Urethane Foams from Animal Fats. II. Reaction of Propylene Oxide with Fatty Acids[1]

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Abstract

Propylene oxide has been reacted with 9,10-dihydroxystearic acid to form polyol components for urethane foams. The alkali-catalyzed reaction proceeds slowly until the first mole of propylene oxide is absorbed and thereafter at a higher rate. For other substrates, the initial reaction proceeds most readily with alcohols and decreases in speed with increasing acidity of the hydroxyl group.

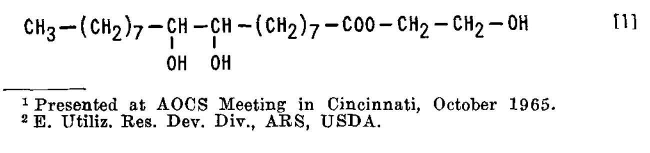
Threo- and *erythro*-9,10-dihydroxystearic acids were reacted with approximately 1, 2, 4, 6 and 8 moles of propylene oxide. Both series of the resulting polyols were liquid, unlike corresponding oxyethylated derivatives, which were solids in the *erythro* series. A small amount of unsaturation was observed in the reaction products in accord with previous studies. The liquid polyols can be used conveniently in the preparation of rigid urethane foams.

Introduction

The preparation of rigid urethane foams from derivatives of *threo-* and *erythro*-9,10-dihydroxystearic acid has been a subject of recent research in our laboratory. In previous work, ethylene oxide derivatives of these acids were used as polyol component in a two-step process of foam preparation (1). The oxyethylated *threo-* derivatives were found to be best suited for conversion to foams because they were liquids or soft pastes depending upon the degree of oxyethylation. On the other hand, the oxyethylated *erythro-* derivatives were waxy solids at room temperature, which led to mixing difficulties just prior to foaming. With all the polyols made by oxyethylation, foaming occurred almost too readily, because of the availability of many primary hydroxyl groups.

It was the purpose of the present investigation to prepare a series of polyols by reaction of 1, 2, 4, 6 and 8 moles of propylene oxide with *threo-* and *erythro*-9,10-dihydroxystearic acid. The resulting polyols were expected to be more fluid, to possess secondary hydroxyl groups predominantly, and therefore to react at lower, more convenient rates with an isocyanate-terminated prepolymer to form urethane foams with modified properties. In addition, it was planned to study and compare the rates of reaction of propylene oxide with various acidic substrates.

Previous evidence has indicated that initial oxyethylation of hydroxystearic acids occurs only at the carboxyl group (2). The acidity of the carboxyl function assures virtually complete conversion of the acid to ethylene glycol monoester before further oxyethylation occurs. Thus:



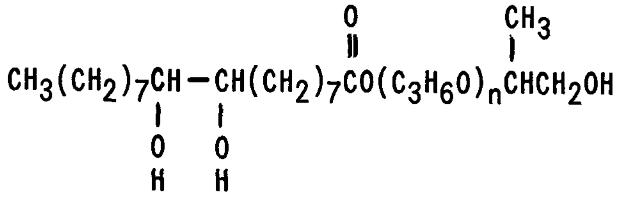
$$CH_3-(CH_2)_7-\underset{OH}{CH}-\underset{OH}{CH}-(CH_2)_7-COOH + \underset{\diagdown O \diagup}{CH_2-CH_2} \xrightarrow{OH^-}$$

$$CH_3-(CH_2)_7-\underset{OH}{CH}-\underset{OH}{CH}-(CH_2)_7-COO-CH_2-CH_2-OH \qquad [1]$$

With additional ethylene oxide, reaction presumably continues to a larger extent at the more acidic β-oxyethanol function and to a lesser degree at the vicinal secondary glycol functions, still disfavored by comparatively low acidities of the secondary hydroxyl groups.

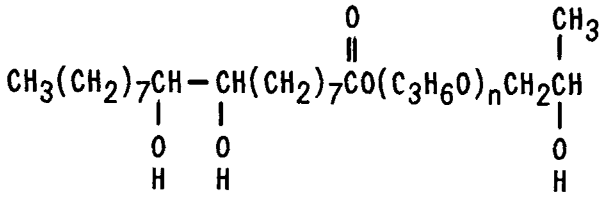
Oxyethylation of fatty acids is complicated by the formation of by-products such as polyethylene glycols and diesters, ascribed to transesterification reactions (3). This was confirmed most recently by Stockburger and Brandner, who investigated the products formed on oxyethylation of oleic acid (4). They observed that after approximately one mole of ethylene oxide had been added the reaction accelerated and transesterification occurred readily.

