[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

THE POLYHYDRIC ALCOHOL–POLYBASIC ACID REACTION. I. GLYCEROL–PHTHALIC ANHYDRIDE

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Introduction

The tendency of the organic chemist to discard the tarry residues or resinous products of a reaction and to explain them away by merely mentioning their formation is unfortunate. It is quite probable that in the study of resin formation many new ideas of space chemistry will be brought forth which, although not revolutionary, will simplify our concepts of materials regarded as complex and at the same time bring about a better correlation between organic chemistry, colloidal phenomena and statistical mechanics.

Although the resinous products of the polyhydric alcohol–polybasic acid reactions have been in commercial application for some time, no systematic study of the reactions has been made until the last four years.

It is probably safe to say that a resinous product results whenever a polyhydric alcohol and polybasic acid are heated together. This has never failed to happen when such characteristic aliphatic alcohols as glycerol, ethylene glycol and mannite have been heated with characteristic polybasic acids as phthalic anhydride, phthalic, isophthalic, tartaric, malic, succinic, citric, sebacic, diphenic[1] and naphthalic[1] acids.

The properties of the resinous products and the methods of promoting the reactions are so similar that any information obtained on the glycerol–phthalic anhydride reaction is very likely to have useful application to the others.

Historical

Although Berzelius reported the formation of a resin from tartaric acid and glycerol in the early days, it was not until 1901 that the reaction between glycerol and phthalic anhydride was reported by Watson Smith.[2] Between 1910 and 1915, M. J. Callahan[3] performed numerous experiments as a result of which new and useful resins were made which showed possibilities for commercial applications. At the same time, W. C. Arsem, E. S. Dawson, Jr., and K. B. Howell[4] studied the general reaction, substituting other alcohols and acids for glycerol and phthalic anhydride,

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[1] Downs and Weisberg, U. S. Patent 1,667,197.

[2] Watson Smith, *J. Soc. Chem. Ind.*, 20, 1075 (1901).

[3] M. J. Callahan, unpublished data and such patents as U. S. Patents 1,108,329 and 1,108,330.

[4] W. C. Arsem, E. S. Dawson, Jr. and K. B. Howell, unpublished data and such patents as U. S. Patents 1,098,777; 1,119,592; 1,098,728; and 1,141,944.

and also the effect produced when other ingredients are added. Since 1924 the authors have been performing quantitative experiments which are probably yielding the first kinetic data on the poly-ester reaction.

Materials

Pure phthalic anhydride was obtained by melting c. p. phthalic anhydride (Selden Co.) in an electrically heated glass container over which a current of dry air was passed which conducted the vapors into a cooled bulb, where dusty cobwebs of pure phthalic anhydride were deposited. The final product had a melting point of 131.8°.

The best water-white glycerol available had a density of 1.2561 by pycnometer measurement, which corresponds to a purity of about 97.7% according to the tables of Bosart and Snoddy.[5] This glycerol was vacuum-distilled in air-tight glass apparatus. Wherever a rubber stopper was used it was isolated from the vapors by thick tin foil, so that no distillate could escape from the rubber into the vapors of the glycerol. Anhydrous sodium sulfate was placed in the distilling flask together with some glass beads to prevent bumping. Hydrogen was passed through a capillary jet which served both to prevent oxidation and minimize bumping. Only the distillate between 160 and 200° was used and redistilled. The final product had a d_{25}^{25} of 1.2598, corresponding to a purity of 99.2% according to Bosart and Snoddy.

Experimental

I. Study of the Products of the Reaction.—If the reaction involves no other mechanism than that of simple esterification, there should be no other products than esters and water. In watching the reaction, however, the most readily noticed phenomenon is the evolution of a white sublimate, shown to be phthalic anhydride, which results from the fact that the reaction takes place at a temperature where the vapor pressure of the anhydride is high. Because of the low apparent density of the sublimed phthalic anhydride, it appears that considerable quantities are evolved, but there actually is relatively very little by weight.

The apparatus which was used to study the products of formation is shown in Fig. 1. The Erlenmeyer flask, heated by a Bunsen burner, contained the reaction mixture and was connected to three traps A, B and C, which were to collect solid, liquid and gas, respectively.

