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Reaction Kinetics of the Model Reaction of Benzoic Acid with Ethylene Carbonate

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ABSTRACT

As a model for several polymer-related reactions, we have re-examined the reaction kinetics of benzoic acid with ethylene carbonate in which various quaternary ammonium salts were used as catalysts. The salt anion appeared to have little or no effect on the rate of reaction. At a 1:1 mole ratio of acid to carbonate, the reaction was zero-order to about 95% reaction. With tetraethylammonium hydroxide catalyst at 0.4 mol% (based on carbonate moles), the activation energy was 20.8 kcal/mol with a preexponential factor of $\ln A = 17.1$ (activation entropy of -26 cal/deg). The activation energy for decomposition of the carbonate alone was 33.0 kcal/mol with a preexponential factor of $\ln A = 27.3$. This rules out previously suggested mechanisms that essentially involved decomposition of the carbonate prior to esterification. The proposed mechanism for the reaction involves the attack of the quaternary salt carboxylate on the methylene carbon of the carbonate. The attack causes ring opening and is followed by proton transfer and carbon dioxide loss from the carbonate half-ester intermediate. Ether linkages (such as diethylene glycol) are postulated to arise from the resultant alkoxide intermediate prior to protonation to give the hydroxyethyl ester rather than by separate postreaction of carbonate with the hydroxyethyl ester.

INTRODUCTION

In 1960, Fischer [1] described the synthesis of some polyesters via a dicarboxylic anhydride and an epoxide, such as ethylene oxide. The reaction was noted to be strongly catalyzed by trialkylamines and quaternary ammonium salts. The proposed mechanism involved activation of the anhydride via a ring opening caused by the catalyst. Later, Schwenk and co-workers and Hilt and co-workers [2], by using cyclic carbonates instead of epoxides, extended and then analyzed this reaction. Catalysts were found to be several acids, some bases, a quaternary ammonium salt, and many alkali metal halides. The initiation step of their proposed mechanism involved the decomposition of the carbonate by the attack of the catalyst anion and the resulting loss of CO_2 to form a haloalkoxide species that attacked the anhydride. In their work, no analysis of the data was performed to obtain rate constants. They indicated, however, that for the first 40 to 60% reaction, a zero-order reaction rate was observed. They also reported solubility problems with various catalyst salts that would have caused difficulties in analyzing for the activation energy of the reaction.

Yoshino et al. [3] examined some of the scope of the esterification of carboxylic acids, mostly benzoic acid, with ethylene carbonate by using various tetraethylammonium halide salts as reaction catalysts. Based on their observations of ester product yields, Yoshino proposed a mechanism for the esterification reaction of benzoic acid and ethylene carbonate that involved the decomposition of the carbonate prior to reaction with the acid. In addition, Yoshino and his co-workers reported an experiment wherein they reacted terephthalic acid with ethylene carbonate to give, presumably, the bis(hydroxyethyl)ester that could then have been polycondensed into poly(ethylene terephthalate).

Subsequently, Wu [4] disclosed a method for making poly(ethylene terephthalate) from terephthalic acid, ethylene carbonate, and catalysts, such as quaternary ammonium salts or phosphonium salts. The reaction mixture was, however, heterogeneous until very near completion of the esterification.

In order to have a homogeneous model reaction showing the mechanism of the terephthalic acid-ethylene carbonate reaction and to help us in understanding the mechanism of the anhydride-ethylene carbonate reactions previously reported, we reexamined the reaction of benzoic acid with ethylene carbonate with a quaternary ammonium salt series as catalysts. We wished to determine the kinetic parameters of the reaction to enable differentiation between the type of mechanism proposed by Fischer [1] and that proposed by later workers [2, 3].

