

# Hydrolysis of Epoxidized Soybean Oil in the Presence of Phosphoric Acid

Yinzhong Guo · Jon H. Hardesty · Vijay M. Mannari · John L. Massingill Jr

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**Abstract** Ring-opening hydrolysis of epoxidized soybean oil in the presence of phosphoric acid was studied under varying experimental conditions. The influence of type and amount of solvents, phosphoric acid content and water content on the rate of ring-opening reactions and the characteristics of the derived products were studied. The soy-polyols prepared were characterized by determination of hydroxyl content, viscosity measurements, determination of average molecular weight and polydispersity index (GPC). The structural confirmation was done by FT-IR and  $^1\text{H-NMR}$  spectroscopy. The study shows that under the reaction conditions employed, a substantial degree of oligomerization due to oxirane-oxirane, and/or oxirane-hydroxyl reaction takes place. It is possible to synthesize soy-polyols having varying hydroxyl content and phosphate-ester functionality by controlling the type and amount of polar solvent and phosphoric acid content.

**Keywords** Ring-opening hydrolysis · Oxirane content · Oligomerization · Epoxidized soybean oil

## Introduction

Vegetable oils are important renewable resources and are increasingly replacing petroleum-derived materials in a variety of fields. The use of vegetable oils and their derivatives in fuels (bio-diesel), polymers, lubricants, surfactants, plasticizers and specialty chemicals is well known [1–6]. Besides their renewable nature, most of these derivatives are biodegradable and environmentally friendly, which make them attractive candidates for development of sustainable technologies [7–9].

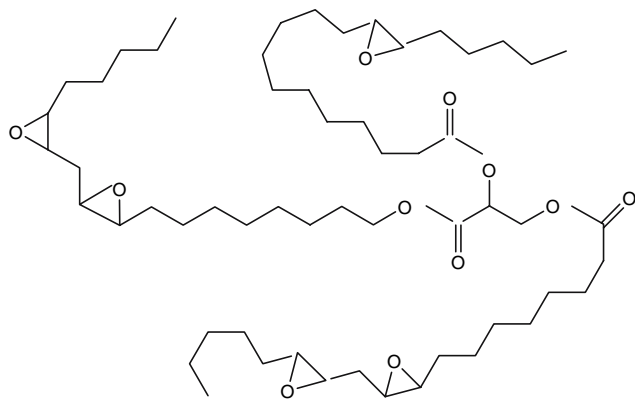
Soybean oil is one of the most abundant and low-cost vegetable oils available in most parts of the world. Epoxidized soybean oil (ESO) can be derived by chemical oxidation of soybean oil and is commercially available. ESO is primarily used as an acid scavenger/plasticizer for poly(vinyl chloride) plastic. Soybean oil consists of a mixture of triglycerides derived mostly from C16 to C18 saturated and unsaturated fatty acids, but with traces of C12, C14, and C20 fatty acids. Figure 1 shows a representative structure of ESO.

A variety of chemical modifications of ESO are possible through the reactive oxirane functionality. By far the most predominant reaction of ESO is the ring-opening reactions with nucleophilic compounds. The reaction of nucleophile water with ESO produces compounds with multiple 1,2-diol structures, depending upon the oxirane content and the extent of hydrolysis. These soy-polyols have interesting properties and applications in a variety of fields. Preparation of polyols from vegetable oils has been extensively reported in the literature [10–19]. Guo et al. [20] reported the preparation of soy-polyols by the hydrogenation of hydroformylated soybean oil and studied the physical and mechanical properties of polyurethanes based on these soy-polyols. Petrovic et al. [21] have reported the preparation

Y. Guo · J. H. Hardesty · V. M. Mannari ·  
J. L. Massingill Jr (✉)  
Institute for Environmental and Industrial Science,  
Texas State University, San Marcos, TX 78666, USA  
e-mail: jm70@txstate.edu

Y. Guo  
The Dow Chemical Co., Midland, MI 48674, USA

V. M. Mannari  
Eastern Michigan University, Ypsilanti, MI, USA



**Fig. 1** Representative structure of epoxidized soybean oil

of a series of polyurethanes from halogenated, hydrogenated, and methoxylated ESO with an average OH functionality of 3.7.

