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N-Tosylaziridine, a new substrate for chemical fixation of carbon dioxide via ring expansion reaction under atmospheric pressure

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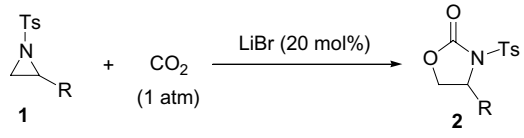
Abstract—*N*-Tosylaziridine was found to be a useful substrate for cycloaddition reaction with carbon dioxide. The reaction was successfully catalyzed by lithium bromide under atmospheric pressure to give the corresponding five-membered cyclic urethane, *N*-tosyl-1,3-oxazolidin-2-one, selectively. It was found that electron-donating nature of the substituent at 2-position of *N*-tosylaziridine accelerated the reaction, and this tendency allowed us to estimate the reaction mechanism.

CO_2 will be an inexhaustible and nontoxic C_1 resource if its highly efficient chemical fixation process is available. For this goal, various reactions of CO_2 to convert it into useful compounds have been studied.[1–4] Among them, cycloaddition of CO_2 with epoxide has been most intensively studied and has become one of the most promising methods for chemical fixation of CO_2.[5–8] We have developed highly efficient CO_2–epoxide cycloaddition catalyzed by alkali-metal halide or quaternary ammonium salt, which enables facile fixation of gaseous CO_2 under atmospheric pressure.[9,10] The obtained products, cyclic carbonates, have been proved to be useful monomers for polymer synthesis.[11] Recently, we have found that *N*–H aziridines react with CO_2 under atmospheric pressure, affording the corresponding cyclic urethanes, 1,3-oxazolidin-2-ones.[12] The reaction can be efficiently catalyzed by alkali-metal halide or quaternary ammonium salt, similarly to the analogous reaction of epoxide.

In the course of our seeking for a new family of substrates for fixation of gaseous CO_2, *N*-sulfonylated aziridine has appeared to be of our great interest. From scientific viewpoints, its reactivity would be much different from that of *N*–H aziridines by the presence of highly electron-withdrawing sulfonyl group on the nitrogen atom, and thus worth challenging as a new target. From much practical viewpoints, its structural diversity and availability is guaranteed by a versatile *N*-sulfonylaziridination reaction of various olefins.[13] This paper describes a new reaction of *N*-(*p*-toluenesulfonyl)aziridine (*N*-tosylaziridine, **1**) with CO_2, using our simple and inexpensive catalytic system.

The reaction system is depicted in Scheme 1. As a catalyst, lithium bromide (LiBr) was used, since it is the most efficient one in the previously studied cycloaddition reaction of *N*–H aziridine with CO_2, and is stable under a wide range of reaction conditions. The substrates, 2-decyl-*N*-tosylaziridine (**1a**) and *N*-tosylaziridines having aromatic substituent at 2-position (**1b**–**e**),



Scheme 1.

Keywords: Aziridine; Cycloaddition; Carbon dioxide; Atmospheric pressure; Carbon disulfide.
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Table 1. Cycloaddition of CO_2 with *N*-tosylaziridine **1** catalyzed by LiBr[a]

Entry	Aziridine	R	Solvent	Temperature	Product	Yield/%[b]
1	**1a**	Desyl	THF	rt	**2a**	42
2	**1b**	Ph	THF	rt		0
3	**1b**	Ph	NMP	100 °C	**2b**	70
4	**1c**	4-ClC_6H_4	NMP	100 °C	**2c**	42
5	**1d**	4-MeC_6H_4	NMP	100 °C	**2d**	76
6	**1e**	4-$MeOC_6H_4$	NMP	100 °C	**2e**	79

[a] Conditions: $[\mathbf{1}]_0 = 1.0$ M, in NMP at 100 °C for 24 h.
[b] Determined by GC.

