Organic Process Research & Development **2006**, *10,* 525–533

Optimization of the Technological Parameters of Epoxidation of Methallyl Chloride by Hydrogen Peroxide over TS-1 Catalyst

Agnieszka Wróblewska* and Eugeniusz Milchert

Institute of Organic Chemical Technology, Technical University of Szczecin, Pułaskiego 10, PL 70-322 Szczecin, Poland

Abstract:

The influence of the technological parameters on the course of epoxidation of methallyl chloride by a 30 wt % hydrogen peroxide over the titanium silicalite TS-1 catalyst has been investigated. The effects of temperature, molar ratio of methallyl chloride to hydrogen peroxide, concentrations of methanol (solvent) and TS-1 catalyst, and reaction time were determined. The optimisation of the technological parameters of methallyl chloride epoxidation was performed by the application of a statistical experimental design method based on a rotatable uniform design. The epoxidation process was described by using the following functions: the selectivity of transformation to 2-methylepichlorohydrin in relation to methallyl chloride consumed, the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, the conversions of methallyl chloride and hydrogen peroxide.

1. Introduction

In recent years, a growing interest in the application of zeolites as the catalysts of many reactions proceeding both in the liquid and the gas phase has been observed.[1] Especially, there is a challenge to develop new epoxidation methods, which would employ the zeolite catalysts and safer oxidants and generate little waste. Heterogeneous zeolite catalysts such as titanium silicalite can be more readily separated from the postreactive mixture than the traditional oxidation catalysts; additionally, they allow the achievement of higher selectivities to epoxide. The possibilities of the utilization of the excellent oxidative properties of the system, TS-1 catalyst/H_2O_2, comprise an impressive achievement. The titanium silicalite TS-1 has the MFI structure with the pore size of 0.56 nm × 0.53 nm. [2−5] A characteristic feature of the TS-1 is the presence of isolated tetrahedral coordinated titanium atoms in a silicalite structure. The TS-1 catalyst can activate hydrogen peroxide in the epoxidation reactions of different alkenes. The application of hydrogen peroxide in the epoxidation process is very attractive from the viewpoint of environmental protection and is economically reasonable. Moreover, hydrogen peroxide is cheap and commonly available, and the only byproduct associated with its use is water.

The epoxidation of allyl compounds over the titanium silicalite catalysts becomes an important method of preparation of epoxide compounds used in the manufacture of various commercial products. One of such compounds is 2-methylepichlorohydrin. This compound is often used in the synthesis of epoxide resins.[6,7] It plays an essential role in the modification of properties of other polymers and in the production of the composition for conductive coatings.[8,9] The epoxide resins based on 2-methylepichlorohydrin are used for the surface protection in the electric and building industries and for the manufacture of chemically resistant compositions. They are used as floor covering and in the production of fibre glass laminates. The photocured resins based on 2-methylepichlorohydrin are used in the production of paints,[10] drawing inks, lacquers, binders, glues, bindings agents for the mineral materials, fillers, and dyes.[11−13] The epoxide resin, based on 2-methylepichlorohydrin and bisphenol A and known under the trade mark of Epicote, was used for the production of glider hulls.[14] This resin is currently replaced by Epidian 52 (based on epichlorohydrin), which exhibits better strength properties. The linear thermoplastic polycarbonates modified by the polymers of 2-methylepichlorohydrin have been also prepared. They are utilized for the manufacturing of small and complex objects owing to their capabilities to fill in the cavities and covings.[15] Polyetherols and their esters based on 2-methylepichlorohydrin are used for the preparation of polyurethanes and polyurethane fibres with the hydrophilic, antistatic, and antistain properties.[16] 2-Methylepichlorohydrin is also used in the production of herbicides.[17]

The objective of this work was to determine the optimal technological parameters of epoxidation of methallyl chloride to 2-methylepichlorohydrin using 30 wt % hydrogen peroxide. We investigated the influence of the following technological parameters: temperature, molar ratio of methallyl chloride to hydrogen peroxide (MAC/H_2O_2), concentration of methanol (solvent), TS-1 catalyst loading, and reaction time. The optimisation of technological parameters was

---

* Corresponding author. Telephone: +48 914494875. Fax: +48 914494365. E-mail: Agnieszka.Wroblewska@ps.pl.