Trap A consisted of a tared flask, Trap B a tared flask connected to a water-cooled condenser and Trap C, a tared flask submerged in liquid air. The circulation of the vapors from the reaction mixture was insured by introducing dry air free from carbon dioxide through a calibrated flowmeter (about 2 bubbles per second) into the reaction flask. As a precaution to prevent the collection of material in the glass tube between the reaction flask and Trap A, a small heating unit of nichrome wire was wound around it.

The reaction mixture, consisting of 46 g. of glycerol and 111 g. of phthalic anhydride, was gradually warmed up to 210° in two hours and twenty-two minutes. After cooling the reaction flask, Trap A was found to contain 7.0 g. of material, most of which was a colorless liquid, water, together with white crystals. On opening the flask a sharp odor also was noticed. The contents of the flask was titrated with $N/25$ potassium hydroxide solution, using phenolphthalein as an indicator. There was found the equivalent of 0.085 g. of phthalic anhydride.

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[5] Bosart and Snoddy, *Ind. Eng. Chem.*, **19**, 506–510 (1927).

Any increase in weight of Trap B was found to be less than the order of the accuracy of the experiment. Trap C contained approximately 0.5 g. of white crystalline solid which melted at 0° to a clear white liquid, probably water although the sharp odor was noticed in this flask also. The water gave no aldehyde test (rosaniline) until near gelation. The reaction mixture itself gave no aldehyde test until gelation.

This, together with the fact that acrolein and phthalic anhydride do not form a resin, makes very doubtful the suggestion of Barry, Drummond and Morell,[6] that intermediate aldehyde formation is the mechanism for the building up of these resins from the polyhydric alcohol–polybasic acid reaction.

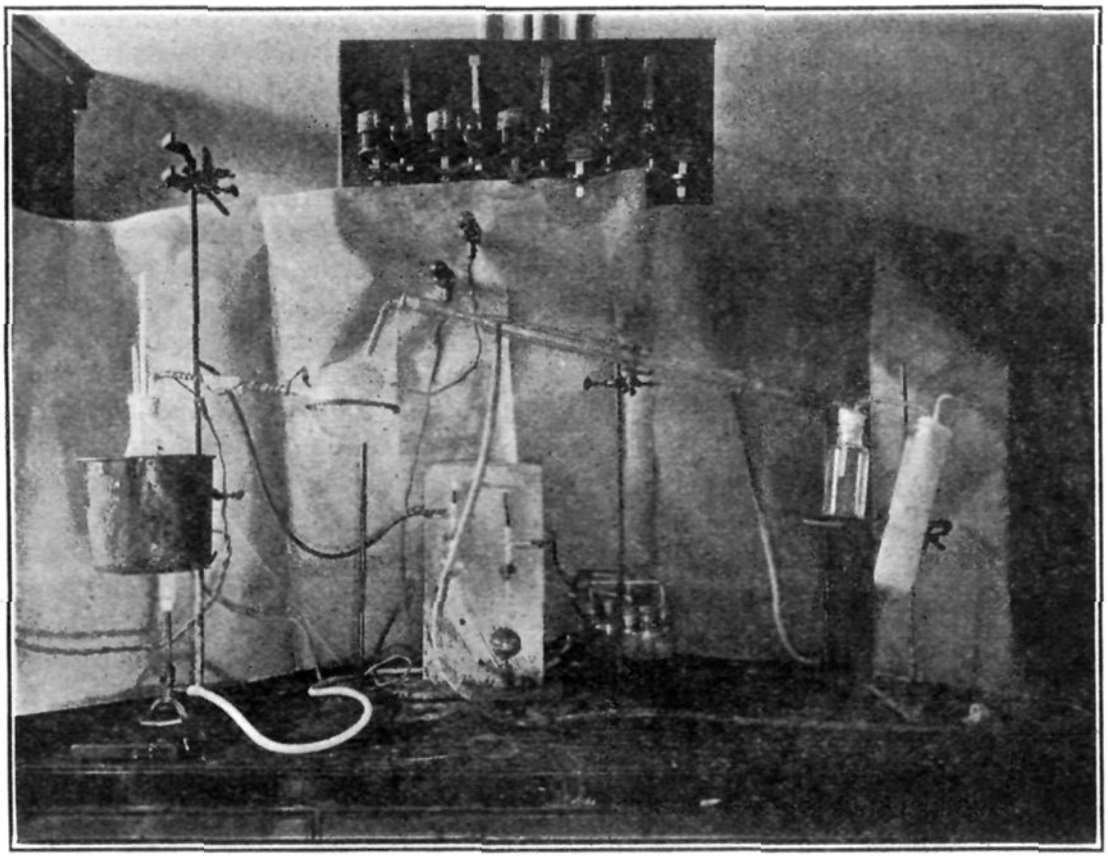

Fig. 1.

