hydroxyl concentration would diminish the hydrogen ion activity and, hence, decrease the rate of the acid catalyzed reaction. It will be noted that velocity constants for the lauryl alcohol reaction are somewhat larger than the others. When one takes into account the lower hydroxyl concentration in these experiments, the rates are found to fall in line with those for the decamethylene glycol reaction.

The Effect of Catalyst Concentration.—In Fig. 3, k' values are plotted against the amount of catalyst added to the polymer. The upper line is drawn through data from expts. 6 and 7 with polymer A; the lower set of results is from expts. 14 to 18, inclusive, with polymer C. In order to avoid effects of varying hydroxyl concentration, in each case experiments are compared in which $\rho^{\infty} - \rho^{0}$ was approximately the same. Over the range shown k' appears to be linear with the catalyst concentration, and both lines possess the same slope.[12]

Assuming that the straight lines in Fig. 3 extrapolate to zero *total* catalyst concentration at $k' = 0$, one obtains for the concentration of catalyst in polymers A and C (in the absence of added glycol) 0.475×10^{-2} and 0.239×10^{-2} mmol. per g., respectively.[13] Total catalyst concentrations given in column five of Table III have been calculated from these values and the amounts of catalyst added to the mixture (column three). The velocity constants k, given in column six of Table III, have been obtained from k' using the ester and total catalyst concentrations given in the table.

Summary

A method for studying the kinetics of polymer degradations from viscosity measurements has been demonstrated. Results with degradations of decamethylene adipate polyesters by decamethylene glycol and by lauryl alcohol are in excellent agreement with theory based on the postulate that ester groups of the polymer molecules are attacked at random.

The method offers a simple means for studying the kinetics of ester interchange. In agreement with previous work, the rate of the reaction has been found to be proportional to the concentration of acid catalyst. The rate constants decrease somewhat with increasing hydroxyl group concentration.

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[12] Proportionality between rate of ester interchange and catalyst concentration was observed by G. B. Kolhatkar and by W. A. Waters, ref. 11.

[13] These values are appreciably less than those calculated from the amounts of catalyst used in preparation of the polymer; the latter values are 0.68×10^{-2} and 0.54×10^{-2} mmol./g., respectively. Apparently much of the catalyst is lost during the rather long time required to carry the preparation reaction to completion.

CINCINNATI, OHIO RECEIVED MAY 31, 1940

[A CONTRIBUTION FROM THE BASIC SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI]

A Comparison of Esterification and Ester Interchange Kinetics

BY PAUL J. FLORY

The similarity between the mechanism of the interchange reaction between an ester and an alcohol

$$R'COOR + R''OH \longrightarrow R'COOR'' + ROH \quad (1)$$

and the mechanism of esterification has been recognized for some time. Kolhatkar[1] pointed out that the rates of alcoholysis of esters and the rates of esterification of acids depend in a parallel manner upon the structure of the reactants. Esterification, hydrolysis and alcoholysis of esters are catalyzed by acids, and the latter two are catalyzed by bases as well. The recent investigation of Roberts and Urey[2] has shown that oxygen exchange between benzoic acid and water should be included in this group of similar reactions.

In comparison with esterification and the hydrolysis of esters, the kinetics of ester interchange reactions have received scant attention, which is probably due to the lack of suitable means by which the progress of such reactions can be followed. In the preceding paper[3] it has been shown that ester interchange reactions with polyesters can be followed conveniently by viscosity measurements. The present paper presents a comparison of rate constants and activation energies for alcoholysis and for esterification, determined by application of the viscosity method.

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[1] G. B. Kolhatkar, *J. Chem. Soc.*, **107**, 921 (1915).

[2] I. Roberts and H. C. Urey, THIS JOURNAL, **61**, 2580, 2584 (1939).

[3] P. J. Flory, *ibid.*, **62**, 2255 (1940).