EXPERIMENTAL

Ethylene carbonate obtained from Union Carbide was vacuum distilled (bp $147^\circ\text{C}/36$ torr) prior to use. Reagent grade benzoic acid ob-

tained from Mallinckrodt was used without further purification. Quaternary ammonium salts were obtained from Eastman Organic Chemicals. Each salt (except for the hydroxide) was dried in a vacuum oven at 70°C under about 0.5 torr pressure for 16 h. Tetraethylammonium hydroxide was obtained from Eastman Organic Chemicals as a 25 wt% solution in methanol and was used without further purification.

The reactions were conducted in 300 mL, 3-neck, round-bottom flasks. The center neck was fitted with a stainless-steel stirring shaft and blade and a stirring seal. One side-neck was fitted with a 400-mm condenser. The top of the condenser was connected via a gas adapter and flexible poly(vinyl chloride) (PVC) tubing to a wet-test meter (Precision Scientific Co.). Prior to each experiment, the wet-test meter was presaturated with CO₂ from a lecture bottle. In a typical reaction, 22.0-g (0.25-mol) ethylene carbonate, 30.5-g (0.25-mol) benzoic acid, and 1.0 mmol (for 0.4-mol% catalyst concentration) of the quaternary ammonium salt were weighed into the flask. The flask was immersed in a Belmont alloy metal bath maintained at the specified temperature (usually 200°C) and immediately timed. Evolved gas (CO₂) vs time readings were recorded and plotted. The volume ratio of CO₂ that evolved per mole of ethylene carbonate varied depending, of course, upon laboratory temperature and atmospheric pressure. The end point of the reaction for determining this ratio was obtained by running the reaction until at least two successive readings of the wet-test meter were identical over 5 to 10 min.

RESULTS AND DISCUSSION

Examination of plots of CO₂ evolution vs time (see Figs. 1-4) showed them all to be approximately zero-order, i.e., the CO₂ evolution rate did not vary with time until upwards of 95% reaction. There was a slight apparent increase in CO₂ evolution rate with time in all runs—the higher the CO₂ evolution rate, the higher the increase. This slight increase or deviation from zero-order kinetics was attributed to formation of ether linkages, diethylene glycol (DEG) in particular. This side reaction resulted in carbonate decomposition not related to the esterification reaction. The plausibility of this explanation was shown by reactions conducted with ethylene carbonate to benzoic acid ratios that were much higher than 1:1, which gave substantially more curvature to the plots and indicated a lower ethylene glycol content (and, therefore, presumably a higher DEG content) of the ester product (see Fig. 1 and Table 1).

DEG could not be separated from benzoic acid with several GC conditions or columns. Ethylene glycol was analyzed and found to be markedly decreasing. This decrease indicated that increasing amounts of DEG were present. The DEG that was formed appeared to be from the reaction of an intermediate with ethylene carbonate rather than a reaction of the final product, hydroxyethyl ester, with the carbonate;

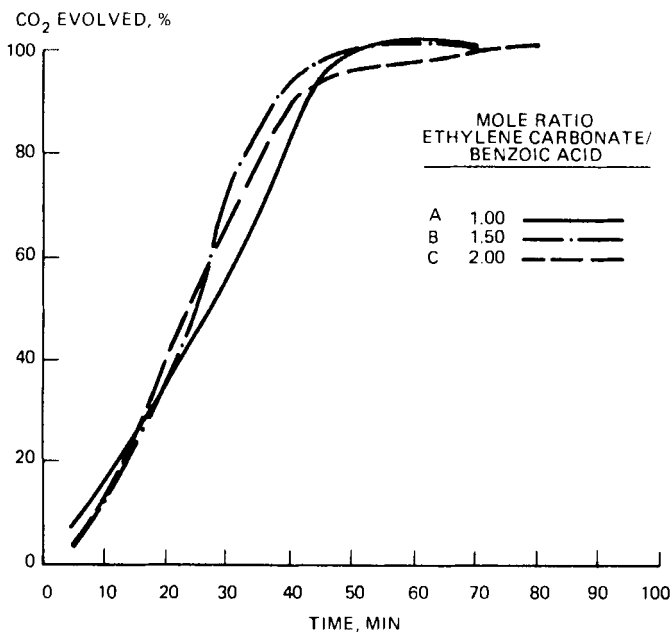


FIG. 1a. Evolved CO₂ vs time for varying ethylene carbonate/benzoic acid mole ratios.