II. Kinetic Isothermal Studies of the Reaction with Time.—It would be extremely gratifying to be able to determine from time to time during the reaction the exact concentration not only of the phthalic anhydride and glycerol but also of the products, water and resin, as well. With such data the reaction velocities could be studied, and with the constants known it might be possible by comparison with data on the heat of reaction and specific heats to obtain free energy relationships for this unusual

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[6] Barry, Drummond and Morell, "Natural and Synthetic Resins," D. Van Nostrand Co., New York, p. 164.

type of reaction. However, none of the standard methods for determination of glycerol or free hydroxyl groups has proved satisfactory. The determination of water content is tedious and uncertain; hence the reaction has been followed from the standpoint of free and combined acid.

Preparation of Samples.—The reaction has been followed by allowing it to proceed at atmospheric pressure, keeping it as nearly isothermal as possible, and by taking out samples from time to time. The theoretical proportion of glycerol, 184.2 g., was weighed out into the reaction vessel and warmed up to the temperature at which the reaction was to be carried out. At the same time phthalic anhydride was melted in an Erlenmeyer flask and raised slightly above the temperature at which the reaction was to take place, to allow for cooling when pouring. When it was desired to start the reaction, the molten phthalic anhydride was poured into the reaction vessel on the balance pan until the theoretical proportion, 444.2 g., was weighed out. The most accurate method of taking the time of the start of the reaction was when one-half of the molten anhydride had been poured in. As soon as the molten phthalic anhydride was added and stirred in, the temperature of the reaction mixture rose very rapidly above the point at which it was desired to run the reaction. Because the reaction was strongly exothermic at the start, it was necessary to cool as quickly as possible with a jet of compressed air, and the reaction vessel was not placed in the insulated oil-bath until the temperature was approximately that of the oil-bath. From then on it was necessary to supply heat to the reaction mixture in order to maintain isothermal conditions.

Samples were taken from time to time by pipetting out a small amount of the fluid into numbered containers; these were allowed to cool rapidly, thus freezing the equilibrium at that point. Samples were taken more frequently in the earlier stages of the reaction than in the latter stages, because the reaction was proceeding so much more rapidly.

The viscosity of the liquid reaction mixture kept increasing until suddenly the mass stiffened and became an irreversible gel. It was much more difficult to take samples after gelation. A heat of gelation might be expected, but no appreciable increase in temperature was noticed. A few samples were taken after the transition and some were left in an oven at 200° to react for a time, infinite in comparison, so that a final equilibrium value could be reached.

(a) **Free Acidity.**—The decrease in free acidity was determined and is reported both as percentage of free acidity, calculated as phthalic anhydride, and as acid value (acid number). The tared samples of about 1 g. each were dissolved in 25 cc. of C. P. acetone which had a low acidity "blank" and then titrated with standardized 0.1 *N* potassium hydroxide solution, using phenolphthalein as an indicator.

Table I shows the data obtained on the decrease of free acidity as the reaction proceeded. While this is as was expected, it is perhaps surprising to note that in every case the free acidity was reduced to approximately one-half within one minute after the start of the reaction. For the first instant the reaction is strongly exothermic. The temperature of the reaction mixture rapidly rises from 15 to 44° above the temperature of the substances when they were poured together. The data indicate that the reaction is about half way through at the end of the first minute, after which it proceeds at a greatly diminished rate until gelation occurs.

In Fig. 2 is plotted the decrease in free acidity with time. It is useful to report the acidity both as acid number and as percentage of free phthalic