(1) Grigoropoulou, G.; Clark, J. H.; Elings J. A. *Green Chemistry* **2003**, *5*, 1.
(2) U.S. Patent 4,410,501, 1983.
(3) Meier, W. M.; Olson, D. H. *Zeolites* **1996**, *17*, 1.
(4) Huybrechts, D. R. C.; Buckens, P. L.; Jacobs P. A. *J. Mol. Catal.* **1992**, *71*, 129.
(5) Millini, R.; Massaro, E. P.; Perego, G.; Bellussi, G. *J. Catal.* **1992**, *137*, 497.
(6) Pat. EP 336724 B1, 1989.
(7) U.S. Patent 4,879,064, 1989.
(8) U.S. Patent 3,867,385, 1975.
(9) U.S. Patent 4,085,018, 1978.
(10) Uemura, I.; Yamada, K.; Sugiura, K.; Miyagawa, H.; Ueno, T. *Tetrahedron: Asymmetry* **2001**, *12*, 943.
(11) U.S. Patent 4,085,018, 1978.
(12) U.S. Patent 4,968,732, 1990.
(13) U.S. Patent 3,507,820, 1970.
(14) U.S. Patent 0074095 A1, 2002.
(15) U.S. Patent 4,168,368, 1979.
(16) U.S. Patent 5,112,940, 1992.
(17) U.S. Patent 5,510,318, 1996.

10.1021/op0600411 CCC: $33.50

performed with the utilization of a mathematical method of experimental design. The optimal parameters of the following functions have been determined: the selectivity of transformation to 2-methylepichlorohydrin in relation to methallyl chloride consumed, the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed, the conversions of methallyl chloride and hydrogen peroxide.

2. Experimental Section

2.1. Preparation of TS-1 Catalyst and its Characteristics. The TS-1 catalyst was prepared by a method of Thangaraj et al.[18] Tetraethyl orthosilicate (Fluka) and tetrabutyl orthotitanate (Fluka) were used as raw materials, whereas tetrapropylammonium hydroxide [TPAOH (Fluka)] was used as the template agent. The gel crystallization was carried out under the static conditions at 175 °C for 8 days. After the separation of crystals from the parent liquid, they were dried at 120 °C for 12 h followed by calcination in a furnace at 550 °C for 24 h. The calcinated catalyst was activated by washing with a 10% aqueous solution of ammonium acetate at 80 °C and recalcinated at 550 °C for 24 h.

The catalyst characterization was performed by using conventional techniques. The chemical composition of the catalyst was established by means of X-ray fluorescence spectroscopy (XRF) on a VRA 30 spectrometer. The catalyst contained 1.7 wt % Ti. The crystalline structure of the sample was confirmed by X-ray diffraction spectroscopy (XRD) using a Siemens D5000 diffractometer with Cu Kα radiation of wavelength 0.154 nm. The XRD pattern was obtained between 5° and 50° 2θ. The spectrum was identical with XRD patterns reported by Perego et al. and Thangaraj et al.[19,20] The FT-IR spectrum of the TS-1 catalyst was recorded on a JASCO FT/IR-430 instrument using the KBr pellet technique. The catalyst concentration in KBr amounted to 1.4 wt %. The absorption band at $\sim$960 cm^{-1} was found for this spectrum. The UV−vis spectrum was recorded on a SPECORD M40 instrument. The UV−vis spectrum reveals the characteristic band at wavelength of 220 nm, which confirms the incorporation of titanium into the crystalline structure of silica. There was no additional band associated with the presence of extraframework Ti. The morphology of the crystals was determined on the basis of the SEM micrographs taken on a JEOL JSM-6100 scanning microscope. The uniform orthorhombic crystallites with a size in the range 0.6−0.8 μm were prepared.