Experimental

Preparation of polymers, measurement of viscosities, and other techniques have been described previously.[3,4,5]

For the determination of rates of esterification, low molecular weight polyesters were prepared by heating exactly equivalent amounts of pure decamethylene glycol and adipic acid, and 0.10 equivalent per cent. of *p*-toluenesulfonic acid at 109° for about 150 minutes. Water produced by the reaction was removed cautiously in order to avoid loss of glycol. Kinetic measurements were carried out on 3 to 5 g. portions of the resulting polymers ($M_n \cong 1500$; $DP_n \cong 10$). These portions were heated at various temperatures, moisture being removed by a stream of nitrogen bubbled through the polymer. From the polymer viscosities measured at intervals during the reaction, weight average chain lengths Z_w were calculated from the empirical relationship

$$\log \eta = -6.147 + 1800/T + 0.1144\, Z_w{}^{1/2} \qquad (2)$$

where T is the absolute temperature. This equation has been shown to be sufficiently accurate within the temperature range in which it is used here.[6]

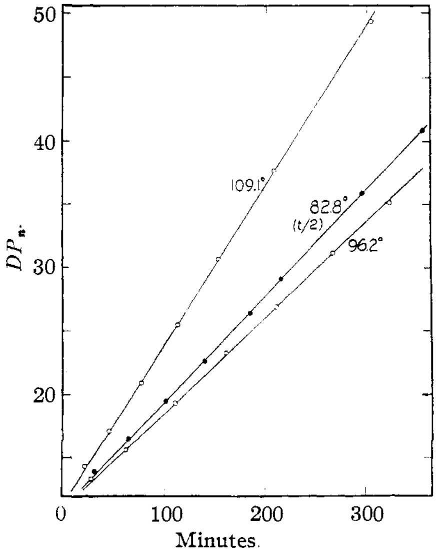

Fig. 1.—Polyesterification in the presence of *p*-toluenesulfonic acid catalyst at three temperatures.

Esterification Rate Calculations.—For an acid catalyzed esterification in which hydroxyl and carboxyl groups are present in equivalent amounts

$$dp/dt = C_0 C_{\text{cat}} k (1 - p)^2 \qquad (3)$$

where C_0 is the initial concentration of hydroxyl or carboxyl groups, C_{cat} is the catalyst concentration, k is the velocity constant, and p is the extent of reaction, *i. e.*, the fraction of the functional groups which have been esterified. Since the degree of polymerization, *i. e.*, the number average number of segments per molecule, is given by[4]

$$DP_n = 1/(1 - p) \qquad (4)$$

the integrated form of the rate expression (3) may be written

$$DP_n = k't + 1 \qquad (5)$$

where $k' = C_0 C_{\text{cat}} k$.

It has been shown previously[7] that

$$Z_w = z(1 + p)/(1 - p) \qquad (6)$$

when hydroxyl and carboxyl groups are present in equivalent amounts; z, the mean number of chain atoms per segment, equals nine for decamethylene adipate. From (4) and (6)

$$DP_n = Z_w/2z + {}^1/_2 \qquad (7)$$

by means of which DP_n may be calculated from Z_w obtained from the viscosity using (2). According to (5) the values of DP_n should increase linearly with time.

Results

Acid Catalyzed Polyesterification.—In a previous publication[4] primarily concerned with the kinetics of "uncatalyzed" polyesterification, a brief discussion of the reaction of diethylene glycol with adipic acid in the presence of *p*-toluenesulfonic acid was included. It was shown that above $DP_n = 10$–15 the process became asymptotically second order in agreement with (5), and continued thus to $DP_n = 90$.

In the present investigation kinetic measurements have been limited to the range beyond $DP_n = 10$. Values of DP_n, calculated from viscosities using equations (2) and (7) as described above, are plotted against t in Fig. 1. In agreement with (5) the relationship is linear, although small deviations from the straight lines are evident below $DP_n = 15$. This behavior is similar to that previously noted in the diethylene glycol–adipic acid reaction.

The experiments shown in Fig. 1 were carried out at atmospheric pressure. Other experiments in which the pressure was reduced to 200 mm. yielded similar results over the initial portions of the curves, but the points fell slightly below the straight lines at larger values of DP_n. These de-

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(4) Flory, This Journal, **61**, 3334 (1939).

(5) Flory, *ibid.*, **62**, 1057 (1940).

(6) See equation (25) of ref. 5. Equation (1') of the preceding paper is the 109° form of (2).

