Urethane Foams from Animal Fats: VII. Reaction of Epoxidized Tallow with Trimethylolpropane and TMP-HBr[1]

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ABSTRACT

Polyols of higher hydroxyl content than previously obtained from tallow were prepared for use in urethane foams. Epoxidized tallow was caused to react with trimethylolpropane with catalysis by p-toluenesulfonic acid (2%). Reaction at 120 C in toluene gave best results. Alcoholysis occurred both at oxirane and at glyceride linkages, the latter reaction conferring hydroxyl functionality even on nonepoxidized glyceride units. Hydroxyl content of polyol products increased with the functional ratio of the reaction mixture, that is, the molar ratio of OH available from trimethylolpropane to oxirane plus ester from tallow. To provide fire retardant polyols, epoxidized tallow was caused to react with trimethylolpropane and gaseous HBr, best at 80 C in benzene. Examined by thin layer chromatography, the polyols showed polarities in the range of mono- and diglycerides.

INTRODUCTION

Previous contributions from this laboratory have described the preparation of polyols, for use in rigid urethane foams, by hydration or hydrohalogenation of epoxidized fats and related glycerides (1-3). Significant fire retardance was obtained by introduction of halogen (2). In polyols based upon lard and tallow, fully saturated components, inert to epoxidation and subsequent hydroxylation, were found responsible for low compressive strength and high open-cell content.

One method of improving these properties was found to be the removal of unhydroxylated material from the polyols by solvent precipitation (3). Although this was effective, we also have sought other ways of accomplishing the same result. For economic reasons the emphasis was on use of tallow, which contains ca. 14% saturated triglycerides (4).

A way was sought to introduce hydroxyl groups by reactions attacking glyceride linkages at the same time as epoxide rings. The preparation of mixed mono- and diglycerides and other esters by alcoholysis of fats and oils with various triols or polyols has been described (5). It, therefore, seemed feasible to alcoholyze epoxidized tallow with polyhydric alcohols frequently used in urethane foam formulation. Under our experimental conditions, trimethylolpropane (TMP) gave products of higher hydroxyl content than either glycerol or pentaerythritol. Moreover, TMP afforded polyols which were liquid at room temperature; the others typically gave solid or semisolid products. TMP was, therefore, selected for the present study. Under appropriate conditions, alcoholysis was expected to occur at both oxirane and ester linkages. Each epoxy group should give rise, by reaction with TMP, to three hydroxyl groups. In addition, alcoholysis of glyceride linkages would confer hydroxyl functionality even on wholly saturated triglycerides, which might otherwise require removal. These reactions would give rise, therefore, to a mixture of products, including diglycerides, monoglycerides, fatty esters of TMP, and TMP-hydroxy-ethers of the foregoing. During the course of the present work, the preparation of polyols by alcoholysis of hydroxymethylated linseed oil with triols and tetrols was reported (6).

Alcoholysis of internal oxirane groups generally is regarded as proceeding faster under acid than basic conditions. Experiments showed this rule to hold for epoxidized tallow. Since a major objective was the full use of the oxirane content, an acid catalyst was used for the present work.

As in other studies from this laboratory, it also was planned to introduce bromine into the polyols for fire retardance. When hydrogen bromide is brought into reaction with epoxidized tallow in the presence of TMP, protonated oxirane groups would be opened in many cases by HBr to give hydroxybromides, in some cases by TMP, to give ether-linked triol groups. Alcoholysis of glyceride links would again give di- and monoglycerides and TMP esters as indicated above.

EXPERIMENTAL PROCEDURES

Materials

The materials listed below were used as received: tallow, fancy (Mutual-Shoemaker Co., Philadelphia, Pa.), iodine value 52.5; TMP (Celanese Corp., New York, N.Y.); p-toluenesulfonic acid, certified (Fisher Scientific Co., Pittsburg, Pa.); hydrogen bromide, gaseous (Air Products Co., Allentown, Pa).

