

Epoxidation of Soybean Oil by the Methyltrioxorhenium- $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}_2$ Catalytic Biphasic System

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ABSTRACT: We studied the methyltrioxorhenium (MTO)- $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}_2$ biphasic system for epoxidizing soybean oil. The reactions were optimized (reactant ratio, time, and temperature), which resulted in a better performance (higher conversion and selectivity) than those described in the literature. Total double-bond conversion and 95% selectivity were obtained in 2 h at room temperature. Furthermore, it was possible to reach desired epoxidation degrees by changing the oxidant and MTO amounts. The rhenium-epoxidized soybean oil remained stable in the absence of stabilizers for up to 30 d when stored at mild conditions.

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KEY WORDS: Epoxidation biphasic system, hydrogen peroxide, methyltrioxorhenium, selective epoxidation, soybean oil.

Vegetable oils are an interesting renewable source for producing useful chemicals and new materials (1,2). Nevertheless, their reactivities need to be enhanced by introducing additional functionalities into the FA molecules. Therefore, a variety of chemical and biochemical reactions have been used for their conversion into value-added products.

Among those reactions, epoxidation plays an important role, since the epoxidized oil, acids, or their esters can be used to prepare different industrially relevant compounds such as plasticizers and stabilizers of PVC resins, polyesters, polyurethanes, epoxy resins, and surface coatings.

Partially epoxidized soybean and linseed oils are more suitable than fully epoxidized ones as reactive diluents for alkyd resins. They are homogeneous liquids with low viscosities and melting points below room temperature. They react through their epoxy groups in epoxy formulations and dry in alkyd formulations through their remaining carbon-carbon double bond. They are attractive reactive diluents for low-volatile organic-compound alkyl and epoxy formulations. Thus, controlling the epoxidation degree allows fine-tuning of viscosity, drying, and compatibility characteristics as well as other properties.

Usually the processes that have been used to prepare epoxidized vegetable oils involve peroxycarboxylic acids, especially the peracetic or performic acids because of their easy availability, low price, and reasonable stability at ordinary temperature (3–5). Nevertheless, these processes are time-consuming, have low selectivity, have hazards associated

with handling the peracids in industrial scale, and present effluent problems (6). In order to overcome these problems and to achieve an easy control of the epoxidation degree, new epoxidation systems continue to be intensively investigated (6–10).

Recently, there have been reports on the use of the methyltrioxorhenium (MTO)- H_2O_2 system in the epoxidation of soybean oil (11,12). The reactions were carried out using concentrated H_2O_2 (30%) and nitrogen-containing bases such as pyridine.

In the present work, we studied the epoxidation of the soybean oil using the biphasic system MTO- $\text{H}_2\text{O}_2/\text{CH}_2\text{Cl}_2$. Reactions were carried out at different temperatures, times, rates of H_2O_2 addition, and proportions of reactants. The results were compared with those obtained with the peracetic system. The epoxidized soybean oil stability was also examined.

MATERIALS AND METHODS

Soybean oil was supplied by CEVAL (Porto Alegre, Brazil) and used without purification. It was characterized by IR, ^1H and ^{13}C NMR, and AOCS standard methods (13). The data obtained were acid value = 0.8 (AOCS Ca 3a-63), PV = 0.9 (AOCS Cd 8-53), and iodine value = 137 (AOCS Cd 1-25). On average, soybean oil has a molecular weight of about 868 g/mol and contains about 4.7 double bonds per TG molecule, both values determined by the ^1H NMR method described by Miyake (14). The H_2O_2 (30%; Merck, Darmstadt, Germany) was diluted to 10% in water just before use. MTO was prepared as described by Herrmann (15). All other solvents were commercial grade and were used without further purification.

The ^1H and ^{13}C NMR spectra were recorded on Varian VXR 200 equipment (Palo Alto, CA), using CDCl_3 as solvent. The reaction conversion was monitored by the area decrease of the double-bond hydrogen signals in the 4.5–5.5 ppm region (14). The degree of epoxidation was calculated by integrating the signals in the 2.9–3.1 ppm region of the ^1H NMR spectra, corresponding to the *cis* epoxy hydrogens. The results were in good agreement with those of the oxirane oxygen standard method (AOCS Cd 9-57). The presence of signals at 53.4 and 55.9 ppm in the ^{13}C NMR spectra was assigned to the *cis* epoxy carbons (16).