TABLE I

ISOTHERMS OF FREE ACIDITY CHANGE WITH TIME

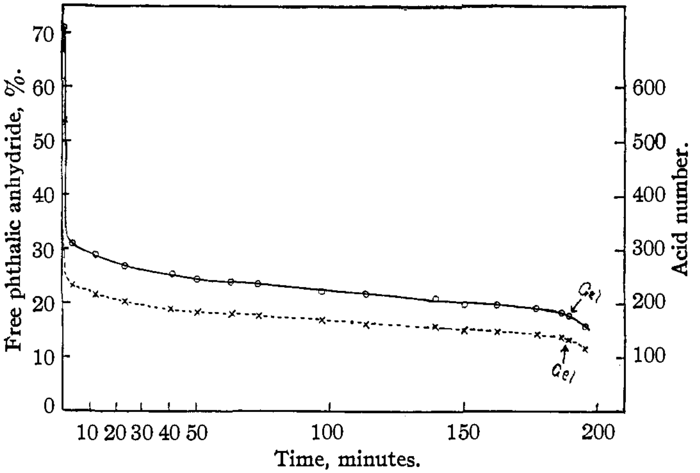
Time, sec.	Time, min.	Free anhydride, %	Acid number	Time, sec.	Time, min.	Free anhydride, %	Acid number
	T = 195°				T = 215°		
0	0	70.67	535	0	0	70.67	535
215	3.58	31.05	235	45	0.75	34.96	264
720	12.16	28.99	218	150	2.50	32.52	246
1,320	23.0	27.02	212	320	5.33	30.46	231
2,440	40.67	25.25	191	575	9.58	27.67	210
3,420	50.0	24.51	185	1510	25.20	26.52	201
3,980	63.0	23.96	181	2175	36.25	24.55	186
4,380	73.0	23.42	177	2855	47.58	22.87	173
5,790	96.5	22.23	169	3855	64.25	20.28	154
6,780	113.0	21.47	163	5430	90.50	17.12	130
8,340	139.0	21.02	159	5520	92.00	15.60	118
9,000	150.0	19.93	151	5640$^+$	98.00	13.93	105
9,720	162.0	19.84	149	∞	∞	0.29	2.2
10,610	177.0	19.18	145		T = 230°		
11,150	186.0	18.31	139	0	0	70.67	535
11,340$^+$	189.0	17.94	136	15	0.25	40.85	318
11,700	195.0	15.81	119	190	3.20	37.98	288
	T = 200°			465	7.75	36.49	276
0	0	70.67	535	700	11.66	33.52	254
20	0.33	36.43	276	1625	27.08	27.24	206
60	1.00	33.86	256	2265	37.75	26.23	198
330	5.50	29.76	226	2505$^+$	41.55	16.87	127
630	10.50	28.25	214	2650	44.20	13.34	101
960	16.00	27.30	207	3465	57.75	11.86	90
1,455	24.25	25.55	194	∞	∞	1.32	10
1,935	32.25	24.26	184		T = 232°		
2,670	44.50	23.62	179	0	0	70.67	535
3,600	60.0	20.22	153	120	2.0	36.42	276
4,830	80.5	20.09	152	300	5.0	31.57	239
6,300	105.0	18.42	139	540	9.0	31.13	236
7,540	125.7	16.74	127	1050	17.5	27.89	211
9,060	151.0	16.25	123	1560	26.0	27.32	206
9,240$^+$	156.0	15.87	120	1860	31.0	24.63	187
9,720	162.0	13.71	108	2160	36.0	17.57	133
10,200	170.0	8.44	64	2220$^+$	37.0	15.72	109
140,400	2360.0	0.57	4.4				

$^+$ Indicates point where gelation took place.

anhydride. The curve illustrates clearly the sudden drop in free acid at the start of the reaction and the subsequent slow continuous change right up to gelation.

(b) **Saponification Number.**—If the resinous product is an ester, it should be saponifiable just as the less complex esters are. The saponification number should remain fairly constant unless affected by change in density of the resin or by volatilization of some free phthalic anhydride.

For the determination, 1-g. samples were refluxed in Erlenmeyer flasks for one hour with 50 cc. of N alcoholic potassium hydroxide solution. Upon cooling titration was made with 0.5 N hydrochloric acid until the pink color of phenolphthalein disappeared; 0.5 N potassium hydroxide solution then was run in until the pink color reappeared.



———, Free phthalic anhydride; - - - -, acid number.

Fig. 2.—Decrease of free acidity with time. T = 195°.

Fig. 3 shows how the saponification value remains fairly constant with time in contrast to the steady decrease in acid number.

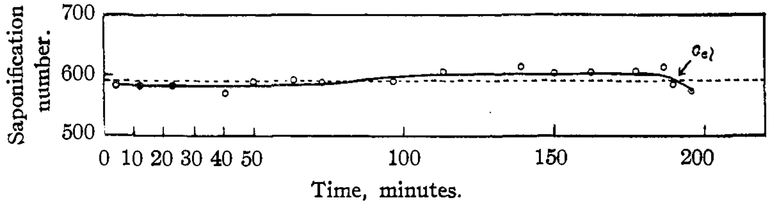


Fig. 3.—Variation of saponification number with time. T = 195°.

