Investigations on Acid Hydrolysis of Polyesters*

E. SZABÓ-RÉTHY and I. VANCSÓ-SZMERCSÁNYI

*Research Institute for the Plastics Industry,
Budapest XIV*

The present investigations aimed at the relationships by which the acid hydrolysis of polyesters can be treated kinetically and consequently effects of the essential variables on the acid-catalyzed hydrolysis of polyesters were determined. In this respect, our results are concerned with hydrolysis of polyesters from different types of dicarboxylic acids and diols in the presence of various acid catalysts under different conditions of reaction variables. In some cases, activation energies were also determined based on temperature dependence of the rate constants. The results may refer to the possible reaction mechanisms.

Several papers have covered the kinetics and mechanism of hydrolysis of monoesters both in acid and in alkaline media. In the fundamental work of *Day* and *Ingold* [1], the possible reaction mechanisms of ester hydrolysis were summarized and classified. The subsequent studies directed principally to supporting these mechanisms or determining the category into which a particular ester hydrolysis can be placed according to the classification reported.

Studies on hydrolysis of polyesters are far less comprehensive. Only a few papers have treated this field being confined merely to investigations of hydrolyses in alkaline media [2—6].

The present paper deals with acid hydrolysis of polyesters connected partly with our previous studies on kinetics and mechanism of polyesterification [7—11].

Experimental

The experiments were performed in inert atmosphere in two ways:

1. Hydrolysis was carried out in a double-walled thermoregulated vessel equipped with a reflux condenser. The temperature was adjusted by an ultrathermostat. The reaction mixture was agitated by means of a magnetic stirrer. Solution of the polyester to be hydrolyzed was placed into the vessel and, as the desired temperature had been reached, the catalyst was admixed. The moment of addition of the catalyst was regarded as the beginning of the hydrolysis. No appreciable hydrolysis was measured without catalyst under the present experimental conditions. Samples were taken by means of a long pipette through the reflux condenser in order to get rid of evaporation losses.

2. The hydrolysis was conducted in a closed system of sealed ampules. The ampules mounted on an appropriate framework were immersed into an ultrathermostat bath. The mixtures were stirred by a continuous rotation of the framework. For sampling, one of the ampules was removed and opened at each stated interval. The moment when ampules were placed into the thermostat was regarded as the beginning of the hydrolysis. The rate of hydrolysis at room temperature was considered negligible under the present conditions.

A mixture of dioxan and water used as solvent in both cases. Hydrolyses were followed by titrations with 0.1 N-NaOH aqueous standard solutions in the presence of thymol blue indicator.

The polyesters were prepared by polycondensations of equimolar mixtures of diols and dicarboxylic acids without catalyst in molten state, up to the acid number of 45 ± 5.

For the hydrolysis, hydrochloric acid or p-toluenesulfonic acid was used as catalyst.

It should be noted that all the experimental results were derived from measurements by method 1. Method 2 was used for control measurements mainly to check some deviating or remarkable results. Considerable differences between these results obtained from both methods were actually not observed.

Calculation method

The percentage extent of hydrolysis was calculated from the concentration of the released acid (in equivalents/1000 g) determined from titrimetric results. Rate constants of the hydrolysis were obtained by further treatment of these data using the following kinetic equation:

$$\ln \frac{E_0}{E_0 - x} = k_1 t \tag{1}$$

and

$$k_1 = k_2 C,$$

where E_0 = initial ester concentration in equivalents/1000 g,

x = concentration of acid produced by the hydrolysis or that of ester hydrolyzed during the period of t minutes, in equivalents/1000 g,

k_2 = rate constant of the reaction in (equivalents/1000 g)$^{-1}$ min^{-1},

C = concentration of catalyst in equivalents/1000 g.

Validity of this kinetic relation was completely verified for these conditions by the experimental results.

It should be noted with respect to the calculation that water concentration is not included in the formula since, under the selected conditions, a great excess of water is usually present. The water concentration is important otherwise as it will recur in interpretation of experimental results.

Experimental Results

According to the above equation, the rate of the acid hydrolysis depends on the initial ester concentration and on the concentration of the acid catalyst. The rate constant should be independent of both concentrations which was proved by several series of experiments. As an example, the effect of changes in concentration of the acid catalyst

is illustrated for hydrolysis of an adipic acid—ethylene glycol polyester in the presence of hydrochloric acid catalyst at 105°C (Table 1).

It is well illustrated in Table 1 that k_1 increases proportionally to concentration of acid catalyst while the other rate constant, k_2, is practically unchanged in a wide range of catalyst concentration.

