

been investigated recently. It was found that the data obtained for these systems could be treated in a manner analogous to the glyceryl phthalate data. It is, therefore, suggested that the essential concepts developed herewith are applicable generally to convertible polymeric systems.

### Summary

1. The reaction between glycerol and phthalic anhydride was reinvestigated. A special apparatus, designed so that the reaction could be carried out under controlled reproducible conditions, was used.

2. The reaction was studied in detail at 200°. Samples were taken at various stages of the reaction and their acid value, saponification value, ultimate analysis, and molecular weight determined. The infrared spectra, rheological properties, and spreading characteristics as monomolecular films were ascertained for each of the samples.

3. As the reaction proceeded at 200°, it was shown that the water evolved was greater than

calculated from simple interesterification considerations.

4. A schematic progress of the reaction is suggested wherein it is proposed that the underlying reactions are essentially interesterification, modified by intraesterification and anhydride formation. Application of these concepts allowed approximate compositions of glyceryl phthalate polymerides to be derived at various stages of polymerization. The several constants calculated from these postulated compositions were found to agree very well with those measured experimentally.

5. Gelation has been shown to occur at a relatively low average molecular weight, suggesting that molecular growth proceeds until a sufficient concentration of intertwined three dimensional molecules has formed, whence arrested motion occurs.

6. Limited data are presented on precipitation and fractionation studies.

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[CONTRIBUTION FROM THE LABORATORIES OF THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY, AND RESEARCH DEPARTMENT, THE CALCO CHEMICAL COMPANY, INC.]

## The Polyhydric Alcohol-Polybasic Acid Reaction. IV. Glyceryl Phthalate from Phthalic Acid

BY R. H. KIENLE, P. A. VAN DER MEULEN AND F. E. PETKE

All the studies on the glyceryl phthalate reaction thus far reported in the literature have been carried out with phthalic anhydride. In the present investigation, data are presented wherein phthalic acid was substituted for the anhydride.

The apparatus used and experimental technique employed already have been described fully.<sup>1</sup> The phthalic acid was obtained from resublimed phthalic anhydride (Selden Division, American Cyanamid Company) by dissolving in carbonate free sodium hydroxide solution, then precipitating with hydrochloric acid, thoroughly washing until the wash water tested free from chloride ion, and finally drying carefully at 60° in the air.

The present investigation was carried out at 190°. This temperature was chosen because it was found that at this temperature no anhydride formation occurred during the preheating period employed before the glycerol was added.

(1) Kienle, van der Meulen and Petke, *THIS JOURNAL*, **61**, 2258 (1939).

### Experimental Data

The detailed data obtained for the glycerol-phthalic acid reaction at 190° are given in Table I.

In Fig. 1 the variations of both the acid value and the water evolved with time of reaction have been plotted. In the case of the water evolved-time curve, the observed points of a second independent experiment under identical conditions have been included to show how well the data could be duplicated. On the acid value-time curve, the values obtained from several independent determinations are also shown. Again they fall quite well on the curve.

The log acid value-log time relationship is shown in Fig. 2. It is strikingly similar in shape to the same relationship for glyceryl phthalate (anhydride) except that for glyceryl phthalate (acid) it has been possible to extend the relationship to much higher acid values.

In Fig. 2 changes in slope are observed at ap-

TABLE I

GLYCERYL PHTHALATE FROM PHTHALIC ACID  
 Glycerol (2/8 mol.), 23.0 g. Phthalic acid (3/8 mol.),  
 62.3 g. Temperature of mixing, 190°. Experiment 63.

Time, min.	Temp., °C.	Water evolved, $V_0$	Water evolved, $V_a$ <sup>a</sup>	Acid value
0	190	..	..	494
2	189	..	..	
5	174	0.31	0.31	
8	174	1.46	1.47	
10	174	2.31	2.31	350
14	185	3.68	3.70	
16	187	4.19	4.21	
18	187	4.77	4.80	
20	187	5.00	5.04	294
24	189	5.44	5.48	
26	189	5.65	5.70	
28	189	6.04	6.09	
30	190	6.19	6.24	259
35	190	6.49	6.55	
40	191	6.71	6.78	235
50	191	7.22	7.31	218
60	190	7.68	7.70	203
70	187	8.08	8.23	190
80	190	8.38	8.55	177
90	191	8.71	8.92	164
100	191	9.28	9.52	155
110	190	9.49	9.72	145
120	190	9.78	10.07	137
130	191	9.90	10.22	132
140	190	10.12	10.48	128