Reaction of Epoxidized Tallow with TMP

Preliminary experiments: Preliminary experiments were performed in a 100 ml three necked flask fitted with reflux condenser, thermometer immersed in the reaction mixture, magnetic stirrer, and heating mantle. The flask was charged with 30 g epoxidized tallow (oxirane 2.9%, saponification no. 198.7, acid no. 2.7), prepared by a method described previously (7), 10 g TMP, 0.6 g paratoluenesulfonic acid (2% based on epoxidized tallow), and 30 ml benzene, toluene, or xylene. Stirred reaction mixtures were refluxed, the solvents providing reaction temperatures of ca. 90, 120,

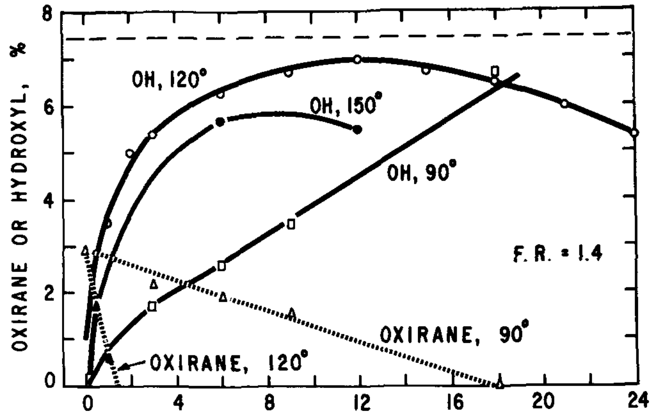

FIG. 1. Reaction of epoxidized tallow with trimethylolpropane at functional ratio 1.4. Effect of temperature upon hydroxyl (or oxirane) vs. time relation.

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TABLE I

Polyol Hydroxyl Content as Affected by Functional Ratio[a] and Time of Reaction[b], at 120 C

$\frac{OH^a}{Ox + E}$	Percent of hydroxyl 6 hr	Percent of hydroxyl 12 hr
1.4	6.3	6.6
2.1	7.5	7.7
4.2	9.3	9.5
6.6	10.1	10.3
8.4	10.3	10.5

[a] Functional ratio = moles OH/ (moles oxirane + ester).

[b] Epoxidized tallow, 6.0 g; toluene, 6 ml; trimethylolpropane as required by functional ratio; 0.12 g p-toluenesulfonic acid.

or 150 C, in this system. The epoxidized tallow used provided 5.4 x 10^{-2} moles oxirane and 10.5 x 10^{-2} moles ester; the TMP provided 22.4 x 10^{-2} moles hydroxyl. The functional ratio, or ratio of moles hydroxyl function provided by the TMP to moles oxirane, plus ester provided by the tallow, was, therefore, 1.4.

At intervals, 2.5 g samples were removed, the aromatic solutions washed with water, the dried solution evaporated to dryness, and the product analyzed for hydroxyl and oxirane. The results are plotted in Figure 1.

Another series of experiments was carried out at the reaction temperature of 120 C, but the functional ratio was varied (by varying the charge of TMP) from 1.4 to 2.1, 4.2, 6.6, and 8.4. Reactions were carried out as before, but on 6 g charges of epoxidized tallow in 6 ml toluene, with catalysis as before. Hydroxyl determinations were made after 6 and 12 hr, as recorded in Table I. A separate synthetic experiment was run for each point.

Preparative experiments: In a 300 ml flask equipped as before, 60 g epoxidized tallow (oxirane 3.0%, saponification no. 190.8, acid no. 2.06) was stirred at reflux in 60 ml toluene and selected amounts of TMP, catalyzed by 2% toluene-sulfonic acid, as summarized in Table II. Reaction time was 10 hr at 120 C. At the end of each reaction, the toluene solution was washed with water to neutrality, dried over $MgSO_4$, and the solvent removed by rotary evaporation. The water washings, after removal of catalyst by passage through an anion exchange column, were evaporated to dryness and weighed.

Reaction of Epoxidized Tallow with TMP-HBr

Reactions of this type were carried out essentially as described above for preparative reactions of epoxidized tallow with TMP. The flask was charged with 60 g epoxidized tallow and 92.7 g TMP for a functional ratio of 6.6. The mixture was stirred at reflux with 60 ml aromatic solvent. The acid catalysis was provided by gaseous hydrogen bromide, which was bubbled slowly through the reaction mixture.

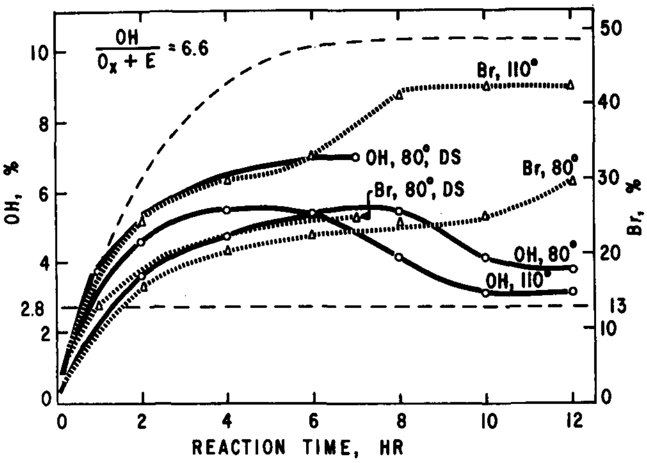

FIG. 2. Epoxidized tallow reaction wiht trimethylolpropane HBr at function ratio 6.6. Hydroxyl and bromine content vs. reaction time at 80 and 110 C. DS: With use of Dean-Stark tube.

