

Reaction Kinetics of the Reaction of Terephthalic Acid and Ethylene Carbonates

DAVID R. FAGERBURG, *Research Laboratories, Eastman Chemicals Division, Eastman Kodak Company, Kingsport, Tennessee 37662*

Synopsis

The kinetics of the reaction of terephthalic acid with a number of ethylene carbonates in the presence of an amine catalyst were examined. All reactions apparently follow first-order kinetics; therefore, the solution rate of TPA is not rate-limiting. With minor adjustments, the mechanism appears to be in accord with that of the model reaction of benzoic acid and ethylene carbonate previously reported. Attack of the carboxylate on the carbonate ring must be the rate-limiting step. Substituent effects (owing to substituents on the carbonate ring) appear to be mostly steric in nature; surprisingly, an *n*-octyl group causes the slowest reaction. Besides being strongly influenced by steric hinderance, the transition state appears to be highly polar. Activation energy (16.0 kcal/mol) and activation entropy (-23.6 cal/deg) are very similar to those of the model reaction.

INTRODUCTION

Work reported by Yoshino et al.¹ (on formation of hydroxyethyl esters of acids by the reaction of the acid with ethylene carbonate) included a short report of the esterification of terephthalic acid (TPA) with ethylene carbonate. Few details were given. Apparently much of the work on this potentially important industrial reaction has been reported only in the patent literature.²⁻⁷ Work has therefore focused primarily on finding faster and more useful catalyst systems for the TPA-carbonate reaction. Therefore, little useful kinetics information is available. The use of a few other cyclic carbonates has also been mentioned in the patent literature, but reaction examples that might aid in the understanding of the reaction mechanism have not been given.

We have recently reported work⁸ that dealt with the mechanism of the benzoic acid-ethylene carbonate reaction, which was intended, in part, to be a model reaction for TPA-ethylene carbonate esterification. Owing to results from the benzoic acid-ethylene carbonate work, a new mechanism for the acid-carbonate reaction was suggested.

We now wish to report on kinetics measurements on the reaction of TPA with ethylene carbonate and substituted ethylene carbonates. This work was undertaken to elucidate the reaction mechanism of these systems in which heterogenous mixtures existed until the reaction was very close to completion. Unlike the catalyst used in previous work, however, tributylamine was used in this work as the catalyst for the reaction so that the catalyst could be removed, and any potential interference of further reactions, such as polycondensation, could be eliminated.

EXPERIMENTAL

Terephthalic acid was high purity grade from Amoco Chemicals. Tributylamine was obtained from Eastman Organic Chemicals and was used without further purification. Ethylene carbonate, obtained from Union Carbide, was purified by distillation under vacuum (bp 113°C/7 torr). Propylene carbonate, Eastman Organic Chemicals, was also distilled under vacuum (bp 104°C/8 torr). Butylene, pentylene, and hexylene carbonates have been recently reported.⁹ Analysis of new carbonates was performed on a V. G. Analytical Model MM-ZAB-1F mass spectrometer by using chemical ionization with methane to give an MH⁺ peak (electron impact failed to give molecular ions). The remainder of the carbonates were prepared by the previous procedure to yield the following results:

Phenylethylene Carbonate. Styrene glycol 300 g (2.17 mol), 350 g diethyl carbonate (3.0 mol), and 0.5 g sodium metal were heated at reflux in a 1-L flask for 2 days with slow distillation of ethanol. Maximum pot temperature was held to 185°C. The cooled reaction mixture was combined with 500 mL diethyl ether and filtered. The product was washed again with 300 mL of cold diethyl ether and filtered again. Yield: 272 g (76.4%).

ANAL. Found (Calcd): C, 65.7% (65.8%); H, 4.7% (4.9%).

