

STRONGLY ACIDIC CATION EXCHANGE RESIN OF SULPHONATED POLYSTYRENE TYPE USED AS CATALYST FOR EPOXIDATION OF CASTOR OIL WITH PERACETIC ACID AND PERFORMIC ACID

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ABSTRACT

Cationic ion-exchange resins are versatile catalysts, which offer several advantages over the homogeneous acid catalysts with respect to corrosion, product recovery, selectivity, etc. In this work, we compared the kinetics of the epoxidation of castor oil with performic and peracetic acid generated *in situ* in the presence of cation exchange resin (Amberlite IR-120) as a catalyst at 30, 50, 70, and 85 °C. The reaction was found to be first order with respect to the conversion of ethylenic unsaturation. The rate constants for the epoxidation with peracetic acid were 0.067, 0.184, 0.55, and 1.12 (h^{-1}) at 30 °C, 50 °C, 70 °C and 85 °C, respectively, while those for the performic acid were 0.125, 0.287, 0.645, and 0.981 (h^{-1}). Activation energies of the epoxidation were found to be 48.2 kJ/mol for the peracetic acid and 35.4 kJ/mol for the performic acid.

INTRODUCTION

Epoxidation of plant oils (triglycerides), commonly referred to as “vegetable oils”, is a commercially important reaction because the epoxides obtained from these renewable resources and from the methyl oleate, (transesterification product of vegetable oil) have wide applications in such materials as plasticisers and polymer stabilizers [1]. On an industrial scale, the epoxidation of plant oils is currently carried out with the “Prileschajew reaction”, in which the unsaturated oils react with a percarboxylic acid, such as peracetic and performic acid, obtained through the acid catalyzed peroxidation of the respective organic acids with hydrogen peroxide [1]. Soluble mineral acids, such as sulphuric acid, are commonly used as catalysts for this reaction. The objective of this work was to find the conditions for maximum epoxy yield and compare the kinetics of epoxidation of castor oil (CO) with peracetic and performic acids formed *in situ*. We were particularly concerned with the stabilization of oxirane ring. The presence of the inert solvent in the reaction mixture appeared also to stabilize the epoxidation reaction and minimize the side reactions, such as the opening of the epoxy ring, especially at higher temperatures [2]. Since the ion exchange resin (IER) has the same effect as a solvent, it is reasonable to assume that the epoxidation of CO may be carried out in bulk with a high SE, i.e. in the absence of an inert solvent, as we have studied in the present work. In this work, we compared the kinetics of epoxidation of castor oil with peracetic and performic acid generated *in situ* in the presence of cation exchange resin as the catalyst. The measured kinetic parameters were the rate constant at 30°C, 50°C, 70°C, 85°C and activation energies.

EXPERIMENTAL DETAILS

Materials

Castor oil was obtained from Mandal Oil Ltd. (Jhargram, West Bengal, India). Glacial acetic acid, 100% (AR Grade), Formic acid (95-97%), aqueous hydrogen peroxide (~30 wt %) and iodine trichloride were procured from Merck India Ltd. (Mumbai, Maharashtra, India). Ion exchange resin (Amberlite IR-120) obtained from SISCO Research Laboratories (Mumbai, India). HBr in acetic acid was obtained from SISCO Research Laboratories (Mumbai, India) and then diluted with glacial acetic acid to prepare 0.1(N) HBr.

Methods

The percentage of oxirane oxygen was determined by the direct method with hydrobromic acid solution in acetic acid. Iodine value was obtained using the Wij's method [3] and glycol content was determined by the method reported by May [4].

Experimental setup

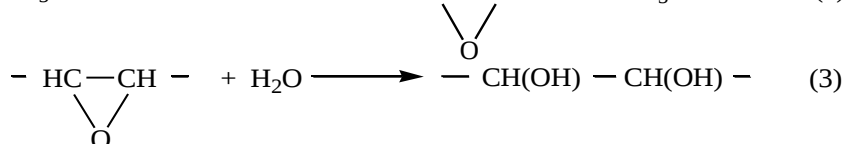
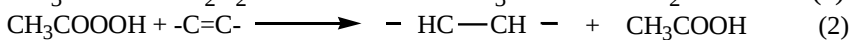
The Epoxidation reactions were carried out in a fully baffled mechanically agitated contactor made of glass (6.5 cm i.d. and 250 cm³ capacity), equipped with a 2 cm-diameter six-bladed glass disk turbine impeller, and reflux condenser. The contactor assembly was immersed in a thermostatic water bath, with temperature control within $\pm 1^\circ\text{C}$.