Table 1

Effect of catalyst concentration on the rate constant of hydrolysis of adipic acid—ethylene glycol polyester catalyzed by HCl at 105°C

C_{HCl} equiv./1000 g	$k_1 \times 10^3$ [min^{-1}]	$k_2 = \dfrac{k_1}{C_{HCl}}$ (equiv./1000 g)$^{-1}$ min^{-1}
0.0140	1.98	0.141
0.0281	4.21	0.150
0.0562	8.51	0.151
0.1754	27.3	0.155

Interrelation between hydrolysis rate of the polyester and chemical structure of the acid component of the polyester was investigated for reactions catalyzed either by hydrochloric acid or p-toluenesulfonic acid. It can be seen in Table 2 that, with hydrochloric acid catalyst, the polyester of adipic acid and ethylene glycol is hydrolyzed 280 times faster than phthalic acid and ethylene glycol under the same conditions. The ratio of these rates is only 18 in the presence of p-toluenesulfonic acid catalyst.

The effect of chain length of the aliphatic saturated dicarboxylic acid incorporated in the polyester is apparent only for the succinic acid in contrast with the other acids where the rate of hydrolysis is practically independent of their chain length. Chain length of the glycol has no effect in all cases. On the other hand, the rate of hydrolysis is dependent on the structure of the chain, in particular, etheric oxygens in the chain of polyesters from

Table 2

Effect of the structure of dicarboxylic acid in polyester on the rate of hydrolysis catalyzed by acid at 105°C

Composition of polyester	HCl catalyst		p-Toluenesulfonic acid catalyst	
	k_2^{*}	$\dfrac{k_2}{k_2(\text{Ft} + \text{Et})}$	k_2^{*}	$\dfrac{k_2}{k_2(\text{Ft} + \text{Et})}$
phthalic acid—ethylene glycol (Ft + Et)	0.00054	1.0	0.0125	1.0
maleic acid—hexanediol-1,6	0.012	22.8	0.0487	3.9
adipic acid—ethylene glycol	0.151	280.4	0.225	18.0

* In (equivalents/1000 g)$^{-1}$ min^{-1}.

diethylene glycol enhance the rate of hydrolysis. The part of steric factors is revealed by the investigations of polyesters containing 2,2-dimethylpropanediol-1,3 where the rate constant is considerably reduced. The irregular behaviour caused by the succinic acid appears in the case of the latter two glycols as well.

As an interesting observation, p-toluenesulfonic acid and hydrochloric acid act almost fully in the same manner in the present cases.

Studying the effect of chain length of the acid on the rates of hydrolysis calculated on the basis of equilibrium polyesterification [9], trends resulted were similar to those described above.

Numerical values are presented in Table 3.

Table 3

Rate constants of acid hydrolyses as a function of the chain length of glycol or the structure of the chain in polyester

Composition of polyester	k_2 (equiv./1000 g)$^{-1}$ min^{-1}	
	HCl catalyst at 105°C	p-TSA catalyst at 90°C
succinic acid—ethylene glycol	0.095	0.0496
adipic acid—ethylene glycol	0.148	0.093
suberic acid—ethylene glycol	—	0.085
sebacic acid—ethylene glycol	0.157	0.089
succinic acid—hexanediol-1,6	0.093	0.046
adipic acid—hexanediol-1,6	0.118	0.085
suberic acid—hexanediol-1,6	—	0.073
sebacic acid—hexanediol-1,6	0.106	0.084
succinic acid—diethylene glycol	—	0.086
adipic acid—diethylene glycol	—	0.135
succinic acid—2,2-dimethylpropanediol-1,3	—	0.024
adipic acid—2,2-dimethylpropanediol-1,3	—	0.055

In the experiments described, a water—dioxan 1 : 5 (v/v) mixture was used as solvent. Interesting and unexpected results were obtained from the experiments with varying ratio of water to dioxan in the solvent.

Our previous investigations in this field [11] showed that the rate constant was practically independent of the water—dioxan ratio in a definite range when p-toluenesulfonic acid was used as catalyst while with hydrochloric acid catalyst, the rate constant decreased considerably as water content was reduced under the conditions used. In a detailed study of this effect, the ratio between the components of the solvent was varied in a wider range. The rate constants obtained as a function of water content are plotted in Fig. 1.
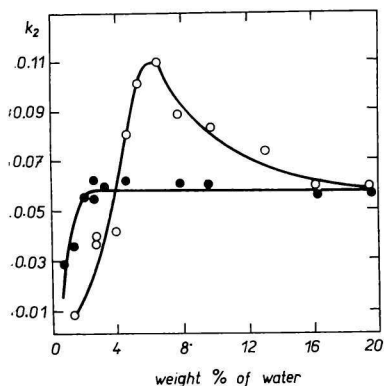
It can be seen that, below a given water concentration, the rate constant increases rapidly with the water content. This critical water concentration is 2% (w/w) of the solvent mixture in the presence of *p*-toluenesulfonic acid. Above this water content, the rate constant is practically unchanged. In the case of HCl, however, the rate constant has a sharp maximum at a water content of 6%.