2.2. Epoxidation Procedure, Apparatus and Analytical Methods. The epoxidation of methallyl chloride was carried out using the following reagents: methallyl chloride (MAC) (98 wt %, Fluka), hydrogen peroxide (30 wt % aqueous solution, POCh, Gliwice), methanol (analytical grade, POCh, Gliwice), and TS-1 catalyst. The epoxidation was performed in a 7-cm^3 capacity stainless steel autoclave equipped with a PTFE insert. The autoclave was charged with reagents in the following order: MAC, hydrogen peroxide, methanol (solvent), and the catalyst. After closing the lid, the autoclave was fixed in a shaker holder and was placed in a temperature-controlled silicone oil bath (±0.1 °C) for the desired period. The mass balance was performed after completing the reaction. The following functions describing the process were calculated: the selectivity of transformation to 2-methylepichlorohydrin in relation to MAC consumed, the selectivity of transformation to organic compounds in relation to H_2O_2 consumed, and the conversion of MAC and H_2O_2.

The quantitative analyses of 2-methylepichlorohydrin were performed chromatographically by the external standard method. A Chrom 5 apparatus equipped with a flame-ionization detector (FID) and a column packed with Chromosorb 101 (60/80 mesh) were used. The column temperature was programmed in the following way: isothermally at 170 °C for 6 min, followed by an increase of temperature at the rate of 15 °C/min, isothermally at 200 °C for 10 min, and then an increase at the rate of 20 °C/min, isothermally at 225 °C for 14 min, and finally cooling to 170 °C. Hydrogen peroxide consumption was determined iodometrically.[21]

3. Results and Discussion

The side reactions that accompanied the main reaction occurred in the epoxidation of methallyl chloride with a 30 wt % solution of hydrogen peroxide over the TS-1 titanium silicalite catalyst and are presented in Scheme 1.

2-Methylepichlorohydrin (MEP) is susceptible to the attack of the nucleophilic molecules, such as water and methanol. As a result of the reaction with water 1-chloro-2-methylpropane-2,3-diol is formed, which undergoes a further hydrolysis with the formation of 2-methylglycerol. 2-Methylepichlorohydrin reacting with methanol forms 3-chloro-2-methoxy-2-methylpropane-1-ol and 1-chloro-3-methoxy-2-methylpropane-2-ol. Moreover, the hydrolysis of MAC to methallyl alcohol may proceeds in an aqueous medium. The MAC forms additional byproducts: 2-methylglycerol, 2-methylacrolein, and dimethallyl ether.

The determination of the influence of technological parameters on the course of the epoxidation process makes it possible to limit the amount of byproducts. The selected parameters were studied in the following ranges: temperature 20−120 °C, molar ratio of MAC/H_2O_2 1.0−5.0 mol/mol, methanol concentration 5−90 wt %, the TS-1 catalyst concentration 0.1−2.0 wt %, and reaction time 30−300 min. The optimisation of the technological parameters of MAC epoxidation was performed according to the mathematical method of experimental design using a rotatable-uniform design.[22−25] Experimental design and the calculations were

---

(18) Thangaraj, A.; Kumar, R.; Ratnasamy, P. *Appl. Catal.* **1990**, *57*, L1-L3.

(19) Perego, G.; Bellussi, G.; Corno, C.; Taramasso, M.; Buonomo, F.; Esposito, A. *Stud. Surf. Sci. Catal.* **1986**, *28*, 129.

(20) Thangaraj, A.; Kumar, R.; Mirajkar, S. P.; Ratnasamy, P. *J. Catal.* 1991, *130*, 1.

(21) Brill, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 141.

(22) Montgomery, D. C. *Design and analysis of experiments*; John Wiley & Sons: New York, 1976.

(23) Nalimow, W. W.; Czernowa, N. A. *Statystyczne metody planowania doœwiadczeñ*; WNT, Warszawa, 1967.

(24) Achnazarowa, S. £.; Kafarow, W. W. *Optymalizacja eksperymentu w chemii i technologii chemicznej*; WNT, Warszawa, 1982.