In the present work, we focused on the study of ring-opening reaction of ESO with water in the presence of phosphoric acid, which not only catalyzes the ring-opening hydrolysis reaction but also chemically combines and becomes a part of the polyol product. Besides eliminating the need for its removal from the reaction mixture, the presence of phosphate ester functionality will add value to the derived soy-polyols for many end use applications, such as in surfactants and coatings. We report some important findings of the study of ring-opening hydrolysis reaction of ESO under varying experimental conditions.

## Experimental

### Materials

Epoxidized soybean oil (Acid Value—0.08 mg of KOH, Oxirane Number—7.0%, Iodine Number—1.35) VIKO-FLEX-7170 was supplied by Arkema, and was used without any purification or treatment. All other chemicals, solvents and reagents used in the study were of laboratory grade and were procured from Aldrich Chemical Co. and used as received.

### Ring-Opening Hydrolysis of ESO

All the hydrolysis reactions reported in this study were carried out by the following general procedure, unless otherwise specified.

To a 500-ml multi-neck reaction flask equipped with a mechanical stirrer, a thermometer, a water cooled condenser and a dropping funnel, a mixture of solvent, phosphoric acid and water, in a specified proportion, was

charged. The mixture was brought to the reflux condition by heating at a slow rate under mechanical stirring. The temperature of the reaction mixture was in the range of 60–120 °C, depending upon choice of solvent. ESO was dissolved in a portion of reaction solvent and added drop wise into the flask over a period of 45 min. After addition of the ESO solution was complete, heating was continued and the reaction sample was periodically tested for the Acid value and the percentage of the oxirane content. Reaction was stopped after 6 h or when the oxirane content was found to be <0.2%, whichever was first. Upon completion of the reaction, the solvent and residual water were removed with a rotary vacuum evaporator.

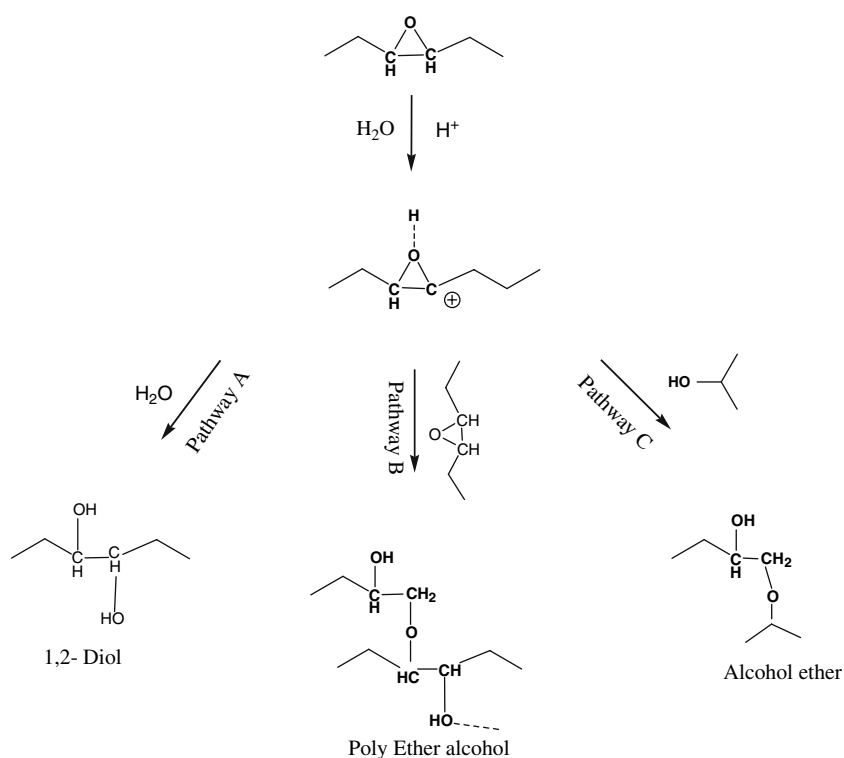
The product was purified to remove unreacted acid by washing its ethereal solution (1:2 by volume) with distilled water using a separatory funnel, followed by drying over anhydrous sodium sulfate.