Table 4

Activation energies for hydrolyses of adipic acid—ethylene glycol and adipic acid—hexanediol-1,6 polyesters in the presence of *p*-toluenesulfonic acid or hydrochloric acid catalyst determined at 60—90°C
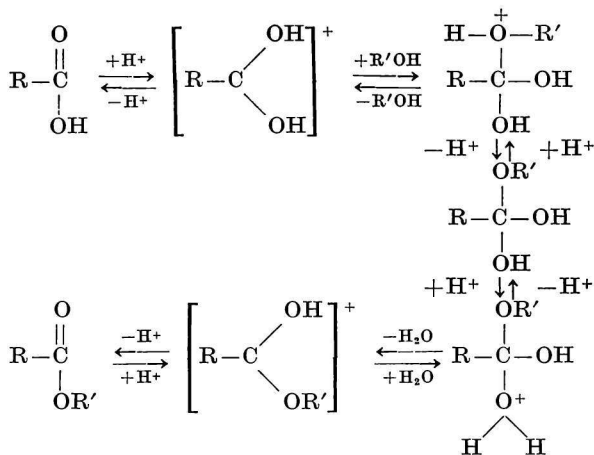
Composition	Catalyst	Activation energy [kcal mol^{-1}]
adipic acid—ethylene glycol	*p*-toluenesulfonic acid	13.3
adipic acid—ethylene glycol	hydrochloric acid	13.1
adipic acid—hexanediol-1,6	*p*-toluenesulfonic acid	12.7

It was found by determinations of activation energies of the hydrolysis that no considerable difference existed in activation energies of hydrolyses catalyzed either by *p*-toluenesulfonic acid or by hydrochloric acid. Activation energies obtained (Table 4) agree well with those of polyesterification reactions [12] and alkaline hydrolysis [9] determined previously.

Discussion

The experimental results are interpreted essentially by two factors: protolytic conditions in the system and steric features of the actual reagents.

Let the starting point be the fundamental mechanism of *Bender* [13] based essentially on carbonyl addition:

$$
\begin{array}{ccc}
\underset{\overset{\displaystyle R-C}{\underset{\displaystyle OH}{|}}}{\overset{\displaystyle O}{\|}}
& \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}}
& \left[\; R-C\!\!\begin{array}{c}OH\\ \diagdown\\ OH\end{array}\right]^+
\end{array}
\quad \underset{-R'OH}{\overset{+R'OH}{\rightleftharpoons}}
\quad
\begin{array}{c}
H-\overset{+}{O}-R'\\ |\\ R-C-OH\\ |\\ OH
\end{array}
$$

$$
-H^+ \;\downarrow\uparrow\; +H^+
\qquad \overset{OR'}{}
$$

$$
\begin{array}{c}
OR'\\ |\\ R-C-OH\\ |\\ OH
\end{array}
$$

$$
+H^+ \;\downarrow\uparrow\; -H^+
\qquad \overset{OR'}{}
$$

$$
\begin{array}{ccc}
\underset{\overset{\displaystyle R-C}{\underset{\displaystyle OR'}{|}}}{\overset{\displaystyle O}{\|}}
& \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}
& \left[\; R-C\!\!\begin{array}{c}OH\\ \diagdown\\ OR'\end{array}\right]^+
\end{array}
\quad \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}}
\quad
\begin{array}{c}
OR'\\ |\\ R-C-OH\\ |\\ \overset{+}{O}\\ \diagup\;\diagdown\\ H\quad H
\end{array}
$$

In connection with this mechanism, the following known facts should be emphasized:

The first step of the reaction is a proton addition to the carbonyl groups. In the present instance, protons are generated predominantly from the acid catalyst. Protons of the acid catalyst can reach the carbonyl groups in two ways. Either of them involves a proton transfer by mediation of an acceptor which receives the proton from the catalyst and passes it on to the carbonyl oxygen. It is well known that water is an excellent proton acceptor; thus it promotes the proton transfer to a high extent and therefore its concentration in the system is of crucial importance.