Isopropylethylene Carbonate. 3-Methyl-1, 2-butanediol 31.1 g (0.297 mol), 416 g diethyl carbonate (4.0 mol), and 1.0 g sodium metal were heated at reflux in a 1-L flask with distillation of ethanol for 1 day. After cooling, the mostly solid mixture was broken up and washed with diethyl ether. The solid was distilled under vacuum to purify the product (bp 105°C/2 torr). Yield: 110 g (28%). M/S obtained 131.0702 *m/e* (theory MH⁺, 131.0705).

***t*-Butylethylene Carbonate.** 3,3-Dimethyl-1, 2-butanediol 115 g (0.975 mol), 130 g diethyl carbonate (1.10 mol), and 1 g sodium metal were heated to reflux in a 500-mL flask with ethanol distillation over 5 h. The mixture after isolation was vacuum distilled to purify the product (bp 75–77°C/0.35–0.4 torr). Yield: 116 g (83%). M/S obtained 145.0841 *m/e* (theory MH⁺, 145.0861).

Cyclohexylethylene Carbonate. 1-Cyclohexyl-1,2-ethanediol 212 g (1.45 mol), 400 g diethyl carbonate (3.39 mol), and 0.6 g sodium metal were heated at reflux in a 1-L flask. The light amber reaction product was distilled under vacuum (bp 118°C/0.5 torr). Yield: 165 g (67%). M/S obtained 171.1018 *m/e* (theory MH⁺, 171.1017).

In all of the above preparations, the IR and NMR spectra supported the structures of the compound sought. Reaction kinetics were determined as described previously.⁸ For the current work, however, 0.125 mol of TPA was substituted for the 0.250 mol of benzoic acid, and the appropriate molar amount of tributylamine was substituted for the quaternary ammonium salt of the previous work. As in the previous work, catalyst concentration was based on the initial moles of carbonate present.

RESULTS AND DISCUSSION

In the model reaction work we reported previously,⁸ an overall zero-order reaction was noted. In the TPA-carbonate reactions, zero-order kinetics

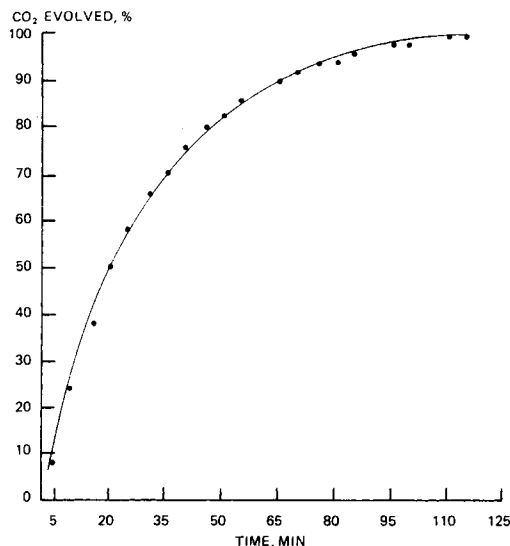


Fig. 1. CO₂ evolution vs. time, pentylene carbonate reaction with TPA.

If, in the above scheme, the first step is very slow relative to all the other steps; i.e., if carboxylate attack on the carbonate ring is rate-determining, then a reaction that is first-order in carbonate and apparently first-order overall is expected.

The overall first-order reaction results, in part, from terephthalic acid having only limited solubility in the reaction medium (the reaction medium becomes clear only after $\approx 96\%$ or greater completion of reaction) and being, therefore, at a constant concentration throughout most of the reaction.

Additionally, the fact that clean first-order kinetics was followed showed that esterification of one carboxy group of terephthalic acid was strictly independent of the other carboxy group, whether reacted or unreacted.