### Characterization

Acid values (A.V.), % oxirane content (O.N.), and hydroxyl values (H.V.) of the product samples were determined by standard methods of ASTM D 1639-90, ASTM D 1652-97, and ASTM D 1957-86, respectively. The viscosities were measured using a Brookfield viscometer at 25 °C. The molecular weight was determined by Gel Permeation Chromatography (GPC) using a polystyrene standard. The products were also characterized with FTIR spectra (Perkin Elmer Spectrum One FTIR Spectrometer) and <sup>1</sup>H-NMR spectra (Unity Inova, Varian 400 MHz Spectrometer) for structural confirmation.

## Results and Discussion

A general reaction mechanism for the acid-catalyzed ring opening hydrolysis of oxirane compounds is shown in Fig. 2. It is essentially a nucleophilic substitution reaction involving the nucleophilic attack of H<sub>2</sub>O on an electrophilic site formed by protonation of oxirane oxygen by an acid catalyst. Under these conditions, the ring-opening hydrolysis reaction results in the formation of 1,2-diol compounds, Fig. 2, pathway A. As shown in Fig. 2, there are two significant competing reactions that take place under the conditions of hydrolysis. First, the reaction between oxirane groups (oligomerization) results in the formation of oligomeric ethers, Fig. 2, pathway B. Secondly, the products of hydrolysis (1,2-diol) or that of oligomerization (hydroxyl functional oligomeric ethers) may react with an electrophilic site to produce ether linkages, Fig. 2, pathway C. The reaction kinetics describing the reaction of hydroxyl or carboxyl groups with

**Fig. 2** Ring-opening pathways of epoxides

cycloaliphatic epoxides has been reported in the literature [22–24]. Wu and Soucek [25] have extensively studied such reactions through kinetic modeling. The extent of various competing reactions depends on several factors such as relative nucleophilicity of reactants, stability of intermediates, solvent, temperature, and relative concentration of reactants, among others.

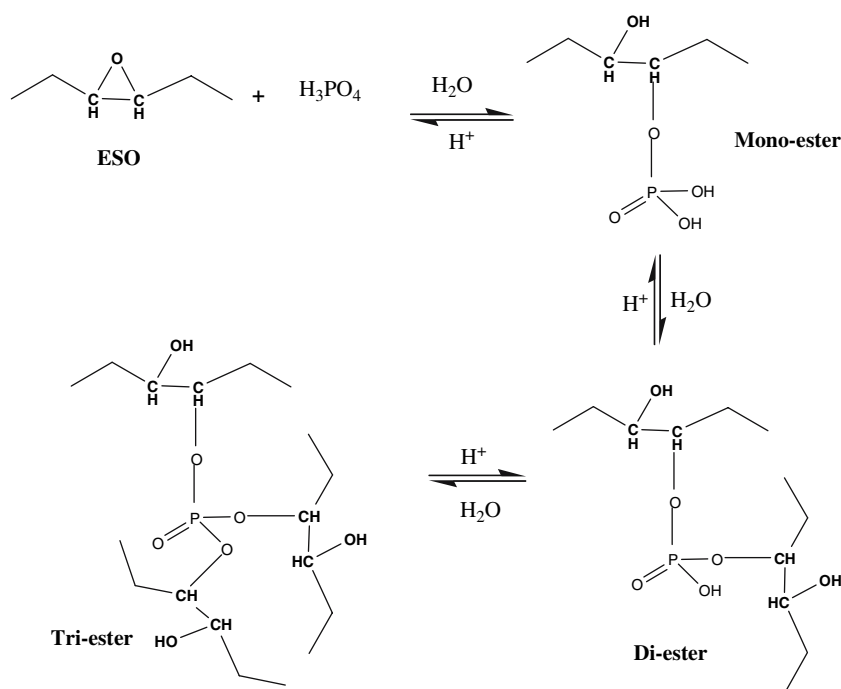
In the present study, phosphoric acid was used as a reactant as well as a catalyst. Phosphoric acid, a polybasic acid has three dissociation constants associated with each of its protons, giving rise to anions having significantly varying nucleophilicity. We believe that under the conditions of the reaction, phosphoric acid reacts with ESO to produce mono-, di-, and tri- phosphate esters as shown in Fig. 3. The formation and hydrolysis of phosphate ester is thought to be dependent upon concentration of the reactants and solvent among other factors. We have, therefore, carried out the reaction using different solvents and varying the relative ratio of solvent, water and phosphoric acid, to study their effect on the characteristics of the resultant product.