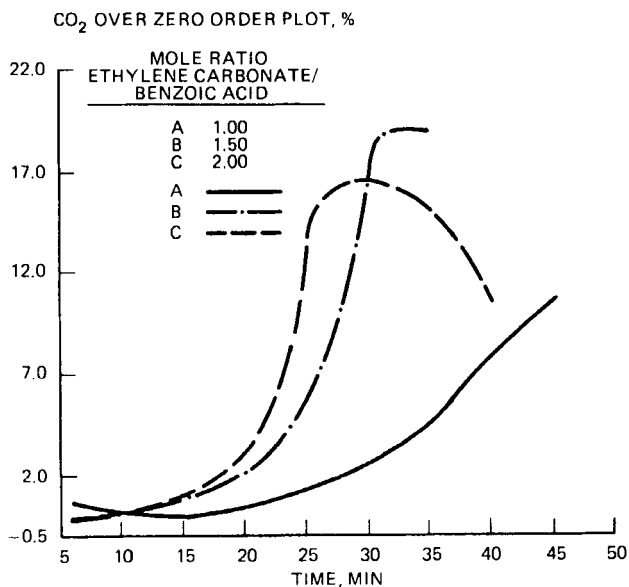


FIG. 1b. Percent CO₂ over zero-order plot of equation of first 15 min of reaction with varying mole ratios of ethylene carbonate/benzoic acid.

TABLE 1. Mole Ratio Effect

Mole ratio ^a ethylene carbonate/benzoic acid	Product ethylene glycol (wt%) ^b
1.00	33.55
1.50	28.38
2.00	21.80

^a0.4 mol% Et₄N⁺, OH⁻ catalyst, 200°C reaction temperature.

^bBy hydrolysis/GC.

that the reaction was apparently of an intermediate with ethylene carbonate was demonstrated when 0.85 additional equivalents of ethylene carbonate were added after completion of the initial reaction (50 min reaction time) and allowed to react for 55 additional minutes. The 0.85 additional equivalents gave a much lower rate of CO₂ evolution than the same amount of carbonate added at the start of the reaction. The ethylene glycol content of the product of the sequential addition reaction was 32.80 wt%—far higher than that expected from the data of Table 1. This increase in ethylene glycol indicated a much lower DEG content for the sequential addition reaction.

The esterification reaction was thus believed to be zero-order, indicating that decomposition of an intermediate species might be the rate-determining step of the reaction. Although this might be true for the mechanism proposed by Yoshino [3], it is highly unlikely for the mechanism proposed by Schwenk and Hilt [2]. The Schwenk and Hilt proposals (as written) should only result in first-order kinetics. The initial haloalkoxy intermediate in the Schwenk mechanism should probably also have very rapid ring closure in competition with the ester formation to form ethylene oxide, some of which would probably escape prior to reaction. This should especially be true with the iodide anion (described later in this paper) and would leave much unreacted benzoic acid in the mixture. We observed essentially very low levels of unreacted benzoic acid, however, as evidenced by the acid numbers of the ester products that ranged from 0.28 to 0.52 mg KOH/g sample. Thus, no more than 0.15% of the original benzoic acid remained after the reaction. Were the Yoshino mechanism operative, one would expect much higher unreacted benzoic acid and ether product levels with iodide salt vs fluoride or hydroxide salts because of this expected ethylene oxide formation. The product acid numbers did not, however, depend on the anion of the quaternary salt, nor did they depend on reaction temperature.