It was anticipated that the dihydroxystearic acids and propylene oxide would lead to products analogous to those obtained with simpler compounds (5). Dihydroxystearic acid would thus form polyols I and II, with II predominating:



$$CH_3(CH_2)_7\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_7\overset{O}{\overset{\|}{C}}O(C_3H_6O)_n\overset{CH_3}{CH}CH_2OH$$

I



$$CH_3(CH_2)_7\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_7\overset{O}{\overset{\|}{C}}O(C_3H_6O)_nCH_2\underset{OH}{\overset{CH_3}{CH}}$$

II

In addition to these triols, the diester tetrols and free mono- or polypropylene glycols formed by transesterification are also reactive toward isocyanate-terminated prepolymers.

Experimental

Starting Materials

Threo- and *erythro*-9,10-dihydroxystearic acid were prepared from oleic acid using conventional procedures (6,7). Oleic acid (99+ % purity) was obtained from Applied Science Laboratories. Stearic acid and remaining substrates were obtained from commercial sources and recrystallized several times before use. Propylene oxide was purchased from Eastman Organic Chemicals and used as received.

Preparative Oxypropylation of Dihydroxystearic Acids

Preparations were carried out by dropwise addition of propylene oxide to the dihydroxy acid and potassium hydroxide (4 mole percent) in a 3-necked flask equipped with a stirrer and reflux condenser and

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[1] Presented at AOCS Meeting in Cincinnati, October 1965.

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TABLE I

Propylene Oxide Polyols from *threo-* and *erythro*-9,10-Dihydroxystearic Acids

Dihydroxy acd	Moles P.O. added	Sap. value		% OH		Physical state, room temp
		Calc'd	Found	Calc'd	Found	
threo-	1.1	147.7	140.8	13.4	13.0	Semi-solid
	1.9	131.6	126.3	12.0	11.7	liquid
	3.5	108.0	101.8	9.82	10.8	liquid
	5.7	86.6	89.6	7.88	7.72	liquid
	7.8	73.5	70.6	6.61	7.37	liquid
erythro-	1.0	149.8	152.6	13.6	9.78	Semisolid
	1.9	131.6	135.7	12.0	9.21	liquid
	4.0	102.2	111.1	9.30	8.75	liquid
	6.0	84.4	91.9	7.67	7.04	liquid
	7.9	72.4	74.8	6.59	6.00	liquid

maintained at 140C. The reaction was followed by measuring the increase in weight of the tared flask. Addition of propylene oxide was continued until the desired amount was absorbed, whereupon the mixture was neutralized with concentrated hydrochloric acid and analyzed.

Rates of Oxyalkylation

In order to follow the rate of uptake of alkylene oxide, an apparatus designed earlier for oxyethylation was employed (8). As previously described, the temperature of the magnetically stirred (380 rpm) reaction mixture was brought to 180C and maintained there by a sensor and heat lamp. The pressure of ethylene or propylene oxide was kept at 7.5-lb gauge by alternate heating and cooling of the oxide reservoir as controlled by a pressure-sensitive switch. For use with propylene oxide, the vapor-carrying tubing was wrapped with heating tapes to prevent liquefaction of the epoxide. The progress of oxyalkylation was followed by the decreasing volume of liquid epoxide in the reservoir. The densities of ethylene and propylene oxide (at their boiling points at 7.5 psig) were taken as 0.860 g/cc (26C) and 0.775 g/cc (54C), respectively.

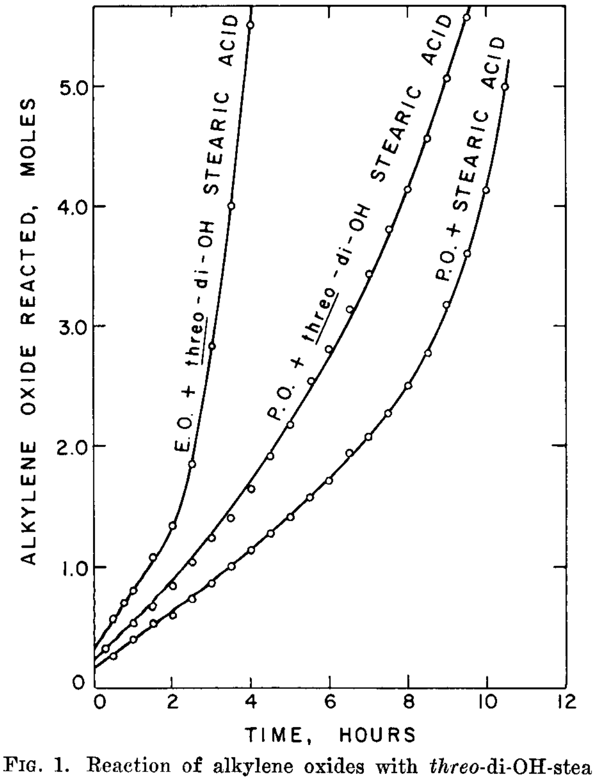

FIG. 1. Reaction of alkylene oxides with *threo*-di-OH-stearic acid and stearic acid.

