measurement of the electron-diffraction photographs.

Summary

The In–C distance in indium trimethyl is found by the electron diffraction method to be 2.16 ± 0.04 Å.

PASADENA, CALIFORNIA
ITHACA, N. Y.

RECEIVED OCTOBER 3, 1940

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

The Polyhydric Alcohol–Polybasic Acid Reaction. VI. The Glyceryl Adipate and Glyceryl Sebacate Polyesters

BY R. H. KIENLE AND F. E. PETKE

No quantitative data appear to have been published for the glyceryl adipate and the glyceryl sebacate polymerization reactions. In the present investigation, data are presented for the formation of these polyesters from glycerol and their respective acids. In addition, when considered jointly with the work published on glyceryl succinate,[1] the effect on the polyester formation reaction resulting from the increase in chain length of the dibasic acid is shown.

The apparatus and the technique used have been described previously.[2] The glycerol used was the same as that employed in all our recent polyester investigations. The adipic acid employed was chemically pure acid (du Pont) which was redistilled under 15 mm. presure, the fraction distilling between 222–224° being taken. The sebacic acid was Eastman Kodak Company purified product. Both polyester reactions were studied at 190°. This temperature was chosen in order that the data might be comparable with the previously published glyceryl succinate (acid) and glyceryl phthalate (acid) investigations.[3]

Experimental Data

The actual data obtained for the glycerol–adipic acid and glycerol–sebacic acid reactions are given in Figs. 1 and 2.

Figure 3 shows the acid value–water evolved relationship for both reactions. When the experimental curves for each polyester are compared with the theoretical curves, which assume that only interesterification occurs, it is found that the water evolved is at all times less than the theoretical. The deviation, however, is greater in the early portion of the reactions than near and at gelation. The acid value–water evolved relationships do not indicate anhydride formation as was found in the case of glyceryl phthalate. There is a suggestion that part of the water formed, especially in the early part of the reaction, is retained by the polyesters.

The log acid value–log time curves for the reactions are similar in shape to the corresponding plots for glyceryl phthalate (acid) and glyceryl succinate (acid). Changes of slope are observed in the curves around 50% esterification and at a degree of esterification corresponding to the formation of the monomer.

Analytical Data

Both of these polyesters were soft, stringy, flexible, very light colored resins. In the early stages they were balsam-like in character. At gelation both were rubbery. Large samples of each polyester very close to gelation were prepared and further examined in detail. The analytical data obtained on these samples are given in Table I.

TABLE I

		Glyceryl adipate	Glyceryl sebacate
Acid value		159.3	118.2
Saponification value		616.1	517.3
% esterification		74.0	77.1
Av. molecular weight		1260	1450
Ultimate analysis	C, %	52.6	60.3
	H, %	6.7	8.6

The infrared spectra from 1–15 μ for these resins have been measured[4] and are plotted in Fig. 4. The spectra show the necessary linkages for polyester formation. In addition, bands are observed around 14 μ which correspond to similar bands found in the free acids from which the polyesters were prepared. Bands such as these were missing in glyceryl succinate.

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[1] Kienle and Petke, THIS JOURNAL, **62**, 1053 (1940).

[2] Kienle, van der Meulen and Petke, *ibid.*, **61**, 2258 (1939).

[3] Kienle, van der Meulen and Petke, *ibid.*, **61**, 2268 (1939).

[4] Acknowledgment is made to Mr. R. R. Brattain for measuring these spectra.