Under these conditions, the solvent benzene gave a reaction temperature of 80 C, and toluene 110 C. In one experiment, water generated was removed continuously by a Dean-Stark tube. As indicated in Figure 2, hydroxyl and bromine content of product polyols was measured as a function of time. At 80 C oxirane disappeared in less than 1 hr. Preparative results, recorded in Table III, were based upon the products after 12 hr or, in one case, 7 hr of reaction.

RESULTS AND DISCUSSION

At the single functional ratio of 1.4, the effect of time and temperature upon the reaction between epoxidized tallow and TMP is shown by Figure 1. At a reaction temperature of 90 C, oxirane disappeared in 18 hr, while hydroxyl content rose to 6.5%. At 120 C oxirane was exhausted in 1.5 hr, whereas hydroxyl content reached ca. 7% in 12 hr and then declined with further heating. The temperature of 150 C resulted in a lower maximum OH than 120 C. The 120 C reaction attained, in a reasonable time, an OH level close to that to be expected (horizontal dashed line), if each oxirane group were opened by TMP and no functionality were lost through side reactions. Consequently, for further exploration, this temperature was chosen. The fact that at 120 C the oxirane was consumed in 1 1/2-hr, whereas the hydroxyl content continued to mount for ca. 12 hr, indicated that an important part of the OH introduced came from alcoholysis of glyceride function. The final decline in hydroxyl suggests some ether or

TABLE II

Polyols Made by Reaction of Epoxidized Tallow with TMP[a]

No.	$\frac{OH^b}{Ox + E}$	TMP, g recovered[c]	TMP, g reacted	Wt increase, %	Hydroxyl %	Hydroxyl no.
TA 1	1.4	4.3	15.4	21	6.6	218
TA 2	2.1	10.7	18.9	28	7.8	257
TA 3	4.6	34.0	25.1	34	9.5	314
TA 4	6.6	63.6	29.1	44	10.3	340
Control	Hydrated epoxidized tallow[d]				4.3	142

[a] In 60 ml toluene, 60 g epoxidized tallow (oxirane 3.0%, ester no. 188.77), 2% p-toluenesulfonic acid (TA), trimethylolpropane (TMP) the sum of columns 3 and 4, 10 hr at 120 C.

[b] Moles OH/ (moles oxirane + ester).

[c] Containing some glycerol.

[d] Unpublished results of this laboratory.

olefin formation with loss of water.

Effect of Functional Ratio

Increased ratios of hydroxyl (provided by TMP) to the sum of oxirane and ester functions (provided by the epoxidized tallow) resulted in higher hydroxyl content in the polyol products. This is shown in Table I, in which hydroxyl content, after 6 and 12 hr reaction, is recorded for five functional ratios. Three increases in ratio caused substantial rise in hydroxyl content, but a final increase from 6.6 to 8.4 generated only a small further rise in OH. For this reason, further work at the functional ratio 8.4 did not seem warranted.

Four polyol products were made on a somewhat larger scale to test in foam formulations. Results on these preparations, carried out by reaction at 120 C for 10 hr, are given in Table II. Data on TMP recovered provided estimates of TMP reacted, or fixed, given in column 3. It is evident that fixation increased with functional ratio. Actual wt increases were a little lower than estimated reacted values, reflecting some losses in washing and handling. Hydroxyl content of the polyols also increased with the functional ratio employed. Percent hydroxyl of these products was 6.6-10.3, compared to 4.3 for a control, epoxidized tallow hydrated with diluted fluoboric acid. The new polyols were liquids at room temperature.

The alcohols recovered by water washing were examined by gas chromatography. Some glycerol was recovered, as well as TMP. This was quite clear in products made at the functional ratios 1.4 and 2.1. At the high ratios, 4.2 and 6.6, the glycerol was not apparent in the presence of a great excess of TMP. The column used was not able to show less than 5% glycerol in TMP, but results at the lower ratios indicated that alcoholysis of glyceride links was one of the effective modes of fixing TMP, even though an acid catalyst was used.