(c) **Degree of Esterification.**—The saponification number is useful in that it may be used to calculate the degree or percentage of esterification. When the acid number is subtracted from the saponification number, the resulting value is known as ester number or ester value, which represents the number of milligrams of potassium hydroxide equivalent to the acid which is combined in the ester.

$$\text{Ester number} = \text{saponification number} - \text{acid number}$$

$$\text{Percentage esterification} = \frac{\text{ester number}}{\text{saponification number}} \times 100 = \frac{(\text{saponification number} - \text{acid number})}{\text{saponification number}} \times 100$$

Fig. 4 shows how the percentage of esterification consistently increases with time. Analytical data show that various batches of glycerol–phthalic anhydride resin in manufacture have an esterification of 75–79% just before gelation.

(d) **Variation of Other Properties with Time: 1. Flow Point.**—The change in flow point[7] with time was one of the earliest studies made in following the formation of the resinous condensate. The flow point[7] is that temperature at which a small sample of resin (0.50″ thick) will flow under gravity a vertical distance of 0.20″ when subjected to a gradual increase in temperature of 2–3° per minute. This value is correspondingly lower than the melting point but is more useful and may be more sharply determined. As the reaction proceeds, the flow point gradually increases until it reaches 115–118°, when gelation occurs. After gelation the resin flows only when pressure is applied. Fig. 5 shows the curve of increase of flow point with time.

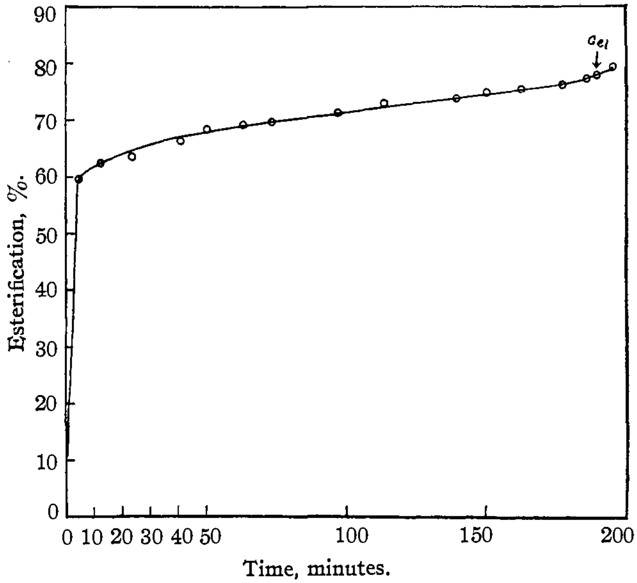


Fig. 4.—Increase of esterification with time. $T = 195°$.

2. **Viscosity.**—The viscosity of the liquid reaction mixture, which probably influences the flow point, has not been followed quantitatively. It is obvious that the viscosity is quite low at the start of the reaction, then gradually increases until at gelation it approaches an infinite value.

3. **Density.**—The density at 15.5/15.5°, as determined by a pycnometer with mineral oil for an insoluble liquid, was found to increase in the early stages of the reaction.

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[7] General Electric Standard Test No. 24.

4. **Color.**—The color changes but slightly in going from a water white liquid to a very pale straw color at gelation.

5. **Refractive Index.**—By comparing the powdered resin with liquids of known refractive index, this value was found to change but slightly from 1.56 in the early stages of the reaction to 1.58 just before gelation.

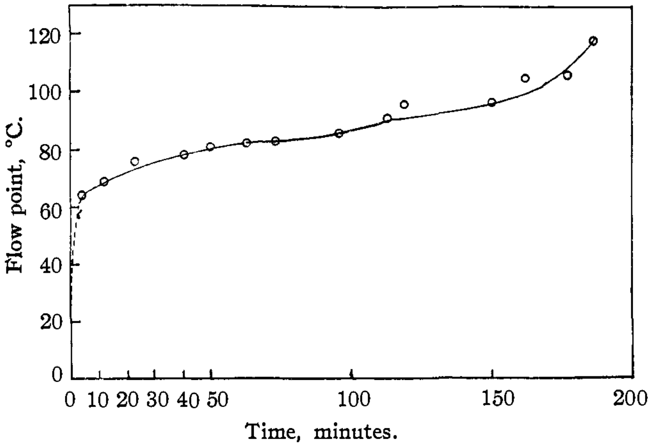


Fig. 5.—Increase of flow point with time. $T = 195°$.