The IR spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer (Madison, WI). Samples were prepared as thin films on KBr disks. The appearance of two bands at 825 and 845 cm^{-1} indicates the presence of an oxirane ring (17,18).

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The epoxidized oil viscosities were measured at $20 \pm 0.1^\circ\text{C}$ by the capillary method, using the starting oil as the standard (19).

Epoxidation with preformed peracetic acid. The epoxidation reaction with preformed peracetic acid was carried out as described by Yadav and Satoskar (6). A solution of preformed peracetic acid was prepared by mixing 286 mL (5 mol) glacial acetic acid, 1.7 mL concentrated sulfuric acid, and 45 mL (0.5 mol) 30% aqueous hydrogen peroxide at room temperature. After 20 h, the pH was raised to 5 with sodium acetate. The content was then filtered to remove sodium sulfate. The peracetic acid prepared (48 mL) was added to soybean oil (10 g, 54 mmol of double bonds) during 30 min at room temperature with vigorous stirring. Afterward, the temperature was raised to 45°C for 1 h. The solution was washed, extracted with an organic solvent, and the epoxidized oil dried under vacuum.

Epoxidation with the MTO- $\text{H}_2\text{O}_2/\text{CH}_2\text{Cl}_2$ biphasic system. In a typical epoxidation reaction, 30 g (34.6 mmol, 162.5 mmol of double bonds) of soybean oil was dissolved in 30 mL CH_2Cl_2 followed by the addition of MTO and H_2O_2 (10% in water) dropwise to the solution. The amounts of MTO and H_2O_2 were calculated according to the double-bond content of the soybean oil. The mixture was vigorously stirred at room temperature. After the desired time, a sodium bisulfite solution (20%, wt/vol) was added and the mixture stirred for 30 min. The organic phase was separated and washed with a saturated NaCl solution. Then it was filtered through an alumina basic column using a (1:1) mixture of hexane and ethylacetate as eluent. The epoxidized oil was dried under vacuum. Catalytic reactions were performed at least three times, in independent experiments, and presented good reproducibility (error <5%).

RESULTS AND DISCUSSION

MTO combined with H_2O_2 is a very active and selective catalytic precursor for the epoxidation of normal olefins, functionalized or not (20), and high molecular weight poly(butadiene) (21). It can be used in homogeneous or biphasic systems (22). The advantages of using biphasic systems are the easy

separation of products and protection of the sensitive epoxides that remain in the organic phase, where they are not in constant contact with the aqueous acidic phase. In some cases, when the epoxide is extremely sensitive to acidic media, the reaction may be performed using bipyridine (12,22).

In our work, we used ^1H NMR to quantify the double-bond and epoxy contents and ^{13}C NMR to verify the formation of side products formed by the opening of epoxy ring. The NMR spectroscopy has been found to be an effective tool for direct, rapid, nondestructive, and automatic oil characterization (13,23). The data obtained presented good reproducibility and agreement with the values determined by standard AOCS methods.

The results obtained with this system are shown in Table 1. In the first reaction, the molar proportions of oxidant and MTO were chosen so that a fully epoxidized soybean oil could be obtained. However, the conversion and epoxidation degrees obtained were not satisfactory. In further reactions, better results were obtained, increasing the time (reaction 2) and the temperature (reaction 3). Nevertheless, higher temperatures are usually not suitable owing to the possibility of opening the epoxy ring.

Therefore, in reaction 4 the same conditions as reaction 2 were used, but the addition of oxidant was made slowly during 30 min and a better result was achieved. Bands characteristic of the hydroxyl group were not observed in any of the IR and ^1H and ^{13}C NMR spectra, showing that this system is very selective.

