

Yield in Epoxidation Reactions

Two new methods have been developed for improving yields in epoxidation reactions—one uses partially preformed acetic acid and the other, agitation control

IN MANY EPOXIDATION procedures, yields are lowered because substantial amounts of epoxide product are converted to cleavage products. Therefore, to improve such yields by reducing cleavage, two methods were developed—in one partially preformed peracetic acid is used, and in the other agitation is controlled. Soybean oil was used as the model olefin, but the results are believed applicable to other water-insoluble olefins such as alkyl oleates.

Experimental Procedure

Partially Preformed Peracetic Acid Method. In conventional in situ peracetic acid epoxidation (2), full quantities of acetic and sulfuric acids are present in the reaction mixture from the start, thus giving maximum opportunity for acid cleavage. Also, peracetic acid is not formed until hydrogen peroxide is added. This prolongs the reaction and results in additional cleavage. In the new method described here, acetic and sulfuric acids are mixed with hydrogen peroxide prior to the reaction, in quantities similar to the in situ method—1.18 moles of acetic acid, 2.35 moles of 51.5% hydrogen peroxide, and 4.63 grams of 49% sulfuric acid (equivalent to 1.0% of sulfuric acid by weight of the acetic acid and hydrogen peroxide). After standing for 20 hours at room temperature to reach equilibrium, the mixture analyzed (3) 20% peracetic acid (about 25% conversion of the hydrogen peroxide) and 25% hydrogen peroxide.

This solution containing a 15% excess of hydrogen peroxide was then uniformly added over a 2-hour period to 400 grams of soybean oil (iodine No. 129.5, 2.04 moles double bond) contained in a 1-liter three-necked flask fitted with a mechanical stirrer, reflux condenser, thermometer, and addition tube. During and after addition, the mixture was stirred continuously at a constant rate and temperature was maintained at 57° C. Samples of 25 ml. were removed each hour from the time that addition of the partially preformed peracetic acid was completed.

These samples were placed in separatory funnels, containing 25 ml. each of

distilled water and hexane, and shaken. The hexane layer was again washed with 25 ml. of water and then brought into contact with 1 to 2 grams of calcium hydroxide for about 2 to 4 hours, dried over magnesium sulfate, and filtered through a fritted-glass funnel filter having a Hyflo Super-Cel (Johns Manville) precoat. The hexane was stripped from the oil by heating at 50° to 70° C. for 1 hour under high vacuum. Oxirane oxygen was determined using hydrobromic acid in glacial acetic acid (7). Iodine numbers were determined by the Hanus method.

In Situ Method. The method of preparation was identical with that for the preformed peracetic acid method, except that sequence of reagent additions was changed—acetic and sulfuric acids were added to the soybean oil in the reaction flask, and then the hydrogen peroxide was uniformly added over a 2-hour period.

Agitation Control. Using the partially preformed epoxidation method previously described, epoxidations were carried out using various stirring rates. Half-moon shaped borosilicate glass

stirring blades, 75 mm. long, were raised 20 mm. from the bottom of a 1-liter three-necked flask. Agitation rates were periodically checked with a tachometer, and in high speed runs, Teflon blades of similar dimensions were used to prevent breakage.

Discussion of Results

Partially Preformed Peracetic Acid Method. After addition is completed, both cleavage and epoxidation reactions proceed at approximately the same rate for both the in situ and the partially preformed method. Maximum oxirane oxygen values are reached when the epoxidation rate equals the cleavage rate. For the partially preformed method, higher oxirane oxygen values result partially from additional oxirane formation during the addition period, as a result of higher peracetic acid concentration, and partially from reduced acid cleavage during the early stages of the reaction. Also, higher oxirane oxygen values are obtained when epoxidation is continued to an iodine number of 4.