(7) P. J. Flory, This Journal, **58**, 1877 (1936); see equation (18) of ref. 5.

viations became more pronounced the higher the temperature. At 129°, even at atmospheric pressure, concave downward curvature was so great as to discourage all efforts to evaluate a velocity constant. Data at this temperature have not been included, therefore. The cause for this behavior is not clear. Perhaps the decrease in rate is due to esterification of the catalyst.[8]

TABLE I

Temp., °C.	k', min.$^{-1}$	k, (mmol./g.)$^{-2}$, min.$^{-1}$
82.8	0.0421	0.85
96.2	.075	1.53
109.1	.126	2.55

The values of k' (see equation (5)) given in Table I have been taken from the slopes of the straight lines in Fig. 1. Values of k in the third column have been calculated from k' taking $C_0 = 1000/142$ mmol./g. and $C_{\text{cat}} = 1/142$ mmol./g. In Fig. 2 (upper line) log k is plotted against $1/T$. From the slope of the straight line we obtain for the activation energy 11,150 cal. This value is in reasonably close agreement with the activation energy, 10,000 cal., which Smith[9] has obtained for hydrogen chloride catalyzed esterifications of normal aliphatic acids in methanol.

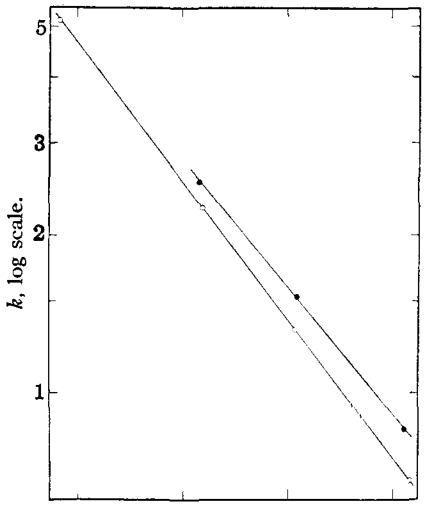

Fig. 2.—Log velocity constant *vs.* reciprocal absolute temperature: ●, polyesterification; ○, ester interchange. Values of k have been multiplied by 10 in the latter case.

Alcoholysis Rates at Several Temperatures.—Rates of the reaction of decamethylene glycol with decamethylene adipate polyester were measured at several temperatures by the viscosity method described in the preceding paper. No catalyst was added to that already present in the polymer, 0.239×10^{-2} mmol./g. (polymer C of the preceding paper), and the concentration of decamethylene glycol added to the polymer was about the same in all of the experiments $(\rho^\infty - \rho^0) \cong 0.060$.

Plots of log $[(\rho^\infty - \rho)/(\rho^\infty - \rho^0)]$ against t, shown in Fig. 3, are approximately linear except at 129.7° where there is a decided upward curvature. This behavior and the difficulties encountered in the study of the esterification reaction above 109° probably have the same origin. The 129.7° straight line in Fig. 3 has been drawn tangential to the initial part of the curve described by the experimental points.

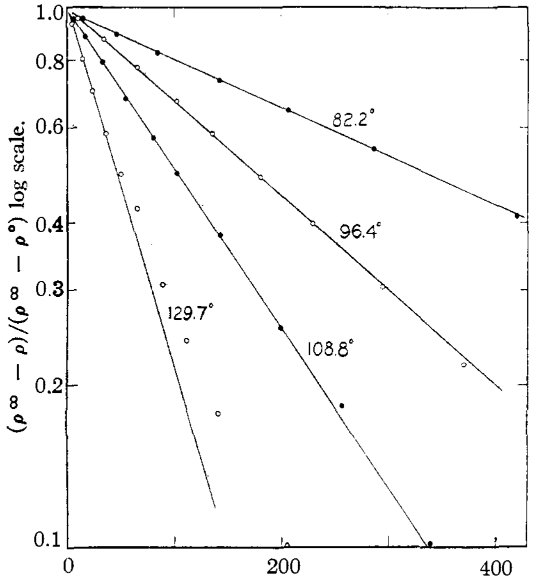

Fig. 3.—Log fraction of decamethylene glycol assimilated *vs.* time at several temperatures.

Velocity constants, evaluated from the slopes of the straight lines in Fig. 3, are given in Table II. Log k is plotted against $1/T$ in Fig. 2 (lower line). From the slope of the straight line drawn through the points the activation energy is 12,150 cal.

TABLE II

Temp., °C.	$k' \times 10^2$, min.$^{-1}$	k, (mmol./g.)$^{-2}$, min.$^{-1}$
82.2	0.205	0.068
96.4	.400	.132
108.8[a]	.685	.226
129.7	1.56	.515

[a] This is expt. 15 of the preceding paper (Table III).

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(8) Similar difficulties encountered by M. M. Davies, *Trans. Faraday Soc.*, **33**, 331 (1937), in a study of the benzyl alcohol-benzoic acid reaction were attributed to esterification of the p-toluenesulfonic acid catalyst.