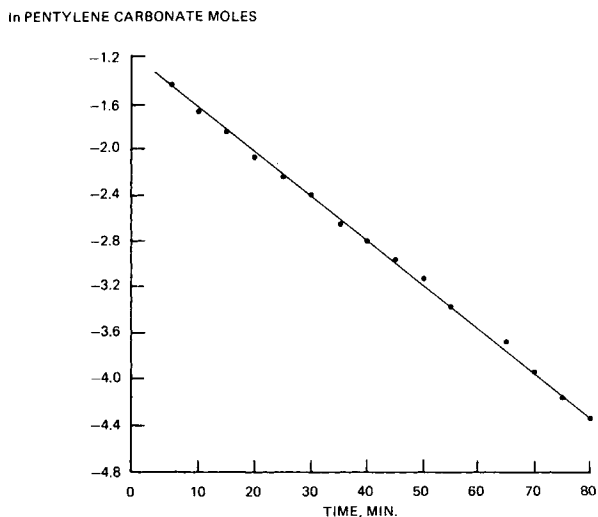


Fig. 2. ln of the pentylene carbonate moles remaining vs. time.

The half-life of reaction for the various carbonates (Table I) showed marked effects of the substituents on the reaction rate. A relatively high reaction temperature was necessary in order to complete the measurements in a reasonable time span for the more sluggish reactions. For the series of straight chain substituents examined, the natural log of the rate constant ($\ln k$) was examined (see Table I, Fig. 3) since it should be related to the free energy of the reaction. From the $\ln k$ data, it was apparent that the largest decrease in rate constant was observed in going from ethylene carbonate to propylene carbonate. Although there were further decreases in $\ln k$ as substituent chain length increased, they were modest by comparison. This would seem to be best explained on the basis of steric hindrance of the alkyl groups, rather than on the basis of their electronic effects. Indeed, reactions with the carbonate substituted with the isopropyl, cyclohexyl, and *t*-butyl groups compared with those substituted with an ethyl group would confirm this and indicate that the rate-determining step was extremely sensitive to steric hindrance.

The *n*-octyl substituent was interesting because the reaction proceeded even slower than the reaction which involved the carbonate with a *t*-butyl group present. This could be due to the long hydrocarbon chain segregating from the more polar carbonate end and coiling on itself to produce a great deal of steric hindrance to reaction. A possible additional factor could be dilution of the polar carbonate moiety, which lowered the overall medium dielectric constant. This would destabilize a highly polar transition state and result in slowing down of the reaction. The phenyl substituent's high rate of reaction would also be in accord with a highly polar transition state.

Lastly, we examined the reaction at 185–230°C with a low level of catalyst (0.4 mol %) in order to determine the activation energy (E_a) and activation entropy (ΔS^\ddagger) (Fig. 4). The data gave an E_a of 16.0 kcal/mol and a natural log of the preexponential factor of 13.4; the latter value resulted in a ΔS^\ddagger of -23.6 cal/deg. Both of these values were relatively close to those calculated for the benzoic acid–ethylene carbonate model reaction ($E_a = 20.8$ kcal/mol, $\Delta S^\ddagger = -26$ cal/deg). The differing activation entropy accounted for ca. two-thirds of the overall faster reaction rate observed in this work as compared with the reaction rate observed in the model reaction work.

TABLE I
Reaction Rates of TPA–Carbonate Reactions

Carbonate substituent	$t_{1/2}$ (min) ^a	$\ln k$
H	1.9	-1.009
Me	7.6	-2.395
Et	14	-3.006
<i>n</i> -Pr	18	-3.257
<i>n</i> -Bu	21	-3.411
<i>n</i> -Octyl	> 500	—
<i>i</i> -Propyl	47	-4.217
Cyclohexyl	56	-4.392
<i>t</i> -Butyl	~200 ^b	-5.665
Phenyl	10	-2.669

^a Reactions conducted at 225°C with 5 mol % Bu₃N catalyst (based on carbonate).

^b Reaction not run more than 2 half-lives.