To determine more about the reaction mechanism, we conducted esterification reactions by using a series of halide anions and the hydroxide ion as counterions for the tetraethylammonium cation. The

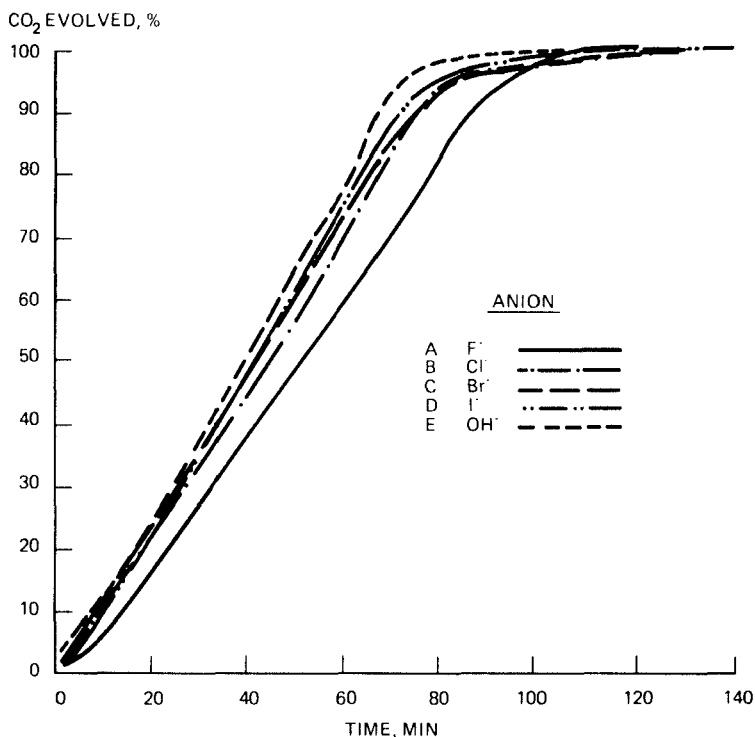


FIG. 2. Percent CO₂ evolved vs time at 185°C for anions.

results (see Figs. 2 and 3 and Table 2) showed that little, if any, real differences in CO₂ evolution rate (and hence carbonate disappearance) existed among the series of anions. With the Yoshino mechanism [3] for the benzoic acid esterification, however, one might expect large differences in reactivity of the haloalkoxy intermediate toward esterification that would probably tend to make the esterification rate-determining in the case of both F⁻ and OH⁻ anions.

To enable us to more fully distinguish between mechanisms, we also determined the activation energy of the esterification reaction over the temperature range of 185 to 230°C with tetraethylammonium hydroxide as the catalyst. The slope of the plot of $\ln(k)$ vs $1/T$, m°K gave an activation energy, E_a , of 20.8 kcal/mol.

The y-intercept gave a natural log of the preexponential factor of 17.1. (If only the two data points obtained by averaging all the rate constants at 185 and 200°C for all anions from Table 2 were used, E_a

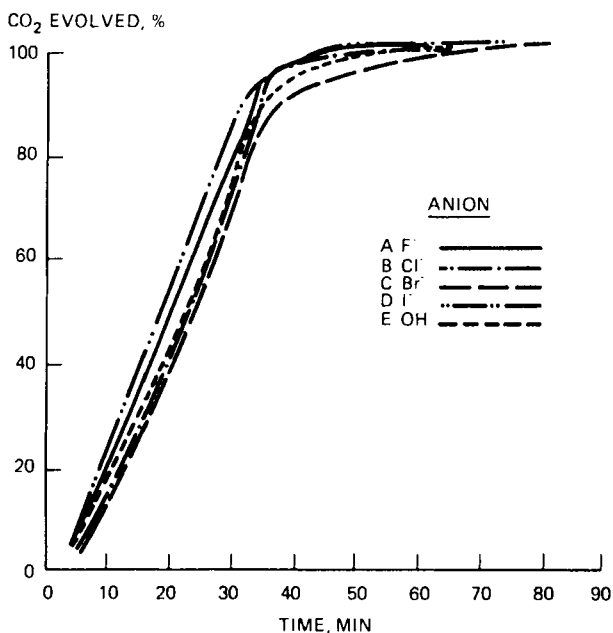


FIG. 3. Percent CO₂ evolved vs time at 200°C for anions.