(9) H. A. Smith, THIS JOURNAL, **61**, 254 (1939).

At 109°, the rate constant for alcoholysis catalyzed by *p*-toluenesulfonic acid is about one-eleventh of that for esterification. The difference, 1000 cal., between the activation energies[10] is greater than the experimental error (about ±300 cal. in each case). This difference is sufficient to account for a 3.7-fold difference in the rates at 109°. Since the ratio of the rates is greater than this factor, the entropy of activation for the esterification reaction probably is slightly greater than that for alcoholysis.

Catalysis by Carboxylic Acid.—In expt. 3 of the preceding paper the viscosity of a mixture of polyester B and decamethylene glycol decreased very slowly in complete absence of *p*-toluenesulfonic acid catalyst. This process has been attributed to catalysis by the free carboxyl groups present in polymer B at a concentration of 3.4×10^{-2} mmol./g. The rate of viscosity decrease was about one-eightieth of the initial rate observed in expt. 8 in which the *p*-toluenesulfonic acid concentration was 0.45×10^{-2} mmol./g.; glycol concentrations were about the same in each experiment. Hence the carboxylic acid end-groups are about one six-hundredth as effective as *p*-toluenesulfonic acid catalyst; for carboxyl group catalyzed alcoholysis at 109°, $k \cong 4 \times 10^{-4}$ (mmol./g.)$^{-2}$ min.$^{-1}$. Approximate evaluation of the rate of alcoholysis from the viscosity decrease when a low and a high molecular weight polyester are mixed (without adding a catalyst) yields a similar value, 6×10^{-4}, for k.[11]

Unpublished results on rates of polyesterification of decamethylene glycol and adipic acid catalyzed by carboxyl groups yield $k \cong 5 \times 10^{-4}$ (mmol./g.)$^{-2}$ min.$^{-1}$ at 109°. Thus, when carboxylic acid is the catalyst, the rates of esterification and alcoholysis appear to be about the same. Compared with *p*-toluenesulfonic acid, carboxylic acid appears to be relatively less effective as an esterification catalyst than as an alcoholysis catalyst. This difference between these similar reactions should be investigated further.

Summary

Rates of polyesterification and of alcoholysis of polyesters have been measured by viscosity methods. When *p*-toluenesulfonic acid is the catalyst at 109°, the rate constant for esterification is about eleven times that for alcoholysis. The activation energies are 12,150 and 11,150 cal., respectively. Preliminary experiments indicate that esterification and alcoholysis rate constants are about the same when carboxylic acid is the catalyst.

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[10] W. A. Waters, *J. Chem. Soc.*, 1014 (1936), has shown that the rates of hydrolysis and alcoholysis of phenyl benzoate in ethanol-water mixtures are approximately equal. The activation energies (16,500 cal.), though larger than we have observed for an aliphatic ester, are approximately the same within the experimental error (±1000 cal.). Since esterification reactions ordinarily are approximately thermally neutral, the activation energy for the formation of phenyl benzoate probably is about equal to that for its hydrolysis. It follows that activation energies for the formation and for the alcoholysis of this ester must be about the same, in harmony with the results reported here.

[11] This estimation of k is based on results of the sort shown in Fig. 6 of ref. 5.

CINCINNATI, OHIO RECEIVED MAY 31, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Quenching of Fluorescence in Solution. II. Temperature and Solvent Effects

BY R. W. STOUGHTON AND G. K. ROLLEFSON

In a previous paper[1] we have shown that the quenching of fluorescence in solution is influenced by ionic strength in the same way as an ordinary bimolecular reaction involving ions. The quenching process may be considered therefore as a relatively simple bimolecular reaction which is readily followed by studying the rate of disappearance of one of the reactants, *i. e.*, the photoactivated molecule. In this paper we wish to present some observations on the effect of changes in the nature of the solvent and of temperature on reactions of this kind.

If we consider the specific reaction rate of a bimolecular reaction as composed of two factors of which one depends on the activation energy and the other is proportional to the number of collisions, it is the latter which may be expected to be dependent on the viscosity of the solvent. Any calculation of the effect of viscosity on the collision number requires assumptions such as that the apparent viscosity of the solvent to a molecule is the same as the macroscopic value. Ölander[2] concluded that the collision number and hence the specific reaction rate should be inversely pro-

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[1] Stoughton and Rollefson, THIS JOURNAL, **61**, 2634 (1939).

[2] Ölander, *Z. physik. Chem.*, **A144**, 118 (1929).