Experimental procedure

The epoxidation method reported in our previous paper [5] was followed in the present work. The required amount of CO was placed in the contactor and suitable amount of acetic/formic acid and cation exchange resin catalyst were added, and the mixture was stirred for 30 min. Then 12.5 g of 30% aqueous hydrogen peroxide was added drop-wise at a rate such that it was completed in half an hour and the reaction was continued further for desired time duration. Samples were withdrawn intermittently, the first being taken after an hour considering the completion of hydrogen peroxide addition as zero time. The collected samples were then extracted with diethyl ether, washed with water until they were acid free and analysed for oxirane content and iodine value.

RESULTS AND DISCUSSION

In situ epoxidations were carried out with 1:0.5:1.5 molar ratio of ethylenic unsaturation: organic acid: hydrogen peroxide. The detailed mechanism of the epoxidation with *in situ* formed peracetic acid is as follows [2,6]:



While organic acid is converted to peracetic acid and then regenerated, hydrogen peroxide is consumed in the process. So an excess of 50 mol % relative to ethylenic unsaturation was considered reasonable. Ion exchange resin was added in amount of 16wt % of the oil phase. Two series of epoxidations at four different temperatures (30°C, 50°C, 70°C and 85°C) were carried out, one with the peracetic acid and the other with performic acid.

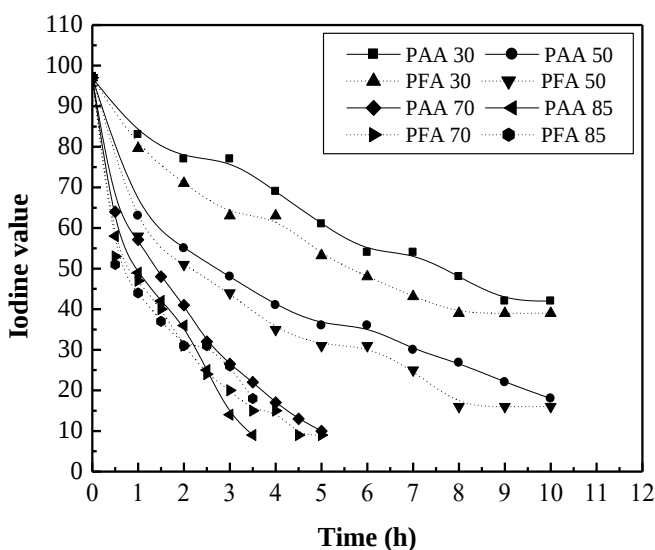
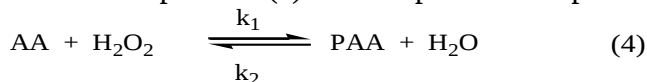


Figure 1: Variation of iodine value with time during epoxidation of CO with peracetic and performic acids.

Variations of iodine values with reaction time for epoxidation with peracetic and performic acid at four different temperatures is presented in Figure. 1. Iodine value is a measure of the concentration of ethylenic unsaturation in the oil. Figure. 1 shows that for the epoxidation with peracetic acid, the conversion of ethylenic unsaturation is very fast at 85°C, final oxirane oxygen content being reached after 3.5 hours and at 70°C after 10 hours. At 50°C, a significant ethylenic unsaturation concentration was found to be present even after 10 hours. Epoxidation with performic acid followed the same

