Kinetics of Acyl Ammonium Salt Formation: Mechanistic Implications for Carbonate Macrocyclization[1]

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Received February 11, 1992
Revised Manuscript Received May 5, 1992

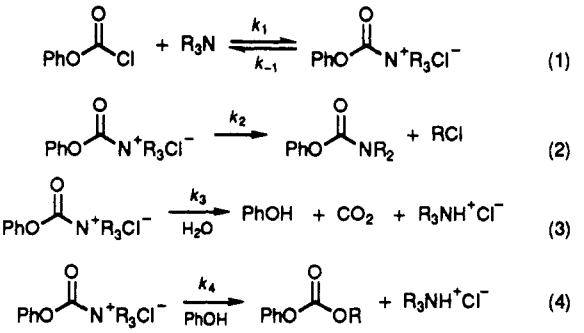
Brunelle and co-workers[2] recently reported the synthesis of cyclic oligomeric carbonates using an amine-catalyzed reaction of Bisphenol A–bischloroformate (BPA–BCF). The process is an interfacial hydrolysis/condensation reaction which can lead to cyclic oligomers, linear oligomers, or polymer depending on the structure and concentration of the tertiary amine. Catalysis by triethylamine (TEA) leads to >85% cyclic oligomers; however, the maximum yield of cyclics is reduced to 27% when the catalyst is diethylmethylamine (DEMA). The profound dependence of macrocyclization on such small structural changes in the amine catalyst is one of the most fascinating aspects of this polymerization chemistry. Mechanism studies by Brunelle and Boden[3] are consistent with the formation of an intermediate acyl ammonium salt (eq 1; Scheme I). The three possible fates for the acyl ammonium salt are urethane formation (eq 2), hydrolysis (eq 3), or condensation (eq 4). It is the complex interplay of these different chemical events that controls the product distribution in the reaction of BPA–BCF. Kosky[4] provided support for major mechanistic components of the macrocyclization by successfully modeling the concentration effects and product distributions. Brunelle and Boden[3,5] studied the reaction of phenyl chloroformate (PCF) with *p*-isopropylphenol in CH_2Cl_2 using a series of different amines. The order of reactivity correlated with the magnitude of the equilibrium constant for acyl ammonium salt formation (measured by proton NMR). Therefore, the concentration of the acyl ammonium salt is an important factor in the outcome of this process. Kosky and Boden[6] studied the formation of the urethane in refluxing CH_2Cl_2 (39 °C). The kinetic model was based on eqs 1 and 2; reversible acyl ammonium salt formation followed by first-order conversion to the urethane. The best fit of their model to the experimental data was obtained for K (k_1/k_{-1}) = 21 L mol^{-1} and k_2 = 0.022 s^{-1}.

In order to further elucidate the mechanism, we have initiated a kinetic study of this process. Our initial goal is to determine the rate of acyl ammonium salt formation and the subsequent conversion to products. Like Brunelle and Boden, monofunctional phenyl chloroformate (PCF) was used to simplify the chemistry.

The data reported here were obtained using a stopped-flow apparatus interfaced to a rapid-scan FT-IR spectrometer.[7] Acyl ammonium salt formation is complete in seconds at 0 °C so it is important to efficiently mix the PCF and amine. The apparatus used here is capable of completely mixing solutions of amine and PCF in 6 ms. Reaction progress was monitored by following changes in the carbonyl region of the spectrum (Figures 1 and 2). A major advantage of this technique is the ability to simultaneously follow changes in the concentrations of PCF (ν = 1786 cm^{-1}, ϵ = 330 L mol^{-1} cm^{-1}), acyl ammonium salt (ν = 1827 cm^{-1}), and urethane (ν = 1712 cm^{-1}, ϵ = 410 L mol^{-1} cm^{-1}). Traces of water in the flow system or reactants lead to diphenyl carbonate (ν = 1786 cm^{-1}, ϵ = 470 L mol^{-1} cm^{-1}) formation. Because the carbonyl absorption maxima of diphenyl carbonate and PCF are the same, solvents (distillation from P_2O_5) and starting materials were carefully dried and solutions were handled in an argon-purged drybox.

