Grasas y Aceites
Vol. 53. Fasc. 2 (2002), 175-178

Reactivity of the biphasic trichloroacetonitrile-CH_2Cl_2/H_2O_2 system in the epoxidation of soybean oil

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RESUMEN

Reactividad del sistema bifásico tricloroacetonitrilo-CH_2Cl_2/H_2O_2 en la epoxidación del aceite de soja.

En el presente trabajo informamos sobre la epoxidación de aceite de soja mediante el sistema bifásico tricloroacetonitrilo-CH_2Cl_2/H_2O_2. La reacción fue realizada bajo condiciones de temperatura ambiente y, lo más importante, en condición no ácida, lo que evita la apertura del anillo oxirano. El aceite de soja fue caracterizado por infrarrojo y RMN de ^1H y ^{13}C. En dos horas se alcanzó una conversión máxima del 81% obteniéndose una selectividad del 86% en grupos epóxidos.

PALABRAS-CLAVE: Aceite de soja – Epoxidación – Nitrilo – Peróxido de hidrógeno - Sistema bifásico.

SUMMARY

Reactivity of the biphasic trichloroacetonitrile-CH_2Cl_2/H_2O_2 system in the epoxidation of soybean oil.

In this work we report on the epoxidation of soybean oil by the trichloroacetonitrile-CH_2Cl_2/H_2O_2 biphasic system. The reaction was carried out at room temperature and, most importantly, in non acid conditions which prevent the opening of the oxirane ring. The epoxidized soybean oil was characterized by infrared, ^1H and ^{13}C NMR. A maximum conversion of 81% was achieved in two hours with 86% of selectivity in epoxy groups.

KEY-WORDS: Biphasic system – Epoxidation - Hydrogen peroxide – Nitrile - Soybean oil.

1. INTRODUCTION

Vegetable oils represent an interesting renewable source for the production of useful chemicals and new materials (Baumann, 1988; Zahler, 1988; Biermann, 2000). Nevertheless, their reactivity needs to be enhanced by the introduction of additional functionalities into the fatty acid molecules. Therefore a variety of chemical and biochemical reactions have been used for their conversion to value-added products. Among those reactions, the epoxidation plays an important role. Usually the processes that have been used to prepare epoxidized vegetable oils involve peroxycarboxylic acids, specially the peroxyacetic or peroxyformic acids because of their easy availability, low price and reasonable stability at ordinary temperature. Nevertheless, these processes are time consuming, present low selectivity, have hazards associated with handling peroxyacids in industrial scale and also involve effluent problems. To overcome these problems, new systems continue to be intensively investigated (Martínez de la Cuesta, 1986, 1988; Ucciani, 1990; Sonnet, 1996; Yadav, 1997; Klaas, 1997; Foglia, 1998; Kozhevnikov, 1998; Sales, 2000).

The peroxycarboxymidic acids formed by the activation of nitriles by hydrogen peroxide seem not to have been used yet in studies of epoxidation of triglycerides, despite their good yields and performance in non-acid conditions for olefins. (Payne, 1961a, b; von Holleben, 1997, 2001). In the first step of the reaction mechanism, the nitrile and hydrogen peroxide react in mild alkaline medium leading to the formation of peroxycarboxymidic acid, which is a highly reactive species. It then immediately reacts either with the olefin (route A), leading to the respective epoxide and amide, or with another molecule of hydrogen peroxide (route B), yielding oxygen, water and amide, as shown in figure 1.

A theoretical study of the structural and electronic features of peroxyformic and peroxyformimidic acids suggested that the reactivity of both species would be quite similar and that the presence of an electron-withdrawing substituent should enhance the reactivity of the peroxycarboxymidic acid on the epoxidation. In fact, experimental studies showed that the reactivity of trichloroacetonitrile-CH_2Cl_2/H_2O_2 system was quite similar to *m*-chloroperbenzoic acid in the epoxidation of unfunctionalized olefins (von Holleben, 2001).