would be 24.8 kcal/mol.) For comparison, the decomposition of ethylene carbonate alone with tetraethylammonium iodide over the same temperature range gave an activation energy of 33.0 kcal/mol and a natural log of the preexponential factor of 27.3. The kinetic results for the carbonate decomposition actually appeared to follow second-order kinetics better than zero-order kinetics, and the rates were so analyzed. Thus, one concludes that the previous mechanisms that assume catalyst attack on the carbonate to form a haloalkoxide must be incorrect, since the activation energy for such a process is much higher than that observed for the esterification reaction.

It is interesting to note that the carbonate decomposition resulted in about 50 wt% loss (in the same reaction time as the esterification) and formation of polyethylene oxide glycols, DEG, and higher molecular weight ether-glycols. Since unreacted carbonate was still present, there must have been some weight loss because of ethylene oxide formation and loss.

To determine the catalyst order, we compared the effects of three concentrations of catalyst (Table 3 and Fig. 4) in the reaction. The slope of the plot of the relative catalyst concentration vs relative CO₂

TABLE 2. Rate Constants vs Anion

Anion	Rate (%/min) ^a	
	185°C	200°C
F ⁻	1.21	3.49
Cl ⁻	1.31	3.14
Br ⁻	1.36	2.98
I ⁻	1.41	3.28
OH ⁻	1.41	3.14
Average	1.34	3.21
Standard deviation	0.084 (6.3%)	0.190 (5.9%)

^aRates were calculated from the first 15 to 20 min of the reaction to avoid effects of the upward curvature of the plots.

TABLE 3. Catalyst Concentration Effect

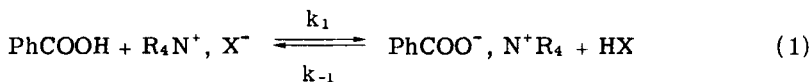
Concentration (mol%)	CO ₂ evolution ^a rate (%/min)
0.133	1.07
0.40	2.03
1.20	5.58

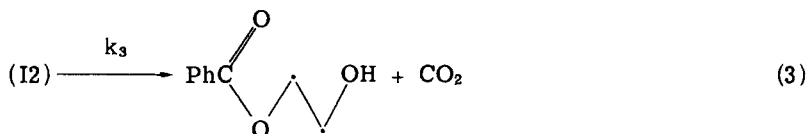
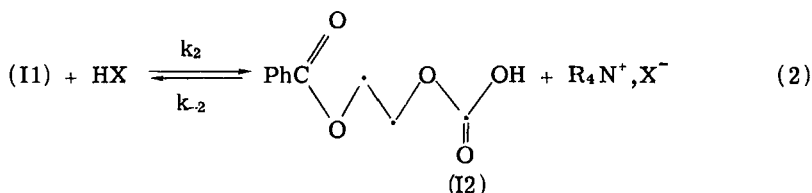
^aRate was calculated from the first 3 or 4 points during the reaction to minimize curvature effects of the plots on the slopes.

evolution rate was not an integer number. This indicated a complex dependency of reaction rate on catalyst concentration.

Several possible mechanisms that might plausibly account for the observations made are shown below.

Scheme I





The side reaction for ether formation is shown only in Scheme I although it operates in all schemes. It should be noted that not one of the schemes provides for the correct catalyst dependency. We have been unable to write a mechanism that has the correct catalyst dependency.