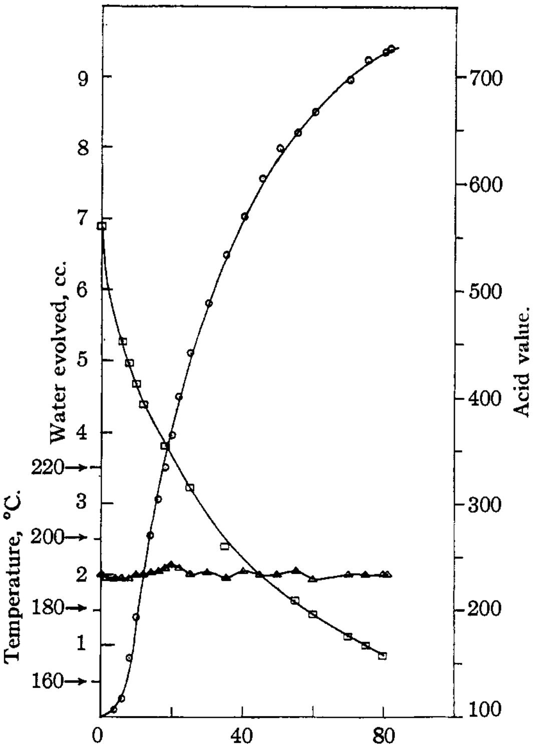

Fig. 1.—Reaction data for glyceryl adipate with proportions of glycerol 23.0 g., adipic acid 54.8 g.: △, temperature; ⊡, acid value; ⊙, water evolved.

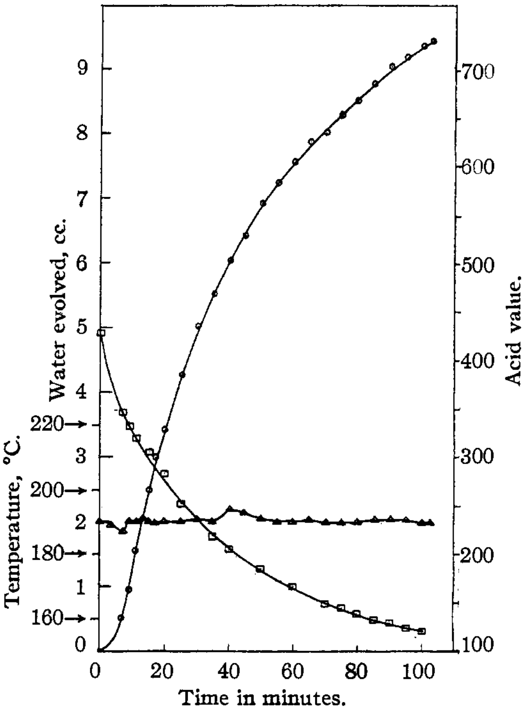

Fig. 2.—Reaction data in glyceryl sebacate; using proportions of glycerol 23.0 g., sebacic acid 75.8 g.: △, temperature; ⊡, acid value; ⊙, water evolved.

The spreading curves of both the glyceryl adipate and glyceryl sebacate polymerides were determined as monomolecular films on 0.001 N hydrochloric acid and are given in Fig. 5. The areas per average molecule, as given in Table III, were obtained from these curves by extrapolation.

In Table II, there have been summarized the sol–gel transition data for the various dibasic acid–glyceryl polyesters thus far investigated.

Discussion

As in the case of the previous dibasic acid–glyceryl polyesters, no initial temperature rise was observed and an appreciable time was required to reach 50% esterification. Also the acid values at which gelation occurred were between that calculated for a dimer and tetramer but nearer the former. Furthermore, the percentage esterifications reached at gelation were very close to the same values previously obtained for other (2,3) polyester systems.

In the case of glyceryl adipate the water evolved to attain gelation was, within experimental limits, the same as that required for glyceryl succinate (acid). This indicates that the same type and degree of reaction has apparently occurred in both systems. In the case of glyceryl sebacate the water evolved is slightly higher but still sufficiently close to indicate approximate equivalence of reactivity.

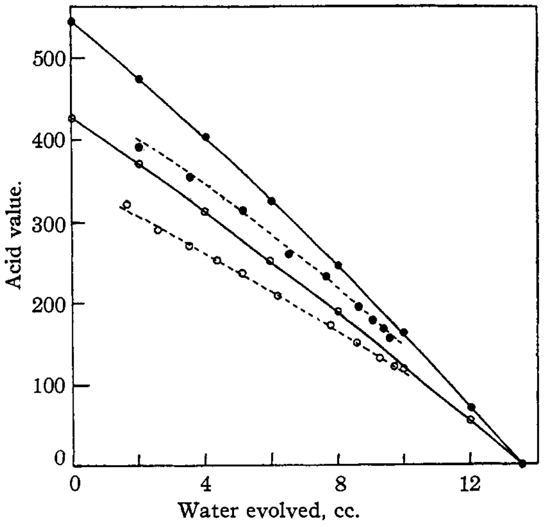

Fig. 3.—Acid value–water evolved relationship: ●, glyceryl adipate; ⊙, glyceryl sebacate; ----, experimental; ——, theory.