2. EXPERIMENTAL

All manipulations were carried out in air. Trichloroacetonitrile (Aldrich), Sodium Bisulfite (Baker), Potassium Bicarbonate (Merck) and H_2O_2 (30% w/v Riedel-de Haën) were used without further purification.

Infrared spectra were recorded as films on KBr disks on a Mattson Galaxy Series FTIR 3000 spectrophotometer. ^1H NMR spectra were obtained on a Varian VXR 200 spectrometer operating at 200

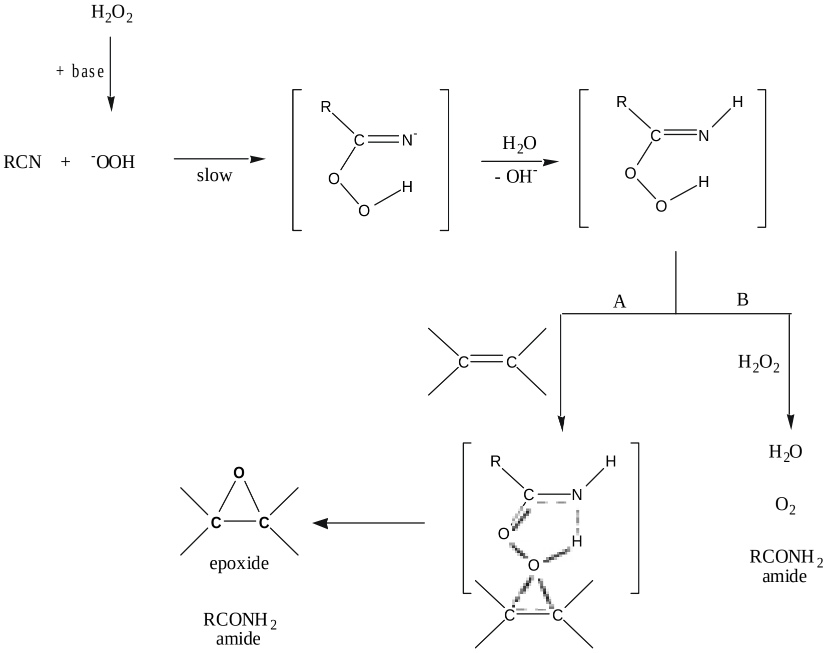

Figure 1
Proposed mechanism for the epoxidation of olefins by the nitrile-CH_2Cl_2/H_2O_2 system.

MHz at room temperature, using $CDCl_3$ as solvent. All chemical shifts are in ppm relative to TMS using the positive downfield convention.

In a typical epoxidation experiment, soybean oil (2 g, 10.8 mmol of double bonds) was dissolved in CH_2Cl_2 (2 mL). Separately, a solution of trichloroacetonitrile (1.12 mL, 10.8 mmol), CH_2Cl_2 (4 mL), water (2 mL), and $KHCO_3$ (0.216 mg, 2.16 mmol) was prepared and added to the soybean oil solution. The biphasic mixture was cooled to 0°C and H_2O_2 (10.8 mmol of a 30% solution in water) was added dropwise. The mixture was vigorously stirred at room temperature. To quench the reaction, a solution of sodium bisulfite (20% w/v) was added. At this point an emulsion was formed and it was extracted with 2 x 6 mL hexane. The organic layer was separated and the solvent was removed under vacuum. The aqueous solution was then filtrated and the trichloroacetamide was isolated.

The epoxidized soybean oil was characterized by the presence of the epoxide ring vibration at 825 cm^{-1} in the IR spectra (Gerbase, 2000; Gregório, 2000), two signals (2.9 and 3.1 ppm,) assigned to the epoxy group hydrogens in the ^{1}H NMR spectra (Miyake, 1998a, b) and two peaks (53.4 and 55.9ppm) attributed to the carbons of the epoxy groups in the ^{13}C NMR spectra (Gunstone, 1993). Bands characteristic of the hydroxyl group were not observed in any of the spectra.