To help differentiate between the above mechanisms, we used a computer program, HAVCHM [5], for reaction simulation of the expected CO_2 evolution vs time for each of the reaction schemes with a 5.0-M concentration of carbonate and acid (this is very near the concentration of the reactants in the bulk). The most favorable ratios of the orders of magnitude of the reaction constants are shown in Table 4. Scheme I resulted in a good fit to the data to about 75-80% reaction, but thereafter the CO_2 evolution began to fall off in the simulation. Scheme III resulted in a better simulation of the actual data (close to zero-order to about 85-90% reaction, see Fig. 5), whereas Scheme II only resulted in first-order kinetics regardless of how the various rate constants were chosen. It would thus seem that Scheme III represents the best proposed mechanism even though the CO_2 evolution rate increase was not modeled by any of the schemes.

In both Scheme I and Scheme III simulations, the proposed mechanisms did not result in a steady-state concentration of either Intermediate 1 or Intermediate 2 (see Figs. 6 and 7 which show Scheme III simulations of these two intermediates).

It is also interesting that the rate constants chosen for the simulations for both Scheme I and Scheme III resulted in a DEG content of ~ 0.13 M out of a 5.0-M initial concentration. This is approximately the expected DEG level based on the DEG levels observed in the reaction of terephthalic acid with ethylene carbonate [6].

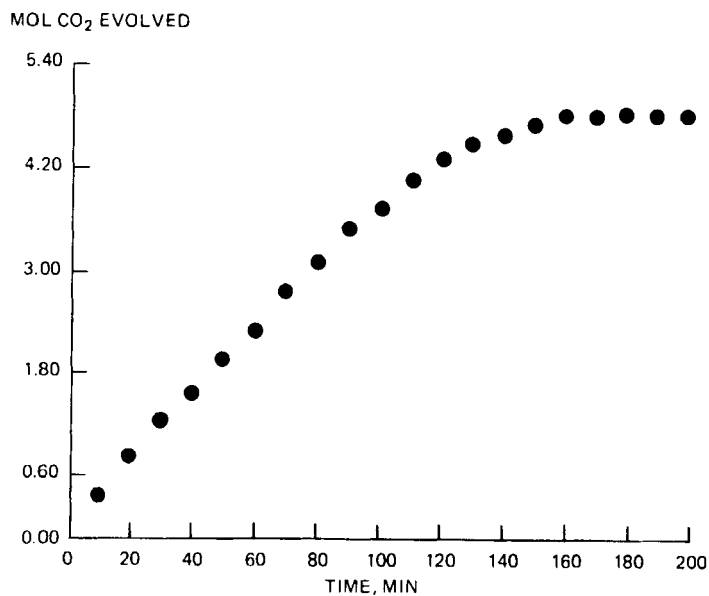
A problem with the Scheme III mechanism is that the first step requires the presence of three species simultaneously, which may be unlikely because of entropy (the preexponential factor for the esterification yields an entropy of activation of -26 cal/deg). On the other hand, both the quaternary ammonium salt and the ethylene carbonate represent strong dipoles, and so the salt may very well be intimately solvated anyway. This may, indeed, lead to the complex catalyst dependency observed.

TABLE 4. Simulation Rate Constants

	Scheme I	Scheme II	Scheme III
k_1	10	1	10
k_{-1}	100	1	1
k_2	10	10	100
k_{-2}	1	100	10
k_3	100	1000	1000
k_{-3}	10	-	-
k_4	1000 ^a	10	10
k_5	10	1000 ^b	1000 ^b
k_6	1000 ^b	-	-

^aLittle difference is seen in the simulation if this number is 100.

^bRate constant for the attack of the alkoxy intermediate, I3 on ethylene carbonate.

FIG. 5. CO₂ evolution rate for Scheme III.