As mentioned before, there are literature reports on the soybean oil epoxidation using MTO systems (11,12). In these papers, the authors used concentrated H_2O_2 (30%) and nitrogen bases to protect the epoxy ring, obtaining a fully epoxidized oil after 7 h. In our study, however, we achieved the same result using milder conditions: a lower H_2O_2 concentration (therefore decreasing handling hazards), a reaction time of 2 h, and an absence of any Lewis base.

Another characteristic of this system is the possibility of tuning the degree of epoxidation, as can be seen in reactions 5–9, Table 1, which is an advantage when partially epoxidized soybean oil is desired. By lowering the MTO proportion and keeping 100 mol% H_2O_2 (reaction 5), selectivity decreased dramatically. This is an indication of the occurrence

TABLE 1
Epoxidation of Soybean Oil with the MTO- $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}_2$ System

Reaction	H_2O_2 (mol%)	MTO (mol%)	Time (h)	Conversion ^a (%)	Epoxidation (%)	Selectivity ^a (%)
1	100	1	1	72 ± 1	68 ± 1	94
2	100	1	2	90 ± 1	82 ± 2	91
3 ^b	100	1	1	92	84	91
4 ^c	100	1	2	100	95 ± 5	95
5 ^c	100	0.2	2	38 ± 2	25 ± 3	63
6 ^c	70	0.7	2	70 ± 3	64 ± 4	91
7 ^c	50	0.5	2	48 ± 1	45 ± 1	95
8 ^c	30	0.3	2	29 ± 1	28 ± 1	96
9 ^c	20	0.2	2	16 ± 1	15 ± 1	94

^aConversion = amount of double bonds converted; selectivity = amount of epoxide formed/amount of double bonds converted, calculated by ^1H NMR, 5% of incertitude.

^bReaction carried out under reflux.

^cSlow addition (30 min) of hydrogen peroxide. MTO, methyltrioxorhenium.

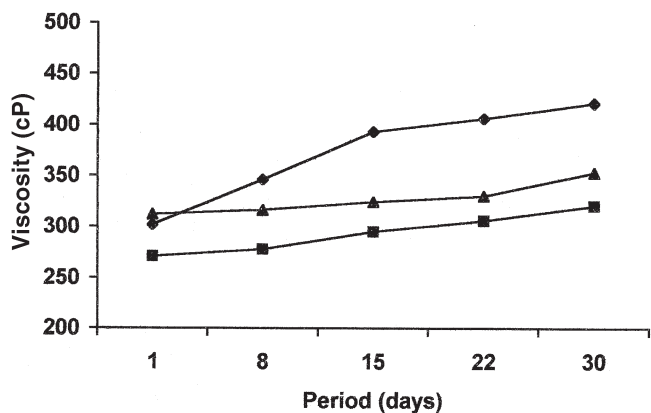


FIG. 1. Viscosity change of the rhenium-epoxidized soybean oil during 30 d when exposed to light at room temperature (◆), protected from light at room temperature (▲), and at 10°C (■).

of side reactions. On the other hand, when both the MTO and H_2O_2 proportions were reduced (reactions 6–9), lower epoxidation degrees could be easily obtained with good selectivity.

Soybean oil epoxidation with a preformed peracetic acid was carried out for comparison. The best result (91% of conversion and 83% of selectivity) was achieved after only 6 h at 35°C.

The degradation of epoxidized vegetable oils can be accelerated when they are exposed to heat and light, especially in the presence of traces of metals. In order to investigate whether the presence of remaining traces of rhenium could favor the degradation process, we monitored for 30 d the acid value, PV, epoxidation degree, and viscosity of fully epoxidized soybean oils kept under different conditions in the absence of any stabilizer. The epoxidized oils were stored three different ways: exposed to light at room temperature, protected from light at room temperature, and at 10°C.

The acid value, the PV, and the epoxidation degree did not change significantly during the period at any of the studied conditions. In contrast, oil viscosities increased for the three samples, mainly for the one kept in the presence of light, as can be seen in Figure 1. The results showed that the rhenium-epoxidized oil is very stable when stored in mild conditions, especially if protected from light.

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