Table II shows a comparison of the variation of the different properties of a set of standard samples taken from time to time, keeping the temperature at 195°.

TABLE II*a*

VARIATION OF PROPERTIES OF PRODUCTS WITH TIME AT 195°

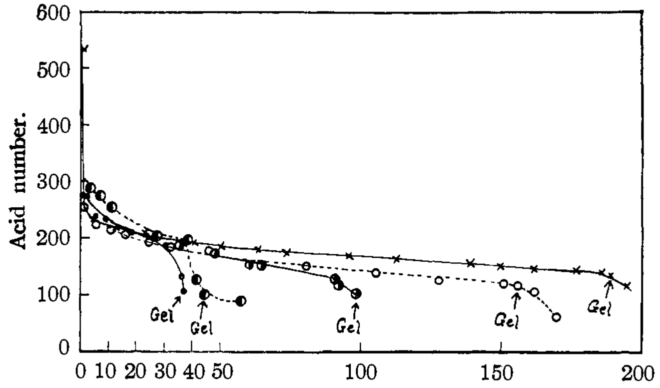
Time, sec.	Time, min.	Flow pt., °C.	Refr. index	Acid number	Sapon. number	Ester value	Ester, %
0	0	...	..	(535)	...	0	0.0
215	3.58	64	..	235	584	349	59.8
720	12.16	69	..	218	582	364	62.5
1380	23.0	76	1.56	212	583	371	63.6
2440	40.67	78	..	191	570	379	66.5
3420	50.0	81	..	185	589	404	68.5
3980	63.0	82.5	..	181	591	410	69.4
4380	73.0	83	..	177	588	411	69.9
5740	96.5	86	..	169	589	420	71.4
6780	113.0	91	..	163	605	442	73.0
8340	139.0	96	..	159	611	452	73.8
9000	150.0	96	..	151	604	453	75.0
9720	162.0	105	..	149	605	456	75.5
10610	177.0	106	..	145	608	463	76.1
11150	186.0	118	1.58	139	614	475	77.3
11340	189.0	Gel	..	136	585	449	77.8
11700	195.0	Gel	..	119	574	455	79.3

TABLE II*b*

VARIATION OF PROPERTIES OF PRODUCTS WITH TIME AT 195°

Time sec.	$d^{15.5°}_{15.5°}$	Hot-plate cure of film at 275°, sec.	Color and consistency	Free phthalic anhydride, %
0	....	...	Mixture of molten components	70.67
215	....	282	Light color, sticky sirup	31.05
720	1.3323	233	Light, sticky balsam	28.99
1380	1.3644	212	Gummy and harder	27.02
2440	1.3687	183	......	25.25
3420	1.4232	163	Reaction mixture viscosity incr.	24.51
3980	....	141	Resin slightly darker	23.96
4380	....	113	Resin harder	23.42
5740	....	98	......	22.23
6780	....	82	......	21.47
8340	....	68	More brittle, less adhesive	21.02
9000	....	47	Water resistance increasing	19.93
9720	....	38	......	19.84
10610	....	28	Mixture still liquid (195°)	19.18
11150	....	16	Beginning to gel	18.31
11340	....	...	Real heat irreversible gel	17.94
11700	....	...	Leathery when hot, flows only with pressure	15.81

III. **Effect of Temperature.**—It is interesting to compare the isothermal curves by plotting the free acidity *vs.* time, Fig. 6. All of the curves are much the same for the early part of the reaction, but the isotherms obtained when the reaction was carried out at higher temperatures require shorter paths to reach gelation. This suggests a relationship between time of gelation and the temperature.



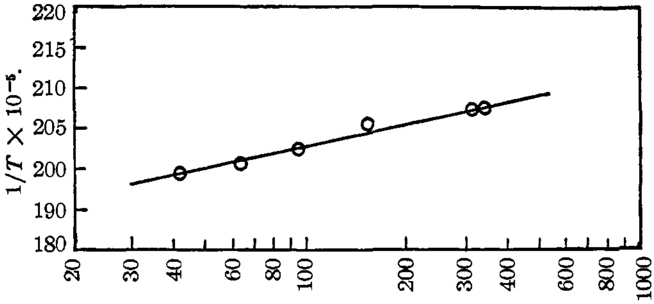
●, 232°; ◐, 230°; ◑, 215°; ○, 200°; ×, 195°.

