

DEGRADATION OF THE OXIRANE RING OF EPOXIDIZED VEGETABLE OILS IN LIQUID-LIQUID SYSTEMS: II. REACTIVITY WITH SOLVATED ACETIC AND PERACETIC ACIDS

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Abstract— The impact of the main process variables (agitation, pH, temperature, concentration levels) on the degradation of the oxirane ring of epoxidized soybean oil (ESO) by attack by solvated acetic and peracetic acids in two-phase (polar-organic) systems when a homogeneous acid catalyst is used, is analyzed in detail. The first degradation reaction is first order with respect to the epoxide concentration and second order with respect to the solvated acetic acid [$k_{AA}(70^\circ\text{C}) = 4.27 \pm 0.12 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ min}^{-1}$; $E_{aAA} = 12.9 \pm 0.64 \text{ kcal mol}^{-1}$]. The degradation increases notoriously the lower the pH of the reacting media is; the increase is directly proportional to the concentration of protons, as is usually found in homogeneous catalysis (for very low pHs the reaction is almost instantaneous). Likewise, the degradation reaction with peracetic acid is first order with respect to the epoxide [$k_{PAA}(70^\circ\text{C}) = 4.31 \times 10^{-4} \text{ l}^2 \text{ mol}^{-2} \text{ min}^{-1}$; $E_{aPAA} = 10.6 \pm 0.38 \text{ kcal mol}^{-1}$] and it also increases linearly with proton concentration. Although the *specific* attack on the ring by the peracid is almost 10 fold harsher, acetic acid is constantly being regenerated during the industrial process, so that its concentration is always far larger than that of peracetic acid. Thus, under process conditions the degradation of the oxirane ring is mostly caused by the carboxylic acid.

Keywords— Epoxidized soybean, degradation of oxiranes, solvated acetic acid, peracetic acid.

I. INTRODUCTION

Epoxidized vegetable oils (EVO) are extensively used by industry, specially as plasticizers in PVC manufacture. Owing to the oxirane ring in the molecule, they also impart thermal and photo-stability to the polymer composite (Kirk and Othmer, 1984). Their main advantage is related to good performance combined with low production costs. Also, and most desirably, EVOs can be obtained from renewable sources.

The epoxidation of any given vegetable oil can be accomplished using organic peracids, either preformed or formed *in-situ*, by reacting a carboxylic acid with concentrated hydrogen peroxide to make a percarboxylic acid, which in turn donates an oxygen atom to the double bonds of the fatty acid carbon chain

of the oil (Reactions 1 and 2 in Fig. 1). Peracetic acid is customarily used in industrial practice, in which case homogeneous or heterogeneous acid catalysts (*viz.*, ion exchange resins) can be used. Together with the main oxygen-transfer reaction, several other, consecutive reactions are always present (Reactions 3-7, Fig. 1). They all imply process losses *via* ring-opening and must be minimized to achieve good yields and high peroxide values of the EVO.

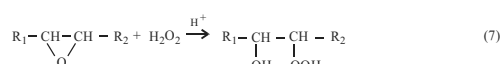
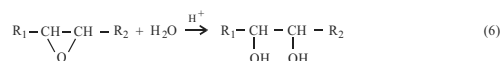
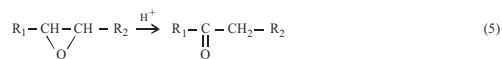
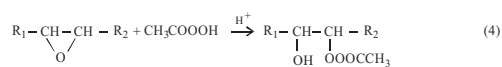
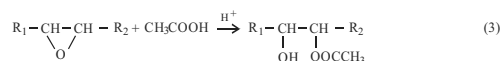
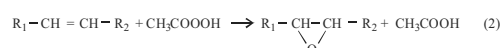


Figure 1: Epoxidation and ring opening reactions of the double bonds of vegetable oils (unsaturated triacylglycerides) in the conventional acetic acid-hydrogen peroxide process.

Until recently, the only oxirane ring opening reaction of oxiranes obtained from vegetable oils (VO) and/or fatty acid methyl esters (FAME) studied with some detail (amongst the set indicated in Fig. 1) was the attack by glacial acetic acid (*i.e.*, in a single organic phase) (Zaher *et al.*, 1989; Gan *et al.*, 1992, Pagès-Xatart-Parès *et al.*, 1999). In the first two works it was found that the reaction is first order with respect to the epoxide concentration and of second order with respect to acetic acid. Zaher *et al.* (1989), who studied the degradation of epoxidized soybean oil, found $k_{AA} = 3.33 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ min}^{-1}$ at 70°C , with an activation energy of $15.84 \text{ kcal mol}^{-1}$. Gan *et al.* (1992) analyzed, instead, the ring opening of a mixture of epoxidized FAME obtained from palm oil. Upon exposing the mixture to glacial acetic acid, they found similar values