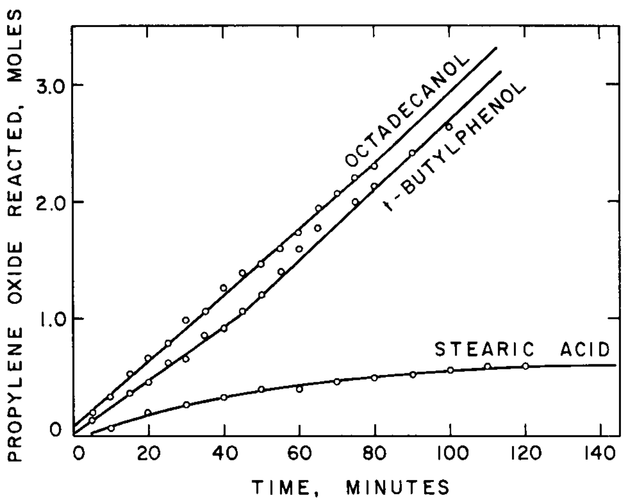

FIG. 2. Reaction of propylene oxide with OH-compounds.

Results and Discussion

In the preparative experiments it was observed that the polyols became more fluid as more propylene oxide was reacted. Although both monooxypropylated dihydroxystearic acids were pastes or soft solids at room temperature, all the other oxypropylates, whether of the *threo-* or *erythro-* acid, were liquids easily mixed with other foam ingredients. This was presumably due to lowering of symmetry by oxypropyl groups. A summary of analytical results is given in Table I.

Previous workers with propylene oxide have noted the existence of unsaturation in reaction products (9), and this was confirmed by us. However, in all the polyols prepared the iodine value was below 2.0. The polyols were suitable for use in urethane foam preparation, and a study of the physical properties of the derived foams has been carried out (10).

In the kinetic experiments, the reaction was found to begin rather slowly with acidic substrates such as stearic or *threo*-9,10-dihydroxystearic acid but increased in speed after the first mole of oxide was absorbed. The results obtained are given in Fig. 1. The change in slope as the reaction proceeded was more marked when ethylene oxide was used with the 9,10-dihydroxystearic acid, as illustrated in the same figure.

For comparison, oxypropylation was carried out under similar conditions using less acidic compounds,

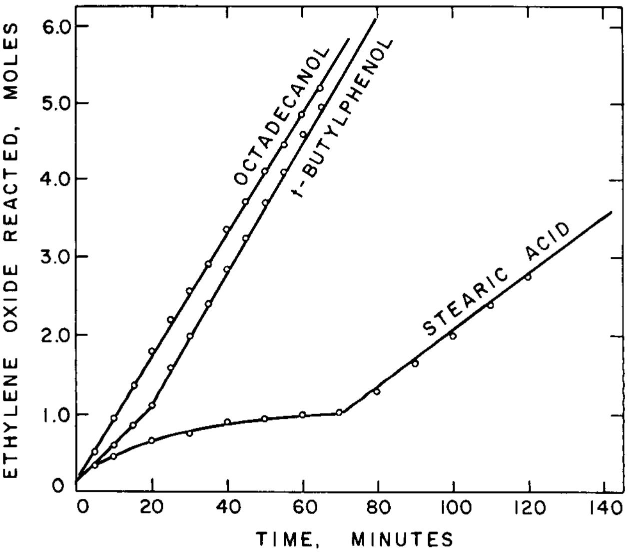

FIG. 3. Reaction of ethylene oxide with OH-compounds.

t-butylphenol and octadecanol, as substrates. With t-butylphenol, absorption of propylene oxide was appreciably faster than with the carboxylic acids mentioned above. Also, the rate of uptake increased after addition of the first mole of oxide. With octadecanol, absorption was even faster, with no change in rate as successive moles of alkylene oxide were added. A plot of the amount of propylene oxide versus the time required for absorption by several hydroxy compounds is given in Figure 2.

The early reaction rate was inversely related to the acidity of the substrates. Thus alcohols were more reactive than phenols, and the latter more reactive than carboxylic acids. Trichlorophenol reacted considerably slower than phenol itself. Since under basic catalysis the opening of epoxide rings involves nucleophilic attack on carbon, it is not surprising that the above sequence of reactivities is in harmony with the order of nucleophilicity $RO^- > PhO^- > RCOO^-$.

TABLE II

Reactivity of OH-Compounds with Ethylene and Propylene Oxide[a]

OH Substrate	Time for fixation of first mole of oxide, sec × 10^{-2}	
	Ethylene oxide	Propylene oxide
Octadecanol	6.6	19.5
t-Butylphenol	10.5	25.5
Stearic acid	36.0	126.0
threo-9,10-Dihydroxystearic acid	48.0	90.0

[a] Catalyzed by 0.04 mole KOH at 180C and 7.5 psig.

In an additional series of experiments, ethylene oxide was used with the substrates mentioned above. As shown in Fig. 3, although ethylene reacted more rapidly than propylene oxide, the sequence of substrate reactivities remained the same. A summary of the time required to fix the first mole of alkylene oxide with various acidic substrates is given in Table II.

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