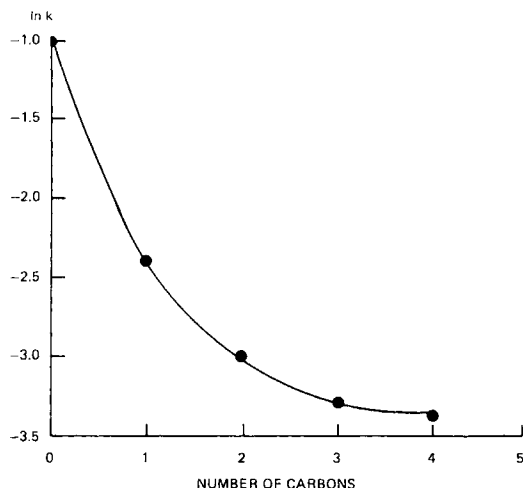


Fig. 3. \ln of the reaction rate constant vs. the number of carbons in the straight chain substituent.

As in the model reaction case, the activation entropy seems on the low side for three molecules being present in coordination for the initial attack. However, as was pointed out previously, the carbonates are strong dipoles which may strongly solvate all species so they are in close proximity for reaction.

CONCLUSIONS

The kinetics of the reaction of a number of substituted ethylene carbonates with TPA were all apparently overall first-order. Thus, solution rate of the TPA into the reaction mixture was not rate-limiting. The mechanism

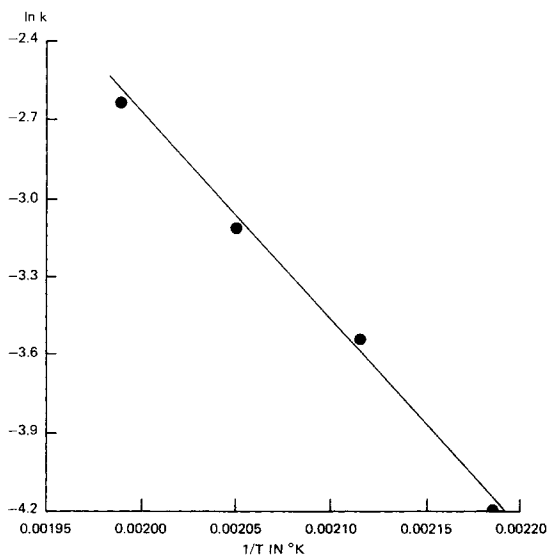


Fig. 4. Activation energy plot for TPA reacting with ethylene carbonate, 0.4 mol % Bu_3N catalyst.

appeared to be in accord with that of the model reaction previously reported. The attack of the carboxylate species on the carbonate ring must be the rate-limiting step and the TPA (owing to its limited solubility in the medium) is at a constant concentration throughout most of the reaction. Substituent effects appeared to be mostly steric in nature, and the surprising result of the *n*-octyl group causing the slowest reaction rate overall was noted. The transition state appeared to be strongly affected by steric hindrance and could be highly polar. Activation energy and activation entropy parameters were similar to those of the model reaction.

The author acknowledges the assistance of Mr. T. R. Walker and Mrs. M. B. Martin for preparation of the carbonates and Dr. E. G. Olsen for helpful discussions.

References

1. T. Yoshino et al., *J. Chem. Soc., Perkin*, 1266-1271 (1977).
2. J. G. N. Drewitt and J. Lincoln, U. S. Pat. 2,802,807 (1957).
3. Chemstrand Corp. Br. Pat. 769,700 (1957).
4. R. Schnegg and H. Pelousek, Ger. Pat. 952,094 (1969).
5. M. V. Wiener, U. S. Pat. 3,462,395 (1969).
6. Y. Wu, U. S. Pat. 4,266,046 (1981).
7. D. J. Swart, U. S. Pat. 4,347,351 (1982).
8. D. R. Fagerburg, *J. Macro. Sci., Chem.*, **A21**, 141-154 (1984).
9. D. R. Fagerburg, *J. Appl. Polym. Sci.*, **29**, 4287-4295 (1984).

Received November 2, 1984

Accepted January 29, 1985