TABLE II

Glyceryl polymeride	Mol. resin	React. temp., °C.	Time to gel, min.	Water evolved, V_a	A. V. at gelation, (obsd.)	A. V. (Calcd.) Dimer	A. V. (Calcd.) Tetramer	% Esterification
Phthalate	1/8	190	160	10.80	120	139	117	78.6
Succinate	1/8	190	64	9.62	178	183	154	76.0
Adipate	1/8	190	83	9.64	152	155	130	75.5
Sebacate	1/8	190	107	9.78	115	119	99	77.7

Increasing the chain length between the carboxy groups of the interacting dibasic acid yields softer resins and changes the solubility characteristics of the polyester.[5] The increase in the time to reach gelation suggests that as the chain length is increased, it is more difficult for the reactive groups on the molecules to come in contact. The degree of molecular complexity necessary for gelation, however, seems to be but slightly affected although apparently, as indicated by the values of v (basicity) in Table III, the molecular complexity at gelation decreases as the chain length increases.

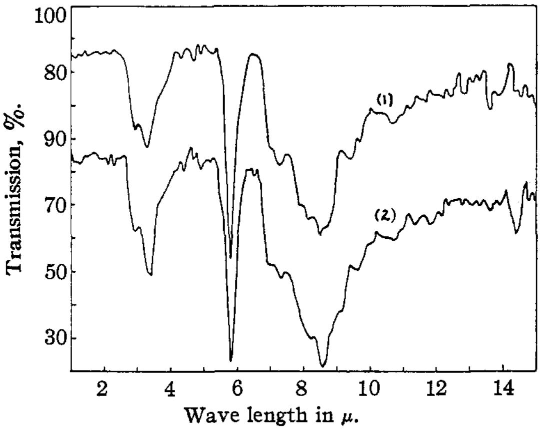

Fig. 4.—Infrared spectra: (1) glyceryl adipate, a. v. 159; (2) glyceryl sebacate, a. v. 118.

TABLE III

Glyceryl polymeride	No. C atoms between COOH groups of acid	Area per av. mol., sq. Å.	Av. mol. weight at gelation	v (basicity) at gelation[6]
Succinate	2	82	1075	3.40
Adipate	4	358	1260	3.38
Sebacate	8	477	1450	3.15

The data for glyceryl adipate and glyceryl sebacate support the viewpoint that in highly polyfunctional polymeric systems, gelation occurs when the average polymeric functionality exceeds 3.0, that is, when a sufficient molar concentration of tetramer or higher polymers has been formed to bring about a state of arrested motion. The data obtained for the average molecular weights and area per molecule just prior to gelation, after the increase in chain length of the interacting dibasic acid has been taken into account, are in accord with this concept.

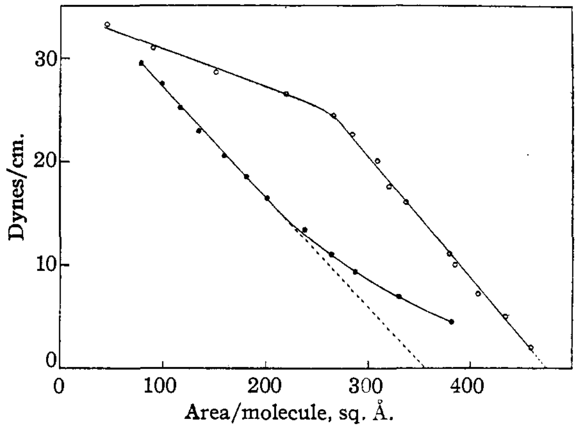

Fig. 5.—Monomolecular film data: T = 15–16°C.; 0.001 N HCl; ●, glyceryl adipate; ○, glyceryl sebacate.

The glyceryl adipate reaction appears to be entirely interesterification. There is no evidence in any of the data of anhydride formation or of intraesterification having occurred. In the case of glyceryl sebacate the reaction is apparently interesterification with possibly a slight amount of intraesterification also occurring.