(25) Polañski, Z.; Górecka-Polañska, R. *Cadex: Esdet 2.2, Podrêcznik użytkownika*; Zakład Postêpu Technicznego i Wdrożeñ, Kraków, 1992.

Scheme 1

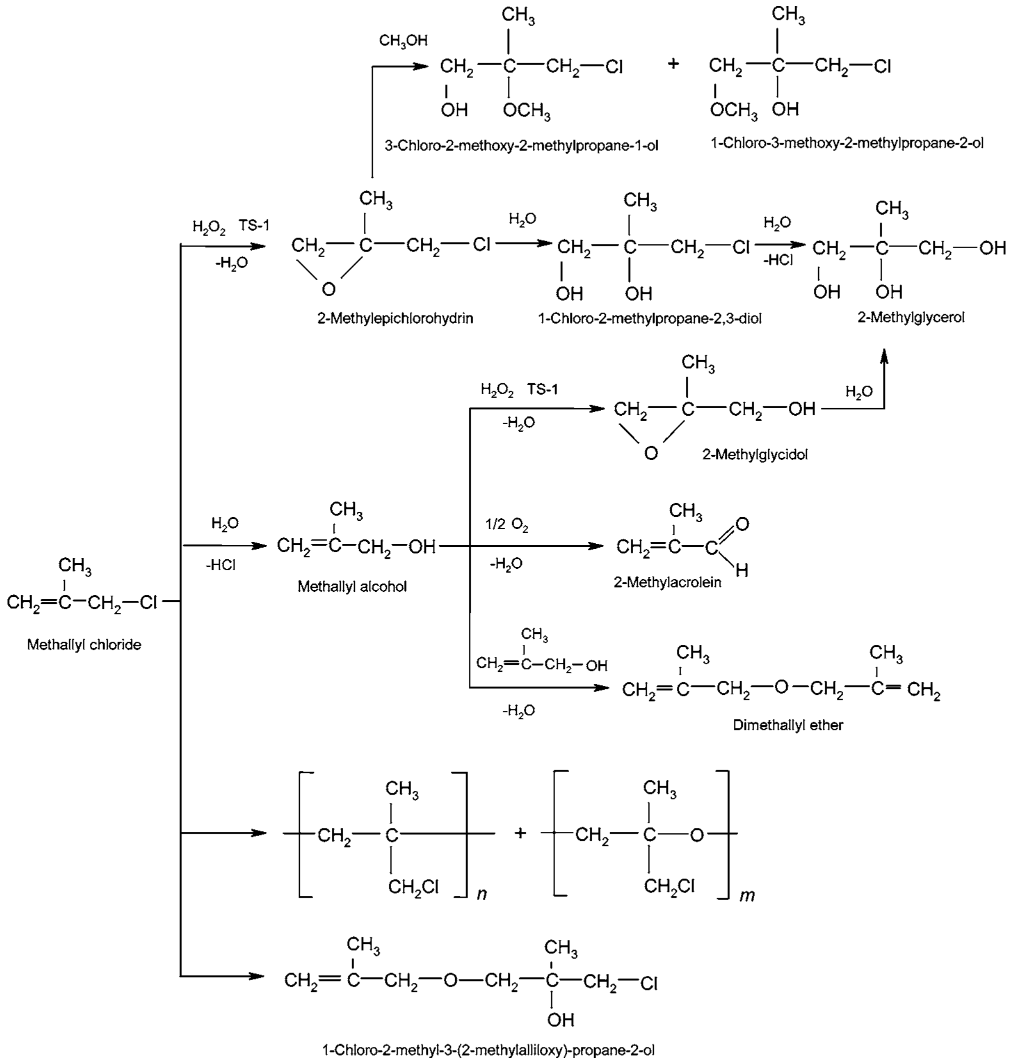

Table 1. Normalized (coded) and real values of the factors (technological parameters)

level	normalized factor X_i	temp (°C) x_1	molar ratio MAC/H_2O_2 (mol/mol) x_2	methanol concentration (wt %) x_3	TS-1 concentration (wt %) x_4	reaction time (min) x_5
basic	0	70	3	48	1.1	83
higher	1	95	4	69	1.5	165
lower	−1	45	2	26	0.6	25
star higher	2	120	5	90	2.0	300
star lower	−2	20	1	5	0.1	30

performed by computer, applying the program Cadex: Esdet 2.2.[26]