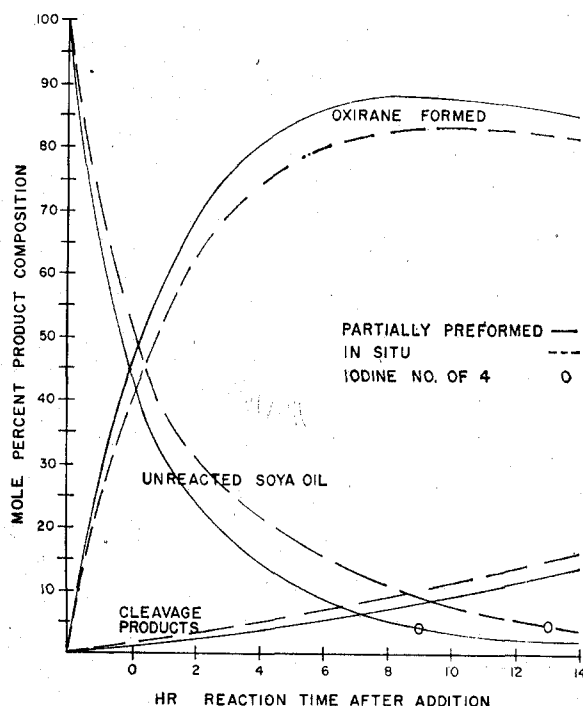


Figure 1. The partially preformed peracetic acid epoxidation method yields a product having higher oxirane content

Epoxidation Yield Data

(AcOH/H₂O₂ mole ratio, 0.5; stirring rate, 275 r.p.m.)

Temp., ° C.	50	57						62		67	
H ₂ SO ₄ concn., %	1	0.75	1.0		1.4	1.8		1.0		1.0	1.4
At max. oxirane oxygen			P	I	P	P	I	P	I		
Oxirane oxygen, %	6.32	6.26	6.55	6.08	6.57	6.59	6.20	6.41	5.77	6.54	6.58
Iodine No.	10.4	10.0	5.7	7.2	6.0	1.1	5.4	6.0	9.4	4.5	2.1
Oxirane, mole % ^b	84.7	84.0	88.2	82.5	88.4	89.6	84.5	86.7	78.9	88.4	89.1
Unreacted, mole % ^b	8.8	8.4	4.9	6.2	5.1	0.9	4.6	5.1	8.1	3.8	1.8
Cleavage, mole % ^b	6.5	7.4	6.9	11.3	6.5	9.5	10.9	8.2	13.0	7.8	9.1
Stirring after addition, hr.	11	9	8	10	6	7	6	6	6	4	4
At iodine No. 4											
Oxirane oxygen, mole %	c	5.90 ^d	6.50	5.95 ^d	6.48	6.58	6.19	6.36	5.40	6.50	6.58
Cleavage, mole %	c	15.0 ^d	8.6	14.5 ^d	8.5	7.5	12.0	10.0	20.0	8.5	7
Stirring after addition, hr.	12	14 ^d	9	13 ^d	7	6	6.5	7.5	9.5	4.5	3

	Mole Ratio AcOH/H ₂ O ₂ ^e			Method ^f		Stirring Rate ^f , R.P.M.				
	0.40	0.45	0.50	2 step	1 step	70	140	275	550	900
At max. oxirane oxygen										
Oxirane oxygen, %	6.50	6.48	6.57	6.54	6.57	6.56	6.68	6.57	6.15	5.95
Iodine No.	6.1	5.4	6.0	5.8	6.0	4.9	2.7	6.0	9.2	12.6
Oxirane, mole % ^b	87.6	87.3	88.4	88.0	88.4	88.4	90.3	88.4	83.0	80.3
Unreacted, mole % ^b	5.2	4.5	5.1	4.9	5.1	4.2	2.3	5.1	7.8	10.7
Cleavage, mole % ^b	7.2	8.2	6.5	7.1	6.5	7.4	7.4	6.5	9.2	9.0
Stirring after addition, hr.	10	9	6	7	6	12	9	6	6	5
At iodine No. 4										
Oxirane oxygen, mole %	6.40 ^d	6.40	6.48	6.52	6.50	6.48	6.68 ^d	6.48	5.60	4.40
Cleavage, mole %	9.5 ^d	9.5	8.5	8.5	8.5	8.0	6.5 ^d	8.5	18.6	32.7
Stirring after addition, hr.	14 ^d	10.5	7	9	7	12	8 ^d	7	11	13

P = partially preformed method; I = in situ. ^a By wt. of acetic acid and 50% H₂O₂. ^b Calculated using equations based on the assumption that the only cleavage product is the hydroxyacetoxy derivative. ^c Not determined. ^d Estimated. ^e Temp., 57° C.; H₂SO₄ concn., 1.4%; agitation, 275 r.p.m. ^f Temp., 57° C.; H₂SO₄ concn., 1.4%; AcOH/H₂O₂ mole ratio, 0.5.