Three different amines were studied. Table I contains the rate values obtained at 0 °C for the formation of the acyl ammonium salt and subsequent conversion to urethane. These two chemical events, which occur on different time scales (Figures 1 and 2), can be treated as discrete reaction steps. We confirmed the validity of this simplification by Runge–Kutta integration of the coupled differential equations. At 0 °C, the equilibrium constants for acyl ammonium salt formation are high[3,8], which is a necessary condition for treating the chemical events as discrete steps.

Scheme I



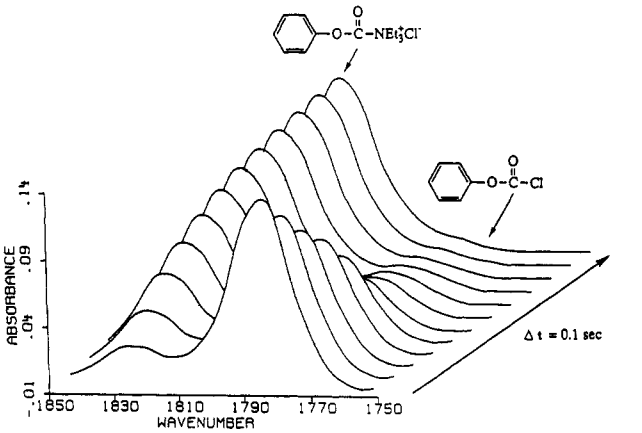


Figure 1. FT-IR stacked plot of acyl ammonium salt formation; CH_2Cl_2, 0 °C, 0.05 M PCF, 0.05 M TEA.

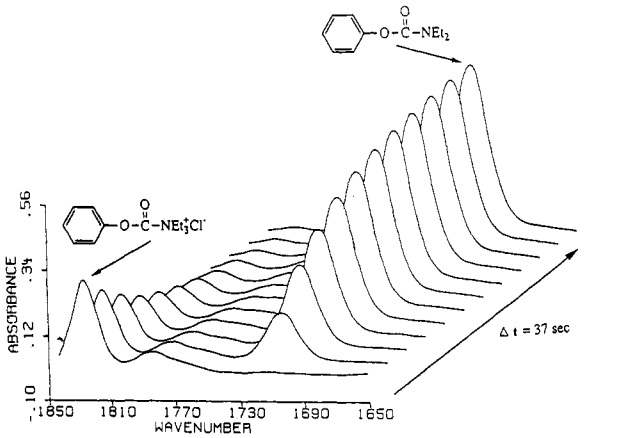


Figure 2. FT-IR stacked plot of acyl ammonium salt conversion to urethane; CH_2Cl_2, 20 °C, 0.05 M PCF, 0.05 M TEA.

0024-9297/92/2225-3827$03.00/0

Table I
Rates[a] of Acyl Ammonium Salt Formation (k_1) and Urethane Formation (k_2); 0 °C, CH_2Cl_2, $[PCF]_0 = [amine]_0 = 0.1$ M

amine	k_1, L mol^{-1} s^{-1}	k_2, $\times 10^4$ s^{-1}
n-Bu_3N	9 ± 1	2.6 ± 0.5
Et_3N	24 ± 3	2.4 ± 0.9
Et_2MeN	>4000	1.9 ± 0.6

[a] Rates are based on the carbonyl adsorption for the acyl ammonium salt, ν = 1827 cm^{-1}; values reflect the average of at least three separate rate determinations.