#### Effect of Solvent

The hydrolysis reaction was investigated using five different solvents: acetone, tetrahydrofuran (THF), 2-propanol (PA), *tert*-butyl acetate (*t*BAC), and *tert*-butyl alcohol (*t*BA). In each case the relative amount of reactants

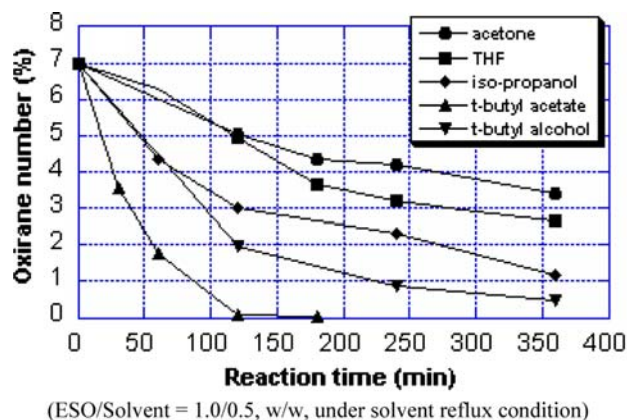
(phosphoric acid 2%, solvent 50% and water 10% by wt. of ESO) were kept constant. The characteristics of soy-polyols obtained after 6 h of completed addition of ESO (or when % oxirane content dropped below 0.2) are presented in Table 1.

In order to follow the extent of ring-opening hydrolysis reaction, the percentage of oxirane content was determined over the course of the 6 h reaction time at 0, 30, 60, 120, 180, 240, and 360 min after completion of the addition of the ESO solution into the flask. As can be seen in Fig. 4, the products derived utilizing acetone and THF as solvents have oxirane contents of 3.41 and 2.64 at the end of 6 h, which corresponds to approximately 51 and 63% completion of the reaction, respectively. The product based on *tert*-butyl acetate shows a much faster rate of depletion of oxirane groups indicating a higher rate of hydrolysis. However, the very high acid value (48 mg of KOH) of the product indicates the probable acid catalyzed hydrolysis of this ester-type solvent resulting in the formation of *n*-butyl alcohol and acetic acid. For the product based on 2-propanol, the rate of oxirane consumption is higher than that for acetone and THF, as indicated by the residual % oxirane contents of their products. It is interesting to note that hydroxyl value of product based on 2-propanol is substantially lower than those when *tert*-butanol or *tert*-butyl acetate were employed as solvents, even after factoring in their difference in % oxirane content. This can be attributed to the possible reaction of 2-propanol with oxirane groups and formation of ethers. The results in Table 1 indicate that

**Fig. 3** Formation and reactions of phosphate esters**Table 1** Characteristics of soy-phosphate polyols prepared using different solvents

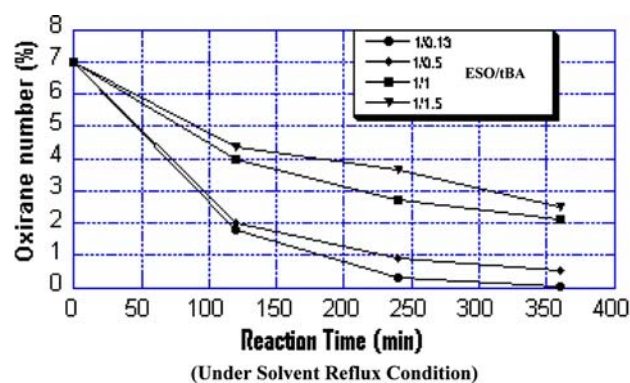
Parameters	Solvents				
	Acetone	THF	2-Propanol	<i>t</i> -butyl acetate	<i>t</i> -butyl alcohol
ESO/solvent (w/w)	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5
Phosphoric acid	2%	2%	2%	2%	2%
Water	10%	10%	10%	10%	10%
% Oxirane content	3.41	2.64	1.16	0.03	0.5
Acid value	1.35	1.96	2.24	48	4.16
Hydroxyl value	–	–	153	235	253
Viscosity (cps)	3,010	3,780	5,310	4,760	3,160
Molecular Wt. (g/mol)-GPC	–	–	4,700	4,018	3,870
Polydispersity index (GPC)	–	–	1.9	3.3	1.8