The plan was realized for five technological parameters (input variables x_1-x_5): x_1 - temperature, x_2 - the MAC to H_2O_2 molar ratio, x_3 - methanol concentration, x_4 - TS-1 catalyst concentration, x_5 - reaction time. The total number of experiments amounted to 32, including 16 in the plan nucleus, 10 in the stars points, whereas there were 6 in the plan centre. The real and normalized values of the technological parameters (input variables) at levels resulting from experimental design are presented in Table 1.

The real values of the input variables x_1-x_5 (parameters) were recalculated on the normalized values (dimensionless) according to the equation:

$$X_k = [2\alpha(x_k - x_{k\,\min})/(x_{k\,\max} - x_{k\,\min})] - \alpha$$

where: $X_k \in [-\alpha, \alpha]$, X_k are normalized input variables, $k = 1,..., i$; i are the number of input variables ($i = 5$); α is star arm ($\alpha = 2$); x_k − real input variable, $x_{k\,\max}$ − maximum value of the real input variable, $k = 1,...,i$; $x_{k\,\min}$ − minimum value of the real input variable.

The following magnitudes characterize the epoxidation process and were assumed as the response functions: z_1 - selectivity of transformation to MEP in relation to methallyl

---

(26) Polañski, Z.; Górecka-Polañska, R. *Cadex: Esdet 2.2, Podrêcznik użytkownika*; Zakład Postêpu Technicznego i Wdrożeñ, Kraków, 1992.

Table 2. **Design matrix of experiments**

	X_1 (temperature)	X_2 (MAC/H_2O_2 molar ratio)	X_3 (methanol concentration)	X_4 (TS-1 concentration)	X_5 (time)
1	−1	−1	−1	−1	−1
2	1	−1	1	−1	−1
3	1	−1	−1	−1	1
4	1	−1	−1	1	1
5	1	1	−1	−1	−1
6	−1	1	1	−1	−1
7	−1	1	−1	−1	1
8	−1	1	−1	1	−1
9	1	−1	1	1	1
10	−1	−1	−1	1	1
11	−1	−1	1	1	−1
12	−1	−1	1	−1	1
13	−1	1	1	1	1
14	1	1	−1	1	1
15	1	1	1	1	−1
16	1	1	1	−1	1
17	−2	0	0	0	0
18	2	0	0	0	0
19	0	−2	0	0	0
20	0	2	0	0	0
21	0	0	−2	0	0
22	0	0	2	0	0
23	0	0	0	−2	0
24	0	0	0	2	0
25	0	0	0	0	−2
26	0	0	0	0	2
27	0	0	0	0	0
28	0	0	0	0	0
29	0	0	0	0	0
30	0	0	0	0	0
31	0	0	0	0	0
32	0	0	0	0	0

chloride consumed ($S_{MEP/MAC}$), z_2 - selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed ($S_{org/H2O2}$), z_3 - MAC conversion (C_{MAC}), z_4 - hydrogen peroxide conversion (C_{H2O2}). The design matrix utilized for the experiments realization was presented in Table 2.

The experimentally obtained values of the response function $z_1 - z_4$ are presented in Table 3.

The influence of normalized independent parameters ($X_1 - X_5$) of the epoxidation process on the values of the response functions was presented in the form of second-order polynomial (regression equations) containing the linear and square components and the double products (interactions):

$$Z = Z(X_k) = b_0 + b_1 \cdot X_1 + ... + b_i \cdot X_i + b_{11} \cdot X_1^2 + ... + b_{ii} \cdot X_i^2 + b_{12} \cdot X_1 X_2 + ... + b_{i-1,i} \cdot X_{i-1} \cdot X_i$$

for X_k×bb $[-2,2]$, where b_i are normalized coefficients of the approximation function, N_b are the number of polynomial coefficients; $N_b = 0.5(i + 1)(i + 2)$, i are the number of the input variables X_k; $k = 1,2,...,i$.