Higher temperatures and sulfuric acid concentrations reduce reaction time and result in higher maximum oxirane content with less cleavage—e.g., at 67° C. using 1.4% sulfuric acid, 6.58% oxirane oxygen is obtained at an iodine number of 2.1. For sulfuric acid, however, less oxirane oxygen was obtained at 0.75% acid, but little difference was obtained over the concentration range of 1.0 to 1.8%.

When acetic acid-hydrogen peroxide molar ratios of 0.33 to 0.75 were used with 1% sulfuric acid, the higher acetic acid concentration caused excessive cleavage. The low concentration decreased the reaction rate so that after 12 hours, the iodine number had been reduced to only 7.5. In the 0.4 to 0.5 range, higher molar ratios should be used when short reaction times are desired. The lower values should be used for low acetic acid usage.

Below the 0.4 molar ratio, the detonable region for acetic acid-hydrogen peroxide mixtures is approached (4), and preparation of a detonable mixture through error can be avoided by withholding some of the hydrogen peroxide and sulfuric acid in the initial mixture. These can then be added following the preformed peracetic acid. The total addition time for this two-step method is the same as for the one-step method.

The two-step method differed in that 1.51 moles of hydrogen peroxide and 4.85 grams of 49% sulfuric acid was used instead of the usual amounts. This mixture containing the acetic acid was added to the soybean oil over a period of 78 minutes, and then 0.84

remaining moles of hydrogen peroxide and 1.66 grams of 49% sulfuric acid were added over a period of 42 minutes. Other than a slightly lower reaction rate for the two-step method, the two procedures differed but little.

Agitation Control. Contrary to expectation, mild agitation produces highest epoxide oxygen. This effect is caused mainly by a sharp increase in cleavage when agitation is unduly increased. Also, when agitation is higher or lower than optimum, both epoxidation rate and epoxide yield decrease. These results can be explained by considering cleavage as a heterogeneous two-phase reaction and epoxidation as a homogeneous single-phase reaction.

Cleavage is catalyzed by sulfuric acid which remains in the aqueous phase. Thus it may be expected that cleavage is a heterogeneous reaction occurring at the interface of the aqueous and oil phases. Increased agitation, therefore, increases cleavage by increasing interfacial area. This theory is supported by Figure 1 which shows that cleavage rate is constant and independent of epoxide concentration. The reaction is thus of zero order with respect to epoxide concentration. Such behavior is typical of heterogeneous reactions.

With mild agitation, decreased epoxidation rates can probably be explained by a sequence of events occurring in the two-phase epoxidation—i.e., peracetic acid formed in the aqueous phase (step 1) is extracted into the oil phase (step 2) where it reacts with the olefin (step 3). Lastly, regenerated acetic acid is extracted into the aqueous phase (step 4).

If agitation is sufficient to maintain steps 2 and 4, at a sufficiently high rate, steps 1 or 3, which are homogeneous, are controlling. However, if agitation is decreased so that transfer of peracetic acid to the oil phase and acetic acid to the aqueous phase is reduced, steps 2 or 4 become rate controlling, and epoxidation rate is decreased because the peracetic acid concentration in the oil phase is reduced. Thus, the reaction is prolonged and more opportunity for cleavage results.

With vigorous agitation, yield is also reduced. Besides consuming epoxide, cleavage also consumes acetic acid, giving a less favorable equilibrium in its reaction with hydrogen peroxide. Therefore peracetic acid concentration in the aqueous phase is reduced; this also reduces epoxidation rate.

Under the conditions used, the optimum rate of about 140 r.p.m. is quite mild. Globules are easily seen in the agitated mixture and the rate is just sufficient to prevent the phases from layering.

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