

# Role of Epoxides in the Oxidation of Allyl Alcohol, Allyl Formate, and Allyl Acetate in Acetic Acid

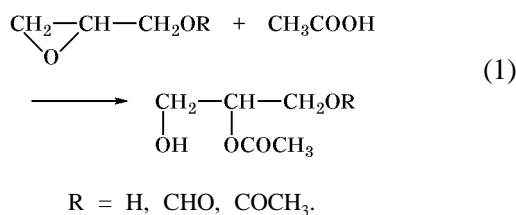
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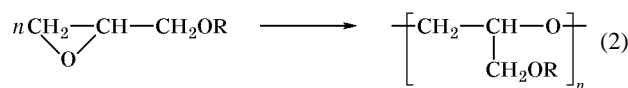
Received January 9, 2001

**Abstract**—The formation of epoxy derivatives as intermediate products in the oxidation of allyl alcohol, allyl formate, and allyl acetate in acetic acid was proved. Intermediate epoxy compounds undergo further transformations: They react with acetic acid to give glycerol esters or are converted into polyethers of glycerol and its esters. The rate constants for transformations of 2,3-epoxypropanol, 2,3-epoxypropyl formate, and 2,3-epoxypropyl acetate along these pathways were measured. Higher selectivity of glycerol ester formation from allyl formate was substantiated.

The simplest procedure for preparation of glycerol is based on oxidation of allyl acetate with molecular oxygen in acetic acid to obtain glycerol esters whose hydrolysis yields glycerol [1–6]. Study of the oxidation of allyl alcohol, allyl acetate, and allyl formate in acetic acid showed that the yield of glycerol esters decreases in the series allyl formate > allyl acetate > allyl alcohol [1, 7–9]. It was presumed [1, 7] that the primary intermediate in these reactions is the corresponding epoxy derivative which gives rise to the final products via reaction with acetic acid:



Intermediate epoxides are likely to undergo concurrent transformations leading to by-products, such as polyethers derived from glycerol esters [7]:



With the goal of substantiating the proposed scheme of oxidation of allyl alcohol and its esters the present article reports the results of studying transformations of intermediate epoxy derivatives under comparable conditions (in acetic acid and in a mixture of acetic and formic acids). It was found

that oxidation products of allyl alcohol and its esters (allyl formate and allyl acetate) in acetic acid contain glycerol esters formed according to reaction (1) and polymeric compounds formed by reaction (2). Figure 1 shows almost complete analogy between the IR spectra of still residues obtained from the reaction mixtures and specially synthesized glycerol polyethers. The yield of polymeric ethers increases in the series allyl formate < allyl acetate < allyl alcohol [7].

Presumably, the ratio of the rates of consumption of intermediate epoxides in the oxidation of allyl alcohol and its esters in acetic acid along concurrent pathways (1) and (2) is responsible for the selectivity of formation of the target products, glycerol esters.

Figure 2 shows the kinetic curves for consumption of epoxides in acetic acid and in a mixture of acetic and formic acids at 344 K. In acetic acid the ratio of the rates of consumption of 2,3-epoxypropyl formate, 2,3-epoxypropyl acetate, and 2,3-epoxypropyl alcohol is 1:5:8. It is qualitatively consistent with the available data on kinetically equilibrated concentrations of these intermediates in the oxidation of allyl formate, allyl acetate, and allyl alcohol in an inert solvent (acetone) at 438 K (2.9 MPa): 0.8, 0.2, and 0.05 M, respectively [9].

Addition to the reaction mixture of formic acid to a concentration of 25 mol % sharply increases the rates of consumption of 2,3-epoxypropyl acetate and 2,3-epoxypropyl formate (Fig. 2; curves 4 and 5). In the case of 2,3-epoxypropyl alcohol, the reaction is so fast that mixing of the reactants at room temperature is accompanied by exothermic effect and the

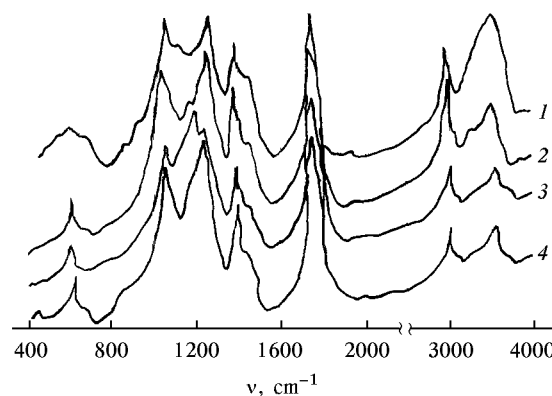
entire epoxy compound is converted into glycerol polyethers.