The coefficients of regression equations for the normalized input variables (parameters) were determined by the least-squares method with the application of matrix calculations. Verification of the adequacy of the approximation functions was subsequently performed on the basis of the relative errors for the particular systems of experimental design and the values of the coefficients of multidimensional correlation R.

The coefficients of normalized regression equations $Z_1 - Z_4$, the values of the coefficient of multidimensional correlation, R, showing fitting of obtained regression equations to the experimental values of the response functions, and the values of both maximum absolute error (Δz_{max}) of performed experiments and calculated functions are presented in Table 4.

The maximum values of obtained regression equations were determined by means of the computer program Cadex: Esdet 2.2 and are summarised in Table 5. Moreover, the real values of parameters (independent variables) corresponding to these values were included in Table 5.

The results presented in Table 5 demonstrate that the maximum values of examined functions, $S_{MEP/MAC}$, $S_{org/H2O2}$, C_{MAC}, C_{H2O2}, were achieved at the following technological parameters: temperature 20 °C (for $S_{MEP/MAC}$, $S_{org/H2O2}$) and 120 °C (for C_{MAC}, C_{H2O2}), the MAC/H_2O_2 molar ratio 1:1−2:1, methanol concentration 90 wt %, catalyst concentration from 1.0 to 2.0 wt %, and reaction time 300 min for $S_{MEP/MAC}$, C_{MAC}, C_{H2O2}. The function $S_{org/H2O2}$ has a maximum after 170 min. The courses of isolines of the selectivity functions: $S_{MEP/MAC}$, $S_{org/H2O2}$ were subjected to analysis to establish the function values at different technological parameters (independent variables). These functions show the influence of the changes of two selected parameters (independent variables) on the values of the examined functions: $S_{MEP/MAC}$, $S_{org/H2O2}$ at the optimal values of the remaining parameters.

Table 3. **Experimental values of response functions z_1-z_4**

	z_1 $S_{MEP/MAC}$	z_2 $S_{org/H2O2}$ (mol %)	z_3 C_{MAC}	z_4 C_{H2O2}
1	41.7	20.6	5.2	50.2
2	0.0	37.5	10.8	57.3
3	3.6	30.6	7.9	50.4
4	5.9	86.1	10.2	22.8
5	6.4	68.7	6.2	35.7
6	0.0	0.0	0.0	80.6
7	61.9	27.7	3.8	51.9
8	48.1	11.8	0.8	25.9
9	21.0	100.0	12.0	20.0
10	29.7	19.1	7.8	81.9
11	93.3	100.0	30.4	58.7
12	90.3	47.0	19.4	79.5
13	81.6	99.4	15.9	61.7
14	20.7	67.1	1.8	10.8
15	45.0	100.0	5.2	19.4
16	33.3	100.0	2.7	9.7
17	77.8	100.0	26.9	80.4
18	78.7	100.0	8.9	26.8
19	22.9	33.4	16.2	48.6
20	19.5	57.9	5.6	46.2
21	77.8	100.0	8.1	23.9
22	71.0	100.0	2.7	62.5
23	35.1	17.2	9.7	69.2
24	57.6	100.0	19.9	62.7
25	77.9	100.0	17.2	50.9
26	62.4	60.4	16.9	82.3
27	56.1	69.4	12.2	52.2
28	72.5	100.0	19.1	57.1
29	55.9	100.0	10.2	30.4
30	59.7	38.4	9.7	75.2
31	58.3	100.0	10.7	30.5
32	53.6	100.0	10.2	30.5

The influence of temperature and the following parameters: MAC/H_2O_2 molar ratio (a), methanol concentration (b), catalyst concentration (c), reaction time (d) on the course of function $S_{MEP/MAC}$ is presented in Figure 1. The values of the constant parameters for both functions of conversion are presented in Table 5. The course of function $S_{org/H2O2}$ during the changes of technological parameters is shown in Figure 2. The presented curves were plotted using the computer program Surfer 5.01.