<sup>a</sup>  $V_0$  = cc. observed.  $V_a$  = cc. when corrected for water loss in gas stream.

proximate acid values 275, 185 and 140. These agree rather well with the approximate acid values at which similar changes are found in the case of glyceryl phthalate (anhydride), namely, 190 and 138. In addition, acid value 275 is reasonably

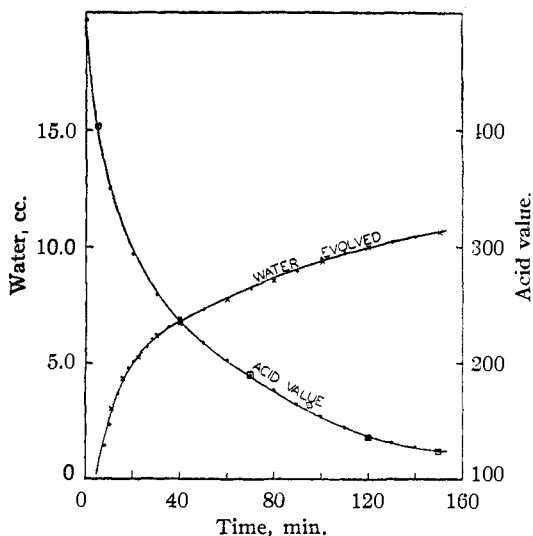


Fig. 1.—Glyceryl phthalate (acid), variation of acid value—water evolved with time,  $T = 190^\circ$ .

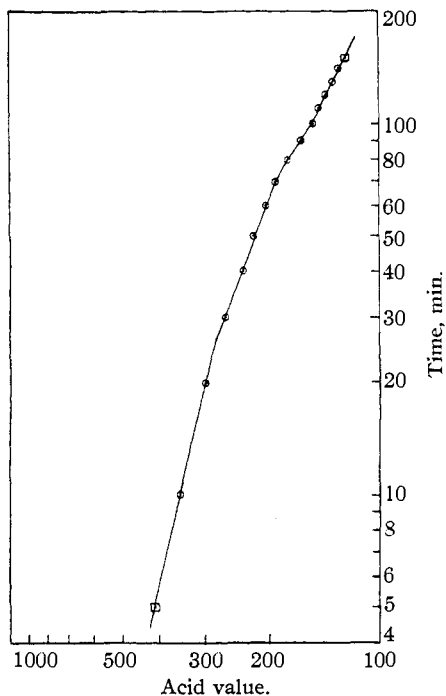


Fig. 2.—Glyceryl phthalate (acid); temperature,  $190^\circ$ .

close to acid value 266, the instantaneous initial acid value always obtained when phthalic anhydride is employed.

The water evolved—acid value relationship is

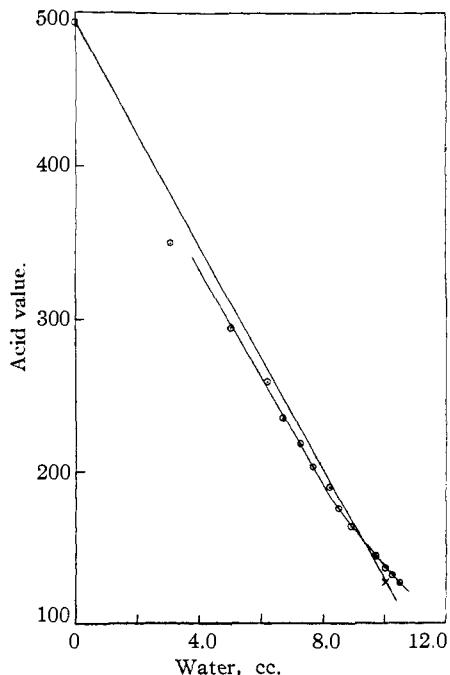


Fig. 3.—Glyceryl phthalate (acid), water evolved—acid value relationship.

given in Fig. 3. There is also included the theoretical relationship for glyceryl phthalate (acid) that should have resulted if the reaction had proceeded by interesterification only. It is interesting to note that the deviations from the theoretical are similar to that observed for glyceryl phthalate (anhydride). This is particularly true from an acid value of 266 on, the acid value representing 50% esterification. In the case of glyceryl phthalate (acid) the curve crosses the theoretical at acid value 155 as compared with acid value 158 observed for glyceryl phthalate (anhydride).