At 0 °C, we have been able to measure the rate of acyl ammonium salt formation for tri-n-butylamine (TBA) and TEA. However, the reaction of PCF with DEMA is complete within the time it takes to acquire one spectrum (50 ms). Therefore, it is only possible to set a lower limit for this rate constant. The order of reactivity for acyl ammonium salt formation for TBA:TEA:DEMA is 1:2.7: >444. It is remarkable that small changes in amine structure (i.e., a single methylene group) result in such profound reactivity changes. It is interesting to recall that the experimentally determined optimum amine concentration for obtaining high yields of cyclics[8] varies with the structure of the amine and, furthermore, that the variations in optimum concentration parallel the differences in the rate of acyl ammonium salt formation for the various amines. The maximum yields of cyclics were obtained at the following amine concentrations: 0.25 M tri-n-propylamine (similar results are obtained for TBA and tri-n-propylamine),[9] 0.1 M TEA, and 0.005 DEMA.[8] That is, the highest yields of cyclics are obtained for a TBA concentration that is 2.5 times higher than TEA which is similar to our difference in the rates of acyl ammonium salt formation.

These kinetic results qualitatively strengthen the mechanistic view that the selectivity toward macrocyclization vs linear oligomer or high polymer formation is related to acyl ammonium salt concentration. Our kinetic results in CH_2Cl_2 also suggest that a specific concentration of acyl ammonium salt will provide the highest yield of cyclic oligomers. Macrocyclization reactions are typically carried out interfacially at pH 10–12 with the concentration of amine kept constant. Since the bischloroformate starting material is added slowly, the concentration of acyl ammonium salt should approximate a steady state. If the formation of acyl ammonium salts occurs too readily, bisacyl ammonium salts may form, which would partition into the aqueous phase and lead to excessive hydrolysis and thus to the formation of linear oligomers. If the acyl ammonium salt concentration is too low, then hydrolysis and condensation reactions will occur too slowly, leading to an increase in reagent concentrations, favoring the formation of linear polymer by intermolecular reactions, rather than intramolecular reactions to cyclic. The yield of cyclic oligomers is optimized when only one end of a bischloroformate-terminated oligomer chain is hydrolyzed to a phenoxide. Such an intermediate can react rapidly with an amine to form an oligomer with a phenoxide on one end and an acyl ammonium salt on the other. If the concentration of that intermediate is low, macrocyclization will be preferred over intermolecular condensation to form polymer. It is a fine balance of relative reactivities toward hydrolysis and condensation and control of inter- vs intramolecular reactions that maximizes the formation of cyclic oligomers.

Rates of urethane formation (eq 2) were determined from first-order plots of acyl ammonium salt concentration versus time. Unlike acyl ammonium salt formation, the rate of urethane formation is independent of the amine structure. The rate constant for urethane formation with TEA was also determined at 20 °C, $k_2 = 2.8 \times 10^{-3}$ s^{-1}. Using the rate constants for urethane formation reported here plus that determined by Kosky and Boden[6] at 39 °C, an Arrhenius plot with a high correlation coefficient (R = 0.998) was obtained showing good agreement from the two laboratories. The activation parameters were calculated from the slope and intercept: E_a = 80 kJ/mol and log A = 13.5.

We are currently studying the kinetics at different temperatures and at different reactant stoichiometry. Also, we are in the process of measuring the rates of condensation between acyl ammonium salt and p-isopropylphenol in order to determine the effect, if any, of the structure of the amine on subsequent reactions of acyl ammonium salts with phenols.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the Ohio Board of Regents for a Research Challenge Enhancement Grant. Financial support for the research was also received from the Research (Faculty Projects) Committee of the University of Akron.

References and Notes

(1) A preliminary account of portions of this work has been reported: Aquino, E. C.; Brittain, W. J.; Brunelle, D. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 1185.
(2) Brunelle, D. J.; Boden, E. P.; Shannon, T. G. *J. Am. Chem. Soc.* **1990**, *112*, 2399.
(3) Brunelle, D. J.; Boden, E. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 399.
(4) Kosky, P. G. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 101.
(5) Brunelle, D. J.; Boden, E. P. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 392.
(6) Kosky, P. G.; Boden, E. P. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 1507.
(7) Brittain, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7440.
(8) Boden, E. P.; Brunelle, D. J. *Curr. Top. Polym. Sci.*, in press.
(9) Brunelle, D. J., unpublished results.