from the top-side inlet. Evolved HCl gas and unreacted Cl_2 gas were trapped by aqueous 1.7 M NaOH solution. After the first eluted solution was discarded for 3 min and then the next eluted solution was collected for analysis. Analysis was carried out using gas chromatography using a capillary column (Agilent J&W DB-5, Φ 0.25 mm × 30 m).

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