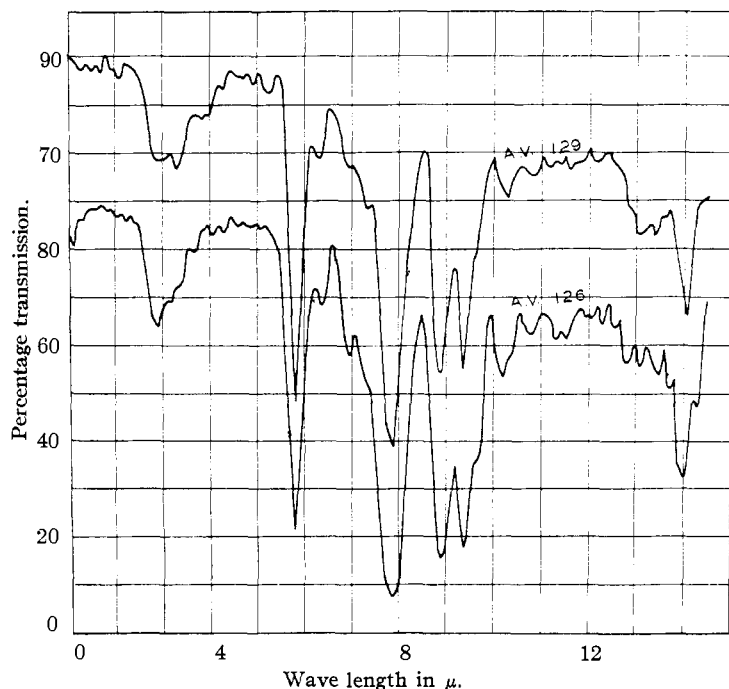


Fig. 4.—Infrared spectra: glyceryl phthalate (acid), A. V. = 129; glyceryl phthalate (anhydride), A. V. = 126.

**Analytical.**—The polymeride obtained just prior to gelation was a light amber, brittle resin similar in physical appearance to that from glyceryl phthalate (anhydride). Its analytical values are given in Table II. In this table there also are

TABLE II  
ANALYTICAL DATA

	Glyceryl phthalate (acid)	Glyceryl phthalate (anhydride)	
		Calcd.	Exptl.
Acid value	129	129	126
Saponification value	560	551	552
% esterification	76.2	76.6	77.2
Av. molecular weight	910	920	1120
Water evolved, cc.	10.48	(10.51)	(10.63)
Ultimate analysis	% C	59.5	59.9
	% H	4.4	4.3

included data for an actual glyceryl phthalate (anhydride) sample of nearly the same acid value and, in addition, the calculated analytical values for glyceryl phthalate (anhydride) of exactly the same acid value determined, by extrapolation, from the curves of the recent glyceryl phthalate (anhydride) study. The water evolved data shown in parentheses for the anhydride samples were obtained by adding to the actual water evolved the water required theoretically to convert the phthalic anhydride to phthalic acid.

The infrared spectrum<sup>2</sup> from 1–15  $\mu$  of the glyceryl phthalate (acid) sample is shown in Fig. 4. There is also included the spectrum obtained for the glyceryl phthalate (anhydride) sample, acid value 126. The general closeness of the two spectra with respect to the over-all shape and positions of the absorption maxima is apparent.

### Discussion

In the glyceryl phthalate reaction, when phthalic acid is substituted for phthalic anhydride, no initial temperature rise is observed and time is necessary to attain 50% esterification. When, however, 50% esterification has been attained, the reaction proceeds further in a manner quite analogous to that observed when phthalic anhydride is used. It appears that equivalent polymerides are eventually formed with quite similar degrees of molecular complexity. This perhaps is illustrated best by the comparison of the various analytical values and is further shown by comparing the water evolved for similar acid values, Table III. In setting up this table, the experimental values for glyceryl phthalate (anhydride) have again been corrected for the amount of water evolved to 50% esterification had phthalic acid been used.