According to the other mechanism recorded in the literature [14], the acid catalyst (HB) is added *directly* to the $C{=}O$ group through a hydrogen bond without any intermediate proton acceptor
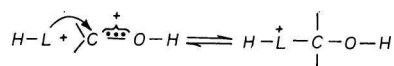
$$
\diagdown\!\!\!\!\!\diagup\;C{=}O \qquad HB.
$$

The elementary steps of the reaction are illustrated by some descriptive symbols as follows:

As a first step, hydrogen bonds are formed

$$
\diagdown\!\!\!\!\!\diagup C{=}\overset{..}{O}\!\!:{+}H-B \;\rightleftharpoons\; \diagdown\!\!\!\!\!\diagup\overset{+}{C}\cdots\overset{..}{O}-H + B^-
$$

followed by the addition of a $H-L$ reagent to the electrophilic carbon atom

$$
H-L + \diagdown\!\!\!\!\!\diagup\overset{+}{C}\cdots O-H \;\rightleftharpoons\; H-\overset{+}{L}-\underset{|}{\overset{|}{C}}-O-H
$$

then by the regeneration of the $H-B$ catalyst

$$
B\!:{+}H-\overset{+}{\underset{|}{L}}-\underset{|}{\overset{|}{C}}-OH \;\rightleftharpoons\; BH + L-\underset{|}{\overset{|}{C}}-OH
$$
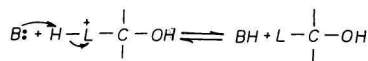
It can be seen from the further analysis of the Bender's mechanism that, after the addition of proton to the $C=O$ group, the trigonal C atom of this group is transformed into tetrahedral one. Thus, this reaction step involves an increase in steric demand. Since the formation of the tetrahedral carbon atom is fairly hindered sterically in succinic acid, it might account for the slower hydrolysis of polyesters from this acid in comparison with those from longer-chain dicarboxylic acids. However, effects of steric factors are observed not only in intramolecular connections but also in the intermolecular proton transfer reactions discussed formerly.

Both of these mechanisms, *i.e.* the proton catalysis by proton transfer and the complex formation through hydrogen bonds, are actually connected with polarity of the $C=O$ group. The mediated proton-catalyzed reaction is governed by the protolytic reaction steps. Besides these factors, the complex formation has to be necessarily affected to a greater extent by individual steric conditions. Possibly, one variant of the basic mechanism and/or the other is realized according to steric characteristics of the reagents, degree of conversion in the reaction, strength and type of the acid catalyst.

The presence of various kinds of the basic mechanisms is suggested by the effects of water concentration. It concerns principally the maximum curve of the rate constant for hydrochloric acid catalyst. The different kinds of the basic mechanisms may also explain the considerable deviations in hydrolysis rates between the use of hydrochloric acid and *p*-toluenesulfonic acid catalyst depending on the structure of the acid component in polyester (Table 2).

The present explanations are obviously not satisfactory for a complete interpretation of the reaction; further improvements are required in the investigations for better elucidation of the reaction.

References

1. Day J. N. E., Ingold C. E., *Trans. Faraday Soc.* **37**, 686 (1941).
2. Fijolka P., Lenz J., *Plaste und Kautschuk* **7**, 336 (1960).
3. Fijolka P., *II. Internationale GFK-Tagung*, I/12, Berlin, 1967. Preprints.
4. Fijolka P., Schulz G., Kriegsmann N., *II. Internationale GFK-Tagung*, I/15, Berlin 1967. Preprints.
5. Schulz G., Fijolka P., *Plaste und Kautschuk* **15**, 407 (1968).
6. Schulz G., Fijolka P., Kriegsmann N., *Plaste und Kautschuk* **15**, 816 (1968).
7. Makay-Bödi E., Vancsó-Szmercsányi I., *Eur. Polym. J.* **5**, 145 (1969).
8. Vancsó-Szmercsányi I., Maros-Gräger K., Makay-Bödi E., *Eur. Polym. J.* **5**, 155 (1969).
9. Vancsó-Szmercsányi I., Makay-Bödi E., Szabó-Réthy E., Hirschberg P., *J. Polym. Sci. A-1*, **8**, 2861 (1970).
10. Szabó-Réthy E., *Eur. Polym. J.* **7**, 1485 (1971).
11. Vancsó-Szmercsányi I., Szabó-Réthy E., Hirschberg P., *J. Prakt. Chem.* **313**, 509 (1971).
12. Vancsó-Szmercsányi I., Makay-Bödi E., *J. Polym. Sci. C*, No. 16, 3709 (1968).
13. Bender M. L., *Chem. Rev.* **60**, 53 (1960).
14. Tchoubar B., *Les mécanismes réactionnels en chimie organique*, p. 171. Dunod, Paris 1968.