The rates of consumption of 2,3-epoxypropyl alcohol, 2,3-epoxypropyl acetate, and 2,3-epoxypropyl formate in acetic acid and of accumulation of the corresponding glycerol esters were examined on variation of epoxide concentration during the process. Figure 3 shows the obtained dependences for 2,3-epoxypropyl acetate and 2,3-epoxypropyl formate. In the initial period ( $c = 3.3$  M) the rate of consumption of 2,3-epoxypropyl acetate, as well as of 2,3-epoxypropyl alcohol, is higher than the rate of accumulation of glycerol esters. As the concentration of initial epoxy compound decreases, the rate of its transformation falls down. The difference between curves 1 and 2 is in fact the rate of formation of glycerol polyethers. This difference is the greatest in the initial period, and it then decreases to zero, though the rate of formation of glycerol esters is still greater than zero. These findings indicate that glycerol polyethers are formed preferentially by polymerization of 2,3-epoxypropyl alcohol and 2,3-epoxypropyl acetate. Had they been formed via addition to oxirane ring of glycerol ester through its hydroxy group, the rates of consumption of the epoxy compound and of accumulation of glycerol ester would be different throughout the process. Increase in the selectivity of transformation of epoxy compounds into glycerol esters by the end of the reaction contradicts the above assumption.

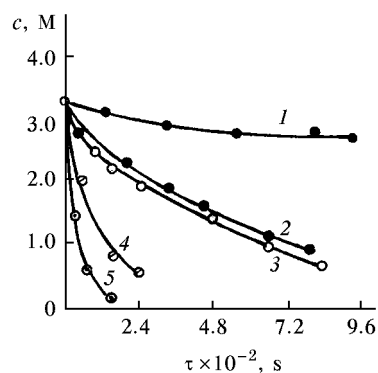
Almost no glycerol polyethers are formed from 2,3-epoxypropyl formate, and the kinetic curves for consumption of the epoxy compound and accumulation of glycerol esters almost coincide with each other (Fig. 3; curves 3, 4).

The overall selectivity of formation of glycerol esters in acetic acid with respect to the consumed epoxy compound is fairly high; by the end of the reaction it attained 98% for 2,3-epoxypropyl formate, 92% for 2,3-epoxypropyl acetate, and 90% for 2,3-epoxypropyl alcohol. One more specific feature of the transformation of epoxides in acetic acid should be noted: the rate of their consumption falls down to zero at some residual epoxide concentration. Obviously, this effect results from increase of the solution viscosity due to accumulation of reaction products.

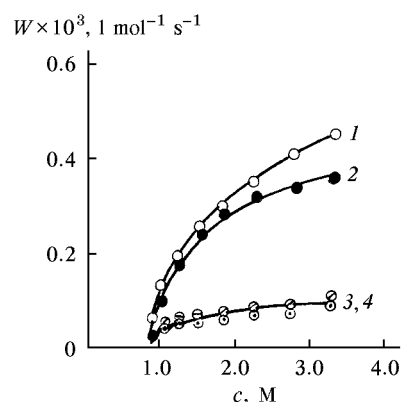
Taking into account that oxidation of allyl alcohol and its esters gives rise to a significant amount of formic acid [7], it was reasonable to examine its effect on the transformations of intermediate epoxy derivatives. As noted above, addition of formic acid to the reaction mixture strongly increases the rate of epoxide transformation (Fig. 2). Comparison of the data given



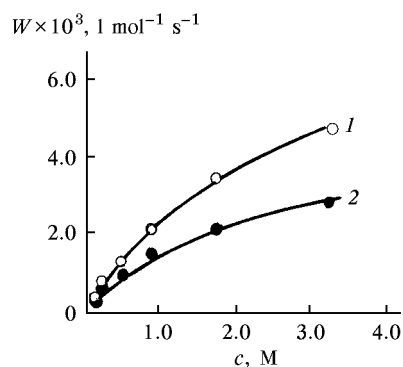
**Fig. 1.** IR spectra of (1) specially synthesized glycerol polyethers and still residues obtained from (2) 2,3-epoxypropyl alcohol, (3) allyl formate, and (4) allyl acetate.