trend. It appeared however, that with performic acid somewhat higher oxirane oxygen content was obtained at 70°C than at 85°C. Figure. 1 shows that the epoxidation of castor oil as followed by the conversion of ethylenic unsaturation is faster in the presence of performic acid than in the presence of peracetic acid at 30, 50, and 70°C, but at 85°C the peracetic acid becomes more efficient than performic acid. The same conclusion is reached when the change in the oxirane oxygen content with time is compared for the two acids and temperatures. Using performic acid, a higher relative conversion to oxirane is achieved at 70°C than at 85°C. The maximum relative conversion to oxirane at 85°C is higher with peracetic acid compared to performic acid, however the rate to achieve it moreover same with both the peracids. The conclusion is that at lower temperatures (30°C, 50°C, and 70°C) performic acid is more efficient for *in situ* epoxidation, while at higher temperature (85°C) peracetic acid is at least as good, if not better. We believe that due to the very high activity of the formic acid at higher temperature, some hydrogen peroxide is decomposed, and the system is depleted of oxygen fairly early, which slows down the reaction. In other words this temperature is very high for performic epoxidation. Thus, for the kinetic studies, only the initial stage of the reaction was taken into account.

In situ epoxidation is characterized by two main reactions involving formation of peracids (d) and formation of epoxides (e) as exemplified with peracetic acid:



where AA is acetic acid; PAA -peracetic acid, EU- ethylenic unsaturation and OO- oxirane oxygen and k_1 , k_2 , and k_3 are reaction rate constants. The first reaction is the acid catalysed formation of peracetic (or performic) acid, while the second is uncatalysed epoxidation of unsaturated castor oil with peracetic acid. At the same time, the side reactions, such as oxirane oxygen opening (3) is shown above.

Kinetics of epoxidation

The results of the work presented above were used to determine the reaction order and also activation energies of the epoxidation reactions carried out with peracetic and performic acids formed *in situ*. The general form of the rate equation for the conversion of ethylenic unsaturation by peracetic acid may be written as:

$$-d[\text{EU}]/dt = k_3 [\text{EU}]^{n_1} [\text{PAA}]^{n_2} \quad (6)$$

Where [EU] and [PAA] are molar concentration of ethylenic unsaturation and peracetic or performic acid, respectively; k_3 is rate constant (see eq. 6), n_1 and n_2 are the reactions order to the ethylenic unsaturation and peracetic or performic acid. It is assumed that the reaction of epoxidation is pseudo first order with respect to the ethylenic unsaturation conversion, and if the rate constant is defined as $k = k_3 [\text{PAA}]$, the rate equation for pseudo-first order in [EU] can be written as:

$$-d[\text{EU}]/dt = k[\text{EU}] \quad (7)$$

The rate data for the epoxidation with peracetic acid are fitted in the above equation.

The same equation is used for fitting kinetics data for epoxidation with performic acid (PFA), except that the rate constant in that case is defined as $k = k_3 [\text{PAA}]$. Hence, after integration, equation (7) becomes:

$$\ln\{[\text{EU}]_0/[\text{EU}]\} = k.t \quad (8)$$

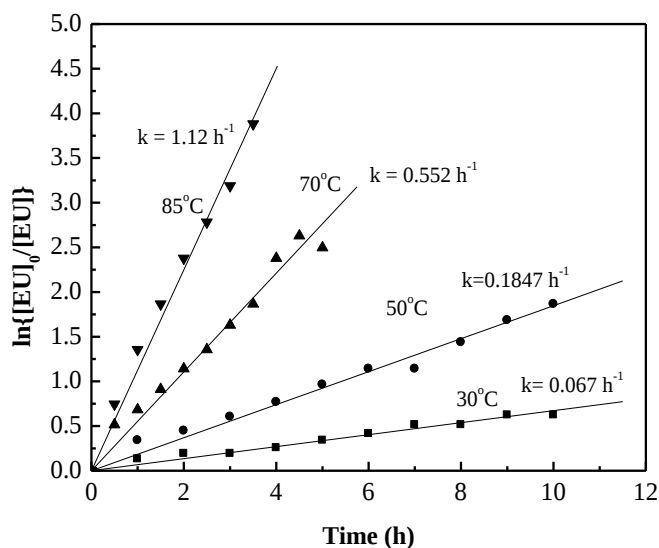


Figure 2: Determination of the pseudo-first order rate constants for epoxidation of CO with peracetic acid at 30°C, 50°C, 70°C, and 85°C.