The double bond content was determined by the integration of the olefinic hydrogen areas in ^{1}H NMR spectra. This value was normalized, dividing by the area per hydrogen (NF) (4.05-4.45 ppm) of the glycerol segment (Miyake, 1998a). The conversion (C) value was calculated using the following equation:

$$C(\%) = \frac{NDs - NDf}{NDs} x100 \quad (eq. 1)$$

where NDs and NDf are the double bond content of the starting and epoxidized oils, normalized.

The quantification of the epoxides was done by equation 2:

$$Epoxide = \frac{E/2}{NFxNDs} x100 \quad (eq. 2)$$

where E is the total epoxide area.

3. RESULTS AND DISCUSSION

The results of the soybean oil epoxidation using this system are presented in Table I and compared with those obtained with the pre-formed peroxyacetic acid method.

When the epoxidation reactions of the soybean oil were carried out under the same conditions used for unfunctionalized olefins (von Holleben, 1997) (entries 1-3), the maximum conversion found was 57% after 2 hours. The longest reaction (entry 3) showed a decrease in selectivity, suggesting the occurrence of the opening of the epoxy group, which is undesirable. This fact was confirmed by the presence of signals assigned to hydroxyl groups in the IR, ^{1}H and ^{13}C NMR spectra (Weber, 1995).

In an attempt to avoid emulsion formation, some reactions were performed using hexane as solvent, but the reactivity fell down significantly reaching a maximum of 23% of conversion. The better result obtained when dichloromethane was used as solvent can be explained by the fact that this solvent stabilizes the intermediate compound, decreasing the activation energy and, consequently, increasing the reaction rate (von Holleben, 2001).

It has been observed in the cyclohexene epoxidation that higher hydrogen peroxide concentrations favours the occurrence of route B (von Holleben, 1997). So, to prevent local high concentration of hydrogen peroxide in the reaction mixture, a slow hydrogen peroxide addition and vigorous stirring is desirable. In our experiment slightly better results were obtained when the hydrogen peroxide addition was made during a longer period (30 min).

Finally, a higher molar proportion of the reagents was employed with better results (entries 4-7). As can be seen in Table I, after two hours the best conversion (81%) was achieved with a good selectivity in epoxide (86%).

The soybean oil epoxidation with a performed peracetic acid was carried out in order to compare the previous results with those using this conventional method. As shown in Table I (entries 8 and 9) the best result (91% of conversion and 83% of selectivity) was achieved only after 6 hours and at the temperature of 35° C.

Table I

Soybean oil epoxidation with the trichloroacetonitrile-CH_2Cl_2/H_2O_2 system[a]

Entry	Addition of H_2O_2 (min)	T (h)	C (%)[b]	S (%)
1	5	1	46	98
2	5	2	57	95
3	5	6	56	86
4[c]	30	1	68	83
5[c]	30	2	81	86
6[c]	30	3	81	88
7[c]	30	6	80	84
8[d]	30	1	40	98
9[d]	30	6	91	83

[a] The reactions were carried out at room temperature, in dichloromethane, with a reagent molar ratio of 1:1:1:0.2 (soybean oil double bonds, trichloroacetonitrile, H_2O_2, $KHCO_3$).

[b] Conversion (C) = amount of double bonds converted; Selectivity (S) = amount of epoxide formed/amount of double bonds converted. Calculated from ^{1}H NMR spectra, with an incertitude of 5%.

[c] Reagent molar ratio of 1:2:2:0.4.

[d] Reaction conditions taken from Yadav, 1997.

4. CONCLUSIONS

The trichloroacetonitrile-CH_2Cl_2/H_2O_2 system reported here was active in the soybean oil epoxidation. This system has many advantages in comparison with the peroxyacetic system: it is much faster, the coproducts are not pollutant, it has a very good performance at room temperature and, most importantly, in non-acid conditions, preventing the opening of the epoxy group.

ACKNOWLEDGEMENTS

The authors thank the CAPES-Brazil for a fellowship.

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Recibido: Enero 2001
Aceptado: Octubre 2001