Reaction of Epoxidized Tallow with TMP-HBr

The hydroxyl and bromine contents of polyols made by action of TMP-HBr, at a functional ratio of 6.6, are related to reaction time in Figure 2. In reactions at 110 C, introduction of hydroxyl was overshadowed at all reaction times by increase in bromine content. Beyond 6 hr reaction, a striking decline in percentage of OH was accompanied by a strong rise in percentage of Br. At 80 C, without provision for removal of water formed, a maximum OH content at 6 or 8 hr was followed by a decline, again accompanied by a rise, though moderate, in bromine content. When at 80 C water was removed continuously by a Dean-Stark tube, the introduction of hydroxyl was more satisfactory; and, up to 7 hr reaction, bromine introduction did not impair hydroxyl content. The dashed, uppermost curve is a plot of data from Table I for the corresponding reaction at 120 C catalyzed by p-toluenesulfonic acid instead of HBr, at the same functional ratio. The horizontal dashed line indicates OH and Br content expected if HBr opening of oxirane function were the only reaction.

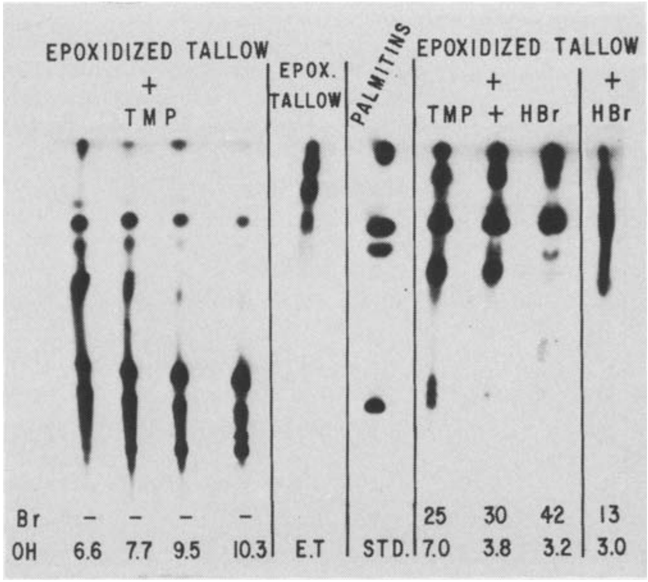

FIG. 3. Thin layer chromatography on silicic acid, developed with benzene-ether-ethanol-acetic acid (80:10:10:1). The standards are, from bottom to top, monopalmitin, 1,2 and 1,3-dipalmitin and tripalmitin.

Table III summarizes the results of the TMP-HBr reactions as polyol preparations. Although the 110 C reaction led to the greatest wt increase in going to product, the resultant polyol had the lowest hydroxyl content; but it had the highest bromine content. The 80 C Dean-Stark tube reaction for 7 hr gave the highest hydroxyl content coupled with a respectable bromine content. The results were an improvement over the control, hypobrominated tallow freed of inert fatty material.

Polarity of Polyol Components

The plyols prepared by the TMP and also by the TMP-HBr reactions were examined by thin layer chromatography. Separations are shown in Figure 3. Epoxidized tallow itself has components with polarity in the range of 1,3-dipalmitin and tripalmitin. The epoxidized tallow-TMP polyols, at the left, identified by percentage of OH, have but little material of polarity like triglycerides. This vanishes in the polyol with 10.3% OH. Components of polarity like monoglycerides became dominant at the highest OH content, while components comparable to diglycerides became unimportant. The epoxidized tallow-TMP-HBr polyols were of much lower polarity. All still had significant amounts of material comparable to triglycerides. Only the polyol with 7.0% OH had appreciable amounts of components near monoglycerides in polarity.

In the unbrominated series, OH content was higher than in previous tallow-based polyols. In the brominated series,

TABLE III

Polyols Made by Reaction of Epoxidized Tallow with TMP-HBr[a]

No.	Reaction conditions temperature, C	time, hr	Wt increase, %	Hydroxyl %	no.	Br %
TX 1	110	12	130	3.2	105	42
TX 2	80	12	65	3.8	125	30
TX 3	80[b]	7	75	7.0	231	25
Control hypobrominated tallow, purified[c]						

[a] At functional rate 6.6; TMP = trimethylolpropane.

[b] Water continuously removed by Dean-Stark tube.

[c] Made (ref. 3) by action of HBr on epoxidized tallow, inert material removed by acetone precipitation.

improved levels of hydroxyl and bromine were attained compared to products from epoxidized tallow treated with hydrogen bromide alone. Liquid character in both series was satisfactory. The preparation and properties of foams from the two series of polyols are described in the following paper.

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