**Fig. 2.** Kinetic curves for consumption of (1, 4) 2,3-epoxypropyl formate, (2, 5) 2,3-epoxypropyl acetate, and (3) 2,3-epoxypropyl alcohol in (1–3) acetic acid and (4, 5) a mixture of acetic and formic acids at a molar ratio of 3:1. Temperature 344 K.



**Fig. 3.** Dependences of the rates of consumption of (1) 2,3-epoxypropyl acetate and (3) 2,3-epoxypropyl formate and (2, 4) of accumulation of glycerol esters on the concentration of epoxy derivative; acetic acid, 344 K.



**Fig. 4.** Dependences of the rates of (1) consumption of 2,3-epoxypropyl acetate and (2) accumulation of glycerol esters on the epoxide concentration in a mixture of acetic and formic acids (molar ratio 1:1); temperature 344 K.

In Figs. 3 and 4 shows that the rate of consumption of 2,3-epoxypropyl acetate in a mixture of formic and acetic acids is higher than in acetic acid by an order of magnitude. An analogous pattern is observed for 2,3-epoxypropyl formate. In the presence of formic acid the kinetic curves for consumption of epoxides and accumulation of glycerol esters are characterized by different courses throughout the reaction (Fig. 4). In this case, epoxy compound is consumed completely. Obviously, formic acid not only accelerates the addition of acetic acid to epoxy compound but also favors addition of the hydroxy groups in glycerol esters to the oxirane ring at deep stages of the process to afford glycerol polyethers. Therefore, in the presence of formic acid the selectivity of epoxide transformation into glycerol esters decreases and is 93–95% for 2,3-epoxypropyl formate and 76% for 2,3-epoxypropyl acetate, while the selectivity for 2,3-epoxypropyl alcohol is close to zero since its entire amount is consumed for formation of polymeric polyether. Thus the examined epoxy derivatives form the following series with respect to their stability

Rate constants for transformations of epoxy compounds in a mixture of acetic and formic acids (344 K)

Epoxide	$k_1 \times 10^4$ , $l \text{ mol}^{-1} \text{ s}^{-1}$	$k_2 \times 10^4$ , $l \text{ mol}^{-1} \text{ s}^{-1}$	$k_3 \times 10^4$ , $l^2 \text{ mol}^{-2} \text{ s}^{-1}$
2,3-Epoxypropyl alcohol	$0.13 \pm 0.02$	$4.0 \pm 1.0$	$62 \pm 15$
2,3-Epoxypropyl acetate	$0.14 \pm 0.02$	$1.5 \pm 0.4$	$0.57 \pm 0.15$
2,3-Epoxypropyl formate	$0.05 \pm 0.01$	$1.1 \pm 0.3$	$0.10 \pm 0.03$

toward formic and acetic acid and selectivity of transformation into glycerol esters: 2,3-epoxypropyl formate > 2,3-epoxypropyl acetate > 2,3-epoxypropyl alcohol. The same order is observed for their precursors (allyl formate, allyl acetate, allyl alcohol) with respect to the maximal concentration of intermediate epoxy derivative and selectivity of formation of glycerol esters in the oxidation by atmospheric oxygen [7–9]. These results confirm the assumptions that 2,3-epoxypropyl derivatives are the main molecular intermediate products in the oxidation of allyl alcohol, allyl acetate, and allyl formate and that their transformations along two concurrent pathways (to give glycerol esters and polyethers) determine the selectivity of formation of the target products.

The equation for the rate of epoxide consumption in a mixture of acetic and formic acids ( $W_{ep}$ ) can be represented as

$$W_{ep} = k_1 c_{ep} c_{aa} + k_2 c_{ep} c_{fa} + k_3 c_{ep} c_{fa} c_{ge} \quad (\text{mol l}^{-1} \text{ s}^{-1}),$$

where  $k_1$ ,  $k_2$ , and  $k_3$  are the apparent rate constants of epoxide consumption for formation of glycerol acetates, glycerol formates and glycerol ethers (the rate of the latter process is the difference between the rates of epoxide consumption and accumulation of glycerol esters);  $c_{ep}$ ,  $c_{aa}$ ,  $c_{fa}$ , and  $c_{ge}$  are the concentrations of epoxide, acetic acid, formic acid, and glycerol esters (M), respectively.