Reaction time 6 h, after complete addition of ESO, under solvent reflux conditions

**Fig. 4** Extent of hydrolysis of ESO in different solvents as function of reaction time

*tert*-butyl alcohol was the best solvent for the hydrolysis reaction, since the rate of oxirane consumption is fairly fast along with a higher hydroxyl value and narrow molecular weight distribution. The relatively low nucleophilicity of *tert*-butyl alcohol promotes a higher degree of hydrolysis as indicated by its high hydroxyl value.

The influence of reactant concentration on the rate of reaction was investigated by varying the *t*BA content in the reaction mixture. As expected, the rate of oxirane consumption decreased with increasing ESO dilution (Fig. 5). Further, decreasing molecular weight with increasing solvent content indicates a decreased tendency of oligomerization (oxirane–oxirane reaction). The subsequent reactions in this study were carried out using ESO/*t*BA of 1:0.5 since this gave a substantial hydroxyl content at a



**Fig. 5** Effect of solvent concentration on extent of reaction

fairly fast rate. Best overall results were obtained at an ESO/*t*BA ratio of 1:0.5.

#### Concentration of Phosphoric Acid

Given the acid-catalyzed nature of this reaction, the amount of phosphoric acid used is expected to have significant effect on the reaction time and the characteristics of the product. A series of reactions with varying amounts of phosphoric acid (ESO/*t*BA = 1/0.5, water 10% by wt. of ESO) were investigated. Phosphoric acid was varied from 2 to 10% (Table 2). As expected, higher concentrations of phosphoric acid gave essentially complete ring-opening in a progressively shorter reaction time. With increasing phosphoric acid content, the products not only showed higher final acid values, but acid values progressively increased during the course of the reaction. This might be due to the progressive hydrolysis of higher phosphate esters to lower esters.

One interesting observation here is the comparison of molecular weight (and viscosity) as a function of phosphoric

acid content (Table 2). The molecular weight and viscosity of the products increases with increasing phosphoric acid content up to 4%. This can primarily be attributed to (a) increased tendency for oligomerization reaction due to higher acid concentration and (b) presence of increasing amount of higher phosphate esters.

The sample obtained from the reaction containing 10% phosphoric acid exhibits lower viscosity and molecular weight along with higher hydroxyl value. These characteristics can be attributed to the significantly lower oligomerization and lower higher phosphate esters in this case. We believe that the reason for this significant drop in oligomerization, despite higher acid concentration, is due to the rapid consumption of oxirane groups in formation of phosphate esters. Since the rate of oligomerization reaction follows second order kinetics with respect to oxirane concentration, drop in the rate of oligomerization is evident. The high hydroxyl value justifies the fact that excessive oxirane groups are not lost in oligomerization. It is important to note that under the conditions of all the reactions, no appreciable glyceryl ester hydrolysis has occurred, as indicated by fairly narrow polydispersity index ( $M_w/M_n$ ) for all the samples. Figure 6 shows the FT-IR spectra of purified soy-polyol samples. The most noticeable feature of the spectra is the increasing intensity of the peak at  $1,020\text{ cm}^{-1}$  at higher phosphoric acid catalyst concentrations, indicating the presence of increasing degrees of phosphate incorporation under the conditions of the reactions.