TABLE III

Acid value	Water evolved, cc.	
	Glyceryl phthalate acid	Glyceryl phthalate anhydride
	8.10	8.47
	9.50	9.55
	10.48	10.51
Gel	10.80	10.74

(2) Acknowledgment is made to Mr. R. R. Brattain for determining this spectrum.

It appears that polybasic acids can be substituted for anhydrides in the polyester reaction to yield finally fairly equivalent polymerides.

### Summary

The glyceryl phthalate reaction has been

investigated substituting phthalic acid for phthalic anhydride. Differences in the early stages of the reaction were observed but the later portions of the reaction to gelation are comparable.

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## The Hydration of Unsaturated Compounds. VII. The Rate of Hydration of Crotonic Acid; the Rate of Dehydration of $\beta$ -Hydroxybutyric Acid; the Equilibrium between Crotonic Acid and $\beta$ -Hydroxybutyric Acid in Dilute Aqueous Solution

BY D. PRESSMAN AND H. J. LUCAS

### Introduction

Crotonic acid has been shown to hydrate slowly in the presence of boiling 20% sulfuric acid to form  $\beta$ -hydroxybutyric acid.<sup>1</sup> This reaction is unlike the hydration of acrylic acid, since the latter occurs in the presence of hydroxide ion<sup>2</sup> while crotonic acid is not affected under these conditions. Moreover, only about 80% of the crotonic acid hydrates, for it appears that at this point it is in equilibrium with the hydroxy acid. The fact that the hydroxyl group enters into the  $\beta$ -position during the hydration is shown by the identical properties of the acid obtained by this method and of  $\beta$ -hydroxybutyric acid obtained by other methods. Also the ethyl ester of the hydroxybutyric acid prepared by this method is identical with that from hydroxybutyric acid obtained by other syntheses.<sup>3</sup>

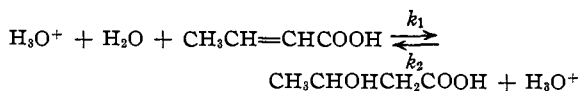
It was desirable to extend the study of the hydration on unsaturated compounds to an investigation of the kinetics of the hydration of crotonic acid, of the kinetics of dehydration of  $\beta$ -hydroxybutyric acid, and of the equilibrium between crotonic acid,  $\beta$ -hydroxybutyric acid, and water. Since it was known that crotonic acid is not hydrated at an appreciable rate at 25° in 1 normal nitric acid,<sup>4</sup> the reaction was carried out in 1.06 and 2.06 normal perchloric acid solutions at 90.03 and 111.31° in order to obtain a measurable rate. These solutions were of 2.06 molal ionic strength. Nitric acid could not be used since its oxidizing power at the elevated temperature was appreci-

able, as evidenced by the liberation of the oxides of nitrogen.

### Data and Discussion

**Kinetics of the Reaction.**—The hydration was found to be first order with respect to crotonic acid since the plots against time of the fraction of crotonic acid unreacted,  $C_t/C_0$ , are practically identical for two runs at hydrogen ion concentration of 1.06 molal where the initial crotonic acid concentration has the values 0.0128 molal and 0.0249 molal. Here  $C_0$  and  $C_t$  are the molar concentrations of crotonic acid at the respective times, zero and  $t$  (Fig. 1). That the reaction is first order with respect to hydrogen ion concentration is evidenced through a comparison of the initial slopes of the plots of  $C_t/C_0$  against  $t$  when the hydrogen ion concentrations are 1.06 and 2.06 molal. The slope at the higher concentration corresponds to a rate constant of 0.014, which is twice that of the lower, approximately 0.007. However, hydrogen ion is not used up in the reaction and thus is constant during any one run.

The independence of the equilibrium value with respect to the hydrogen ion concentration, except for small second order differences, is clearly evident from Fig. 2, which shows the complete runs of which Fig. 1 contains only the first portions. The equilibrium value of the crotonic acid fraction remaining is practically identical for both acid concentrations. The reaction then may be considered to be



where  $k_1$  is the specific reaction rate constant of

(1) Kaufel and Basel, *Monatsh.*, **53**, 122 (1929).

(2) Linnemann, *Ber.*, **8**, 1095 (1875); Erlenmeyer, *Ann.*, **191**, 281 (1878).

(3) Dewael, *Bull. soc. chim. Belg.*, **34**, 341 (1925).

(4) Winstein and Lucas, *THIS JOURNAL*, **59**, 1461 (1937).