Substitution into the above equation of the rates of epoxide consumption and the corresponding component concentrations from the obtained experimental data leads to a system of linear equations. Solution of this system by the least squares procedure gave the apparent rate constants given in table.

2,3-Epoxypropyl formate is the most stable in a mixture of acetic and formic acids, and it shows the highest selectivity in the formation of glycerol esters. Therefore, the greatest yields of glycerol esters are obtained just in the oxidation of allyl formate. 2,3-Epoxypropyl alcohol is the least selective in the formation of glycerol esters, and the selectivity of their formation in the oxidation of allyl alcohol does not exceed 30%.

It should be taken into account that oxidation of allyl acetate or allyl formate in acetic acid gives rise to considerable amounts of formic acid and water, thus creating favorable conditions for hydrolysis of these esters to form allyl alcohol. As a result, the selectivity of formation of glycerol esters as target products is reduced. To prevent formation of allyl

alcohol, it is advisable to perform the oxidation process in the presence of dehydrating agents, e.g., acetic anhydride. In this case the selectivity of formation of glycerol esters can be raised by 5–10%.

### EXPERIMENTAL

**2,3-Epoxypropyl alcohol** was obtained by distillation of the commercial product of pure grade, a fraction with bp 338–339 K (0.34 kPa) being collected. The purity of the product was 99%.

**2,3-Epoxypropyl acetate** was synthesized from epichlorohydrin and potassium acetate according to the procedure described in [10]. The purity of the product was 98% (determined by chemical and chromatographical analysis).

**2,3-Epoxypropyl formate** was synthesized by the procedure described in [10]. A mixture of 92.5 g (1 mol) of distilled epichlorohydrin and 84 g (1 mol) of dry potassium formate was refluxed for 20 h under stirring. The reaction mixture contained a compound whose retention time (in a column charged with Polisorb-1) was greater than for epichlorohydrin but smaller than for glycerol. The temperature of the mixture rose by 10°C. The mixture was distilled, and a fraction distilled next to epichlorohydrin, bp 348–353 K (5 kPa), was collected. The unreacted epichlorohydrin was combined with the still residue. This procedure was repeated three times. In such a way, about 10 ml of the above fraction was obtained. It contained 70% of 2,3-epoxypropyl formate which was then purified by preparative gas chromatography on a PAKhV-07 instrument using a column packed with Polisorb-1. The purity of the product was 96%, bp 426 K (atmospheric pressure).

Polymeric products accumulating in the oxidation of allyl alcohol, allyl formate, and allyl acetate were identified by IR spectroscopy using a Specord M-80 instrument.

**Polymeric products** having a structure implied by reaction (2) were synthesized from 2,3-epoxypropyl alcohol and acetic and formic acids. The latter was added taking into account that it is formed in appreciable amounts in the oxidation of allyl alcohol, allyl acetate, and allyl formate [7]. A solution of 0.13 mol of acetic acid and 0.03 mol of 2,3-epoxypropyl alcohol was added dropwise at 363 K to a mixture of 0.17 mol of acetic acid and 0.02 mol of formic acid. The mixture was refluxed for 1 h and distilled so that

all products boiling up to 380 K (0.2 kPa) were removed. The residue was the product of glycerol polymerization followed by esterification of free OH groups with acetic and formic acids.

**The kinetics** of consumption of epoxy derivatives in acetic acid or in a mixture of acetic and formic acids were studied using a microreactor equipped with a jacket (to maintain a required temperature), stirring device, and reflux condenser. Samples of the reaction mixture were analyzed by chromatography on an LKhM-8MD instrument equipped with a thermal-conductivity detector and a 2-m column packed with Polisorb-1, grain size 0.15–0.25 mm; carrier gas helium, flow rate 2.5 l/h. The temperature conditions were selected depending on the initial epoxy derivative. Chlorobenzene was used as internal standard.

The experimental kinetic dependences  $c_i = f(\tau)$  were approximated using Chebyshev's orthogonal polynomial whose numerical differentiation gave an analytical dependence of the reaction rate  $W_i$ ,  $\text{mol l}^{-1} \text{s}^{-1}$ , on the reaction time:  $W_i = \varphi(\tau)$ , where  $\varphi(\tau) = f'(\tau)$ .

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