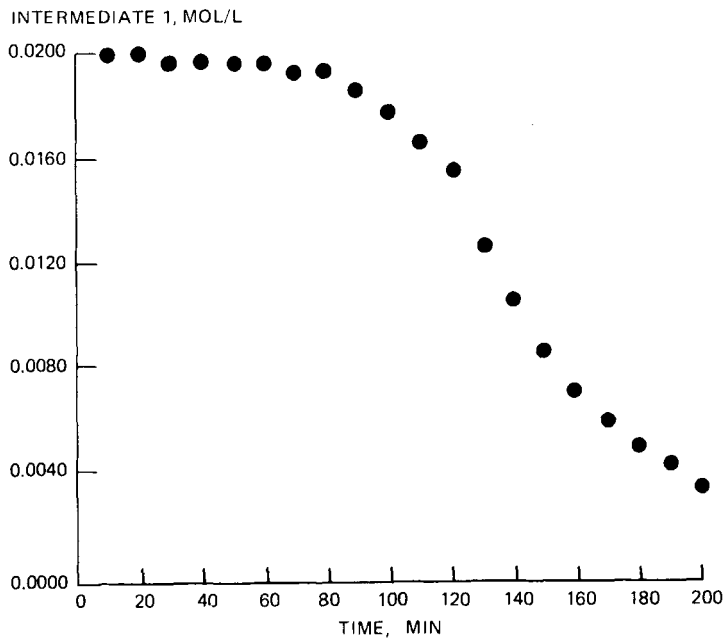


FIG. 6. Concentration of Intermediate 1, Scheme III Simulation.

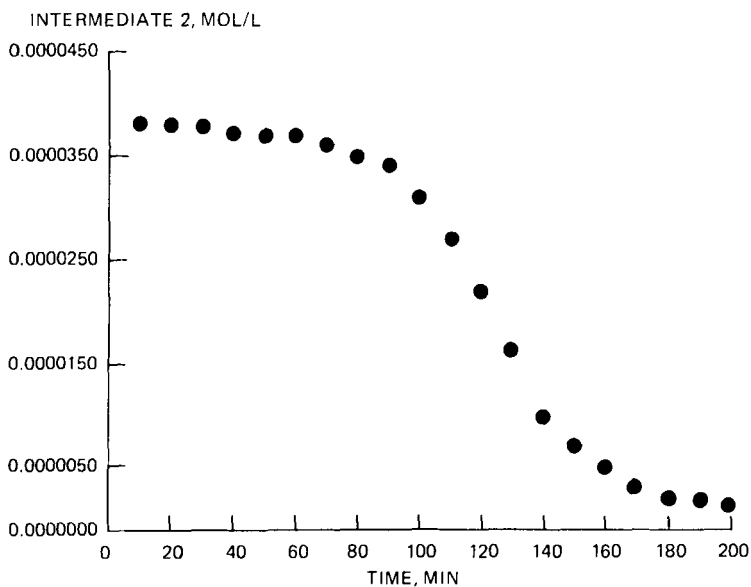


FIG. 7. Concentration of Intermediate 2, Scheme III Simulation.

At any rate, both Schemes I and III proceeded through attack of the carboxylate species on the methylene carbon of the ethylene carbonate and seemed to fit the data better than the previous mechanism of Yoshino [3]. Our proposed mechanisms are very similar to the one of Fischer [1].

CONCLUSIONS

Because of the apparent lack of sensitivity of reaction rate to the quaternary ammonium salt anion and the activation energies determined for the esterification reaction vs the carbonate decomposition, the previously proposed mechanism for the benzoic acid esterification by ethylene carbonate was ruled out. Two new mechanisms were proposed that involve the attack of a carboxylate species on the methylene carbon of ethylene carbonate. The benzoic acid esterification data would indicate that the phthalic anhydride-ethylene carbonate mechanism previously proposed is also unlikely since very similar reactions are involved. The complex catalyst dependency has not yet been resolved. Ether species appeared to arise from reaction of an alkoxide intermediate with ethylene carbonate rather than reaction of the hydroxyether ester product with the carbonate.

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