were synthesized from the corresponding olefins by aziridination reactions with chloramine-T.[13] The reaction of aziridine **1a**, which has an alkyl substituent, was performed in tetrahydrofuran (THF) at ambient temperature (entry 1 in Table 1). CO_2 was supplied to a reaction vessel from an equipped balloon with atmospheric pressure. GC analysis of the reaction mixture revealed that the reaction proceeded slowly, and the corresponding cyclic urethane, 4-decyl-3-(4-toluenesulfonyl)-1,3-oxazolidin-2-one (**2a**) formed in 42% yield. The corresponding regioisomer, 5-alkyl substituted one, was not detected at all by GC and 300 MHz ^{1}H NMR analyses of the crude mixture. The other aziridines **1b–e** can also be used as a substrate for the present reaction system, if the reaction conditions were chosen appropriately. Although these aziridines did not react with CO_2 at ambient temperature, they did at 100 °C (entries 2–6 in Table 1). In order to elevate the reaction temperature, *N*-methylpyrrolidone (NMP) was employed as a less volatile solvent. In all cases, only the corresponding cyclic urethane and the aziridine were detected by GC and 1H NMR, indicating that decomposition of the aziridine and other side reactions such as alternate copolymerization were negligible. No regioisomer was detected by NMR analysis.

The time-conversion dependence was analyzed in the reactions of the aziridines having several aromatic substituents **1b–e** by GC in order to investigate how the substituent effects on the reaction rate. In all cases, the time-conversion curve reached saturation before complete conversion. The reason for this tendency is not clear at present but it should not be caused by side reactions. As shown in Figure 1, the order of the reaction rate is roughly **1e > 1d > 1b > 1c**, if the induction periods of the reaction are neglected. This order suggests that the reactivity of *N*-tosylaziridine increases when the substituent X at *para*-position of the aromatic substituent is an electron-donating one. The fact that the aziridine **1a** having a relatively electron-donating alkyl substituent reacted with CO_2 without heating is in good accordance with the order. It is noteworthy that this order is opposite to that found in the reaction of epoxide with CO_2, indicating that the rate-determining step in the present reaction is different to that in the analogous reaction of epoxide (vide infra).[10]

Figure 2 shows the first order time-conversion relationships of the reactions of **1b–e**, based on the aforementioned time-conversion plots. Although some plots were deviated from the approximated first order kinetics due to the presence of the induction period, the rate constants k were calculated based on the equation $-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = k[\mathbf{1}]_0 t$, in order to obtain more detailed information on the reaction behavior. The calculated constants for **1b**, **1c**, **1d**, and **1e** were 1.3, 0.6, 1.8, and 2.1 ($\mathrm{L\,mol^{-1}\,min^{-1}}$), respectively. Based on these values,

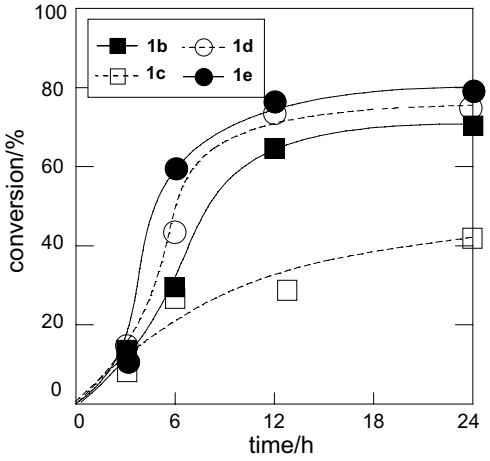


Figure 1. Time-conversion plots for the reactions of *N*-tosylaziridines **1b** (R = Ph), **1c** (R = 4-ClC_6H_4), **1d** (R = 4-MeC_6H_4) and **1e** (R = 4-$MeOC_6H_4$) with CO_2 in NMP at 100 °C, catalyzed by 20 mol% LiBr.

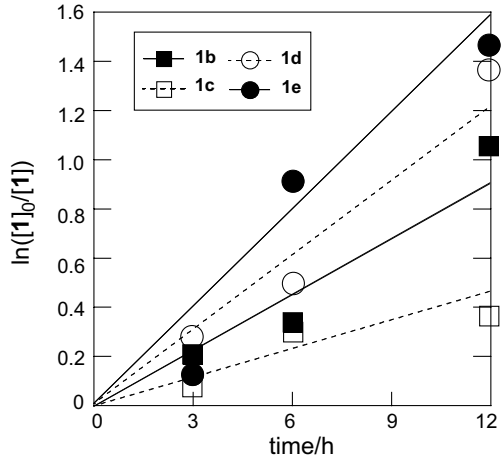


Figure 2. First order time-conversion plots for the reactions of *N*-tosylaziridines **1b** (R = Ph), **1c** (R = 4-ClC_6H_4), **1d** (R = 4-MeC_6H_4) and **1e** (R = 4-$MeOC_6H_4$) with CO_2 in NMP at 100 °C, catalyzed by 20 mol% LiBr.