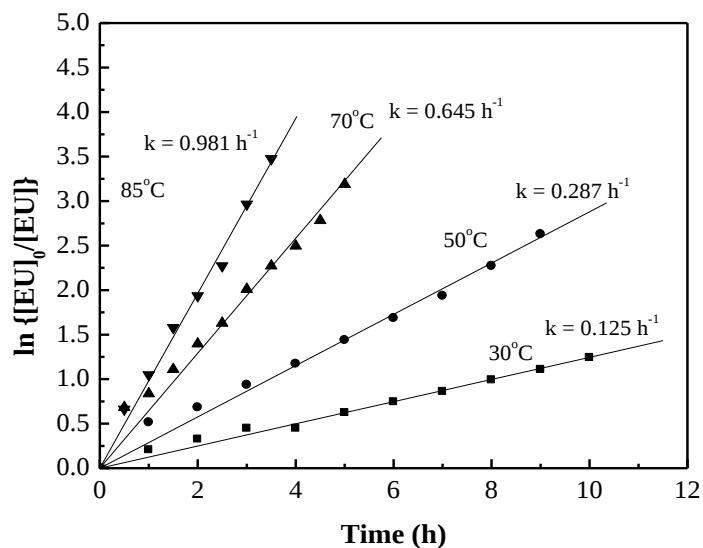


Figure 3: Determination of the pseudo-first order rate constants for epoxidation of CO with performic acid at 30°C, 50°C, 70°C, and 85°C.

The slope of the plot in $\ln([EU]_0/[EU])$ vs. reaction time points to the pseudo first order reaction. The results of the rate constant determinations for epoxidations with peracetic and performic acids at four temperatures are shown in Figures. 2 and 3, respectively. Straight lines in Figures. 2 and 3 indicate that the epoxidation with both acids is the pseudo first order with respect to the ethylenic unsaturation. Activation energy for the epoxidation process was determined from the rate constants at different temperatures, assuming Arrhenius type temperature dependence. The activation energies for epoxidation with both peracetic and performic acids were calculated from the slope of the $\ln(k)$ vs. $1/T$ dependencies (Figure. 4). The value of the activation energy for peracetic acid (48.2 kJ/mol) is higher than that for the performic acid (35.4 kJ/mol). Our values for activation energy of epoxidation with peracetic and performic acid are lower than those reported for epoxidation of palm oil methyl esters with peracetic acid of 63 kJ/mol or epoxidation of natural rubber with performic acid of 55 kJ/mol [2,7].

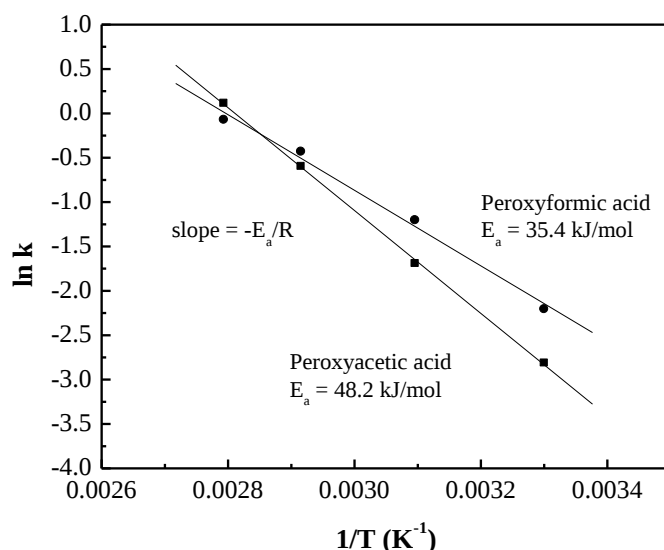


Figure 4: Determination of activation energy for epoxidation of castor oil with peracetic acid and performic acid.

CONCLUSIONS

Epoxidation of castor oil was carried out with *in situ* formed peracetic and performic acids as the oxidizing agents. A general rate equation was proposed and the kinetic parameters were determined in the temperature range of 30- 85°C. Activation energies of the epoxidation were found to be 48.2 kJ/mol for the peracetic acid and 35.4 kJ/mol for the performic acid. It was found that extent of the side reaction is negligible with peracetic acid in the entire temperature range and somewhat higher with performic acid at 85°C.

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