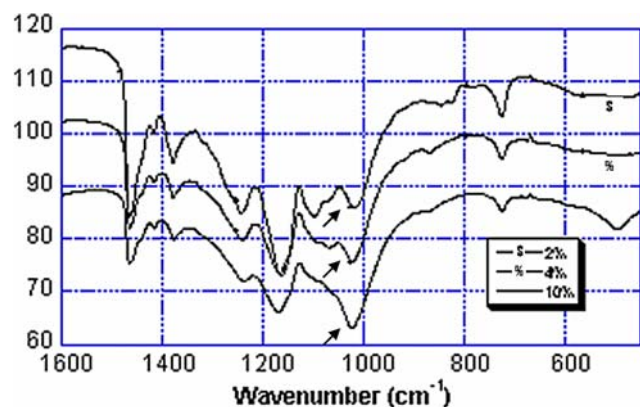
#### Concentration of Water

Comparison of samples (Table 2) of 10% water with those of 20 and 30% water indicates that besides a small increase in the rate of hydrolysis, the amount of water does not seem to be a significant factor.

**Table 2** Characteristics of soy-phosphate polyols

Parameters	<i>t</i> -butyl alcohol									
	1/0.15	1/0.5	1/1.0	1/1.5	1/0.5	1/0.5	1/0.5	1/0.5	1/0.5	1/0.5
ESO/solvent	1/0.15	1/0.5	1/1.0	1/1.5	1/0.5	1/0.5	1/0.5	1/0.5	1/0.5	1/0.5
Phosphoric acid	2%	2%	2%	2%	3%	4%	10%	2%	2%	2%
Water	10%	10%	10%	10%	10%	10%	10%	20%	30%	30%
% Oxirane content	0.03	0.5	2.13	2.5	0.13	0.05	0.04	0.05	0.04	0.04
Acid value	10.2	4.16	4	3.45	8.25	20.5	104	4.3	4.4	4.4
Hydroxyl value	245	253	–	235	231	242	262	261	259	259
Viscosity (cps)	3,290	3,160	2,670	1,820	3,890	4,240	2,850	2,950	2,913	2,913
Molecular wt. (g/mole)	5,830	3,870	3,375	3,032	7,171	6,212	2,679	2,983	2,960	2,960
Polydispersity index	2.4	1.8	2.1	1.9	2.8	2.3	1.6	1.6	1.6	1.6

*t*-butyl alcohol as solvent, reaction time 6 h. After complete addition of ESO, under solvent reflux condition



**Fig. 6** FT-IR spectrum of soy polyols-increasing phosphate ester content ( $1,020\text{ cm}^{-1}$ ) with increasing % phosphoric acid content

### Characterization of Products

The products of various reactions were characterized by their FT-IR spectrum for qualitative confirmation of functional groups. In some instances, FT-IR spectra were used to monitor the progress of ring-opening reaction by following the disappearance of the signal at  $824\text{ cm}^{-1}$ , indicating the loss of the oxirane groups. All the products showed two characteristic signals at  $3,400$  and at  $1,020\text{ cm}^{-1}$ , indicating the presence of hydroxyl and phosphate ester groups, respectively. While the % oxirane content was used to calculate the overall conversion, the extent of the hydrolysis reaction (leading to the formation of 1,2-diols) was monitored by the determination of hydroxyl values of the products and comparing them with the theoretical value of  $495\text{ mg of KOH/g}$ . The theoretical value is based on the molecular structure if all of the oxirane groups of ESO were to have opened up giving rise to two -OH groups per oxirane group. The experimental hydroxyl values determined by chemical method (ASTM 1957-86) as well as by spectroscopic method by calculating peak areas of  $5.27\text{ ppm}$  and  $2.68\text{ ppm}$  in  $^1\text{H-NMR}$  spectrum. We found good correlation between hydroxyl values determined by chemical and spectroscopic methods.

Comparison of the theoretical hydroxyl value of  $495\text{ mg KOH/g}$  with experimental values in Table 2 clearly indicate that under these experimental conditions, on an average, about 50% of the hydroxyl groups are lost, primarily in the formation of oligomeric ethers. The comparison of average molecular weights (Table 2) of the products with theoretical molecular weight ( $\sim 1,000\text{ g/mol}$ ) clearly indicates the oligomeric nature of the products of these ring-opening hydrolysis reactions.

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