Fig. 6.—Isotherms of free acid *vs.* time, showing effect of temperature.

Fig. 7 shows that when gelation time is plotted against the reciprocal of the absolute temperature, the result is a straight line.

Discussion

The data indicate that as the glycerol–phthalic anhydride reaction proceeds, the changes in the various properties are gradual and continuous. This makes it rather doubtful whether the reaction takes place in certain steps, such as the formation first of a monoglyceride, then a diglyceride and finally a triglyceride. It is more likely that a heterogeneous complexity of esters results, and finally the formation of more complex structures.



Gel time, minutes.

Fig. 7.—Gel time *vs.* reciprocal of absolute temperature.

Increase in temperature promotes the rapidity of this reaction, as in the case of the simpler esters. Regardless of the temperature at which this reaction is carried out, it does not seem possible to carry this reaction to completion, since gelation (with obstruction to mobility) invariably occurs between 75–79% esterification.

In the study of this resin-producing reaction, no evidence was found to indicate that anything but simple esterification occurred. This fact, together with the others just mentioned, must be taken into account in any theory of resinification, which is a problem that the authors hope in the near future to discuss in detail.

Summary

1. The glycerol–phthalic anhydride reaction proceeds by esterification, since water was the only product collected. No intermediate aldehyde was detected until near gelation.

2. The reaction went very rapidly at the start, evolving heat, and was apparently about one-half complete within one minute.

3. As the reaction proceeded under isothermal conditions, the free acidity decreased, the saponification number remained fairly constant and the percentage of esterification increased. The changes in other properties with time were noted.

4. Similar resinous products result if other polyhydric alcohols are substituted for glycerol, or if other polybasic acids are substituted for phthalic anhydride.

5. At whatever temperature the glycerol–phthalic anhydride reaction is carried out, gelation occurs before the esterification has an opportunity to complete itself.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

STRUCTURE OF BETA-GLUCOCHLORALOSE[1]

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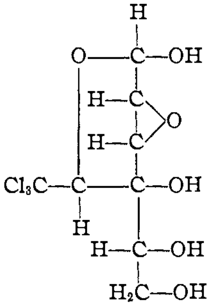
Two crystalline chloral derivatives of glucose were reported by Heffter[2] in 1889 but were not named. More detailed studies of the chloral derivatives of the various carbohydrates have been made by Hanriot[3] and his associates, by Meunier,[4] by Petit and Polonowski,[5] and by Pictet and Reichel.[6] The most recent formula for the β-glucochloralose is that of Pictet and Reichel (Formula III). Most of the standard handbooks give the older formula of Hanriot (Formula I) or of Polonowski (Formula II).

The evidence regarding the structure of β-glucochloralose is conflicting. The absence of reducing properties, the failure to combine with hydroxylamine and phenylhydrazine and the resistance of the compound to hydrogenation all indicate that the free aldehyde groups of both the glucose and the chloral have been modified in their union. The formation of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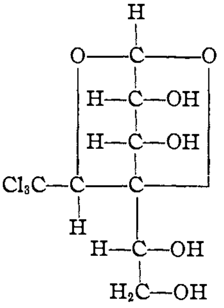
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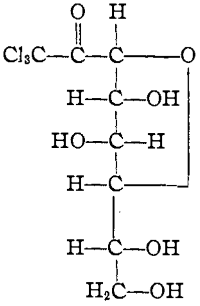
III

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[1] This compound is also called "Parachloralose."

[2] Heffter, *Ber.*, **22**, 1050 (1889).

[3] Hanriot and Richet, *Compt. rend.*, **116**, 63 (1892); **117**, 734 (1893); **122**, 1127 (1896); *Bull. soc. chim.* [3], **9**, 947 (1893); [3], **11**, 37, 258, 303 (1894); Hanriot, *Ann. chim. phys.*, **18**, 466 (1909); Hanriot and Kling, *Compt. rend.*, **152**, 1398, 1596 (1911); **156**, 1380 (1913).

[4] Meunier, *Ann. chim. phys.*, [6] **22**, 413 (1906).

[5] Petit and Polonowski, *Bull. soc. chim.*, [3] **11**, 125 (1894).

[6] Pictet and Reichel, *Helv. Chim. Acta*, **6**, 621 (1923).