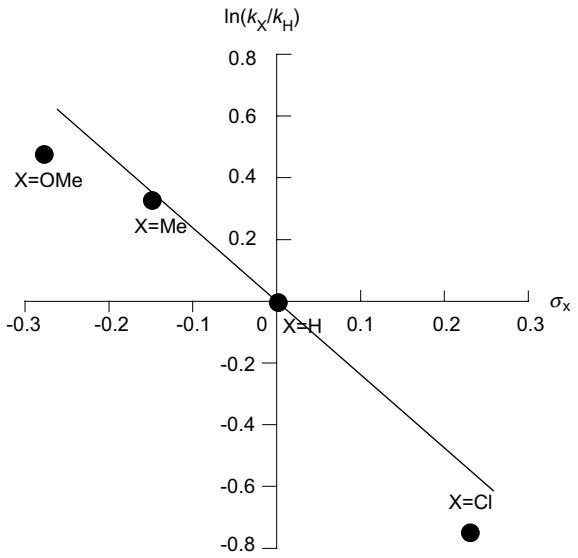
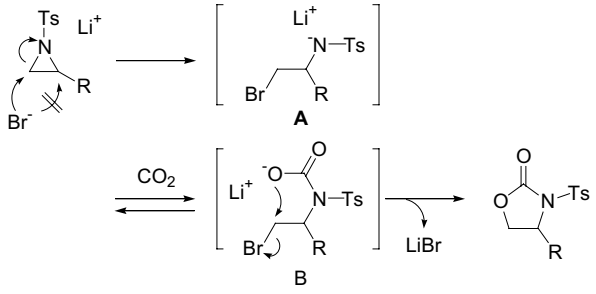


Figure 3. Hammett plots for the reactions of *N*-tosylaziridines **1**.



Scheme 2.

relative ratios of the rate constants are plotted against the Hammett's σ values of *para*-substituents[14] to find a virtually linear relationship as shown in Figure 3.

As shown in the Hammett plot, the reactivity of *N*-tosylaziridine in its reaction with CO_2 is increased by introduction of electron-donating substituent. This tendency is opposite to that found in the reaction of epoxide with CO_2.[10] Scheme 2 depicts a plausible mechanism for the present reaction, which is convenient for us to understand the difference in the electronic effect of substituent between the reaction of *N*-tosylaziridine and that of epoxide. The first step of the reaction of *N*-tosylaziridine would be ring-opening reaction by nucleophilic attack of bromide anion from the catalyst to give the intermediate A, analogously to the reaction of epoxide. Regioselectivity in this ring-opening reaction leads to the regioselective formation of the final product, five-membered cyclic urethane. In the case of the reaction of epoxide, this step is considered to be the rate-determining step, because the reactivity of epoxide is enhanced by electron-withdrawing substituent. On the other hand, since the reactivity of *N*-tosylaziridine is suppressed by electron-withdrawing group, this ring-opening step should not be the rate-determining one. The next step is reaction of anionic nitrogen with CO_2 to form the intermediate B, whose intramolecular cyclization gives the product. Since this step might be in equilibrium between A and B, the final cyclization step might be the rate-determining one in the reaction of *N*-tosylaziridine, which is accelerated by electron-donating substituent. The possible reason for this acceleration can be inductive effect by the neighboring aromatic group.

In summary, *N*-tosylaziridine was found to be a useful substrate for cycloaddition with CO_2. The reaction can be easily operated under atmospheric pressure by employing lithium bromide as a catalyst. This hopeful method for chemical fixation of CO_2 will be further studied to clarify its mechanism in order to develop further efficient chemical transformation of CO_2 into valuable products.

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