Both glyceryl adipate and glyceryl sebacate, in contrast with glyceryl succinate, have present near gelation a small percentage of the first formed acid esters. The appearance of the bands around 14 μ in the infrared spectra investigation is in harmony with this suggestion. Still better evidence in support thereof is the microscopic examination of the polyesters after standing approximately six months. At the end of this period glyceryl phthalate, glyceryl maleate and glyceryl succinate were still perfectly clear transparent resins. The glyceryl adipate and glyceryl sebacate resins, however, had become cloudy. When these polymerides were examined microscopically as thin films the cloudiness was found to be due to very

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(5) Ellis, "The Chemistry of Synthetic Resins," Vol. II, Reinhold Pub. Corp., New York, N. Y.

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

fine crystals. These crystals were especially evident under polarized light. In glyceryl adipate they were small aggregates of needles; in glyceryl sebacate spheroid clusters.

Summary

1. The changes in acid number and water evolved as the glyceryl adipate (acid) reaction proceeds at 190° have been measured. No temperature increase was observed on initial mixing and an appreciable time was required to reach 50% esterification. The reaction appears to be only interesterification. Gelation occurs when approximately 30 mole per cent. of tetramer or higher polymer has been formed. There is evidence that, at gelation, a small amount of the initially formed acid esters is still present.

2. The glyceryl sebacate reaction has been studied at 190°. It apparently progresses like the glyceryl adipate reaction but there is some evidence that, in this case, a small amount of intraesterification as well as interesterification has occurred. Gelation takes place at a slightly lower degree of molecular complexity than in the case of glyceryl adipate. The initially formed acid esters indicated as present in glyceryl adipate at gelation also appear to be present in glyceryl sebacate.

3. Data comparing the effect of increasing the chain length in the polybasic acid portion of glyceryl polyester reactions are presented. As the chain length increases, the time to attain gelation increases, the average molecular weight and area per average molecule increases, the average basicity at gelation decreases, the molecular complexity at gelation decreases.

BOUND BROOK, NEW JERSEY

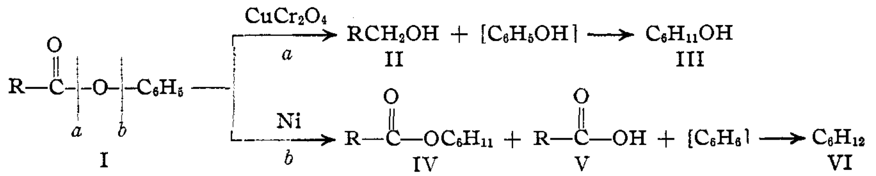
RECEIVED OCTOBER 16, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF PENNSYLVANIA]

The Hydrogenation of Aryl Esters[1]

BY WM. R. MCCLELLAN AND RALPH CONNOR

The formation of hexahydrochroman[2] by the hydrogenation of coumarin over Raney nickel suggested that the formation of ethers might be characteristic either of lactones or of aryl esters (I). Since the latter had apparently not been hydrogenated over either nickel or copper chromite, their behavior over each catalyst was investigated. The main reactions are shown in the flow diagram.



Over copper chromite the esters (I) of phenol gave results similar to those observed with esters of alcohols. The details are given in Table I. Without considering the specific mechanism, the net result was hydrogenolysis of the ester grouping with cleavage between oxygen and acyl (*a*), giving alcohols (II) and phenol. The latter was converted to cyclohexanol (III).[3,4] Hydrogenation of the lactone (VII) of *o*-hydroxyphenoxyacetic acid gave β-(*o*-hydroxyphenoxy)-ethyl alcohol (VIII) without any apparent attack of the aromatic ring over copper chromite. The formation of toluene from phenyl benzoate and of methanol and cyclohexanol from phenyl carbonate are the expected results of the continued hydrogenolysis and hydrogenation of the initial products.

The details of the results using Raney nickle as a catalyst are given in Table I. No ethers were isolated. Excepting the hydrogenations of phenyl carbonate, phenyl benzoate and the lactone of *o*-hydroxyphenoxyacetic acid (VII), two major competitive reactions were observed over Raney nickel. One of these was the hydrogenation of

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[1] This communication is constructed from a thesis submitted by Wm. R. McClellan in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania in June, 1940.

[2] De Benneville and Connor, THIS JOURNAL, **62**, 283 (1940).

[3] The presence of a phenolic group has been reported to labilize aromatic nuclei to hydrogenation over copper chromite.[4]

[4] Adkins, "Reactions of Hydrogen, etc.," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 61.