3.1. Influence of Process Parameters on the Selectivity of Transformation to 2-Methylepichlorohydrin in Relation to Methallyl Chloride Consumed ($S_{MEP/MAC}$). Analysis of the influence of temperature and the parameters MAC/H_2O_2 molar ratio, methanol concentration, TS-1 concentration, and reaction time indicates that it is advantageous to run the process at temperature 20 °C (Figure 1). Elevation of temperature from 20 to 120 °C causes a decrease of the selectivity of transformation to MEP from 100 mol % to a few percent, at the constant values of the remaining parameters. An increase in temperature has a strong influence on the hydration rate of MEP to 1-chloro-2-methylpropane-2,3-diol. The maximum selectivity $S_{MEP/MAC}$ is achieved at the molar ratio of MAC/H_2O_2 = 2:1 (Table 5). However, the course of function in the parameters system: temperature - MAC/H_2O_2 molar ratio (Figure 1a) indicates that the application of the excess MAC is not necessary, because at temperature 20 °C the maximum of function $S_{MEP/MAC}$ is also reached at the molar ratio of MAC/H_2O_2 = 1:1. Similarly, the methanol concentration of 90 wt % (Table 5) is not necessary to achieve the highest selectivity $S_{MEP/MAC}$. This function reaches the maximum (Figure 1b) at the methanol concentrations above 30 wt %, at temperature 20 °C and the values of the remaining parameters presented in Table 5. Moreover, the maximum of function $S_{MEP/MAC}$ can also be achieved at the lowest concentration (0.1 wt %) of the TS-1 catalyst (Figure 1c). Based on the curve of isolines (Figure 1d) for the parameters: temperature - time it was found, that the reaction time necessary to reach the function maximum at temperature 20 °C amounts at least 1 h. A prolongation of time over 1 h does not decrease the selectivity to MEP, if the temperature of 70 °C will not be exceeded. The most advantageous parameters for reaching the maximum selectivity of transformation to MEP ($S_{MEP/MAC}$ = 100 mol %) in relation to MAC consumed are as follows: temperature 20 °C, the molar ratio of MAC/H_2O_2 = 1:1, methanol concentration at least 30 wt %, TS-1 concentration above 0.1 wt %, and reaction time at least 30 min.

3.2. Influence of the Process Parameters on the Selectivity of Transformation to Organic Compounds in Relation to Hydrogen Peroxide Consumed ($S_{org/H2O2}$). The maximum of function $S_{org/H2O2}$ = 100 mol % is reached at the following technological parameters: temperature 20 °C, the molar ratio of MAC/H_2O_2 = 2:1, methanol concentration 90 wt %, TS-1 concentration 2.0 wt %, and reaction time

Table 4. **Coefficients of regression equations in the normalized form and statistical parameters of equations Z_1-Z_4**

coefficients	Z_1 $S_{MEP/MAC}$	Z_2 $S_{org/H2O2}$	Z_3 C_{MAC}	Z_4 C_{H2O2}
b_{00}	63.21[a]	87.85[a]	12.87[a]	48.33[a]
b_{01}	−10.87[a]	11.01	−2.59[a]	−15.48[a]
b_{02}	0.19	3.46	−3.68[a]	−5.41
b_{03}	5.54[a]	10.51	1.76	5.60
b_{04}	6.40[a]	17.37[a]	2.03[a]	−5.29
b_{05}	2.94	−0.54	0.08	3.27
b_{11}	0.84	0.62	0.61	−0.45
b_{12}	8.65[a]	8.08	1.09	−1.56
b_{13}	−1.31	−5.15	−2.74[a]	−5.24
b_{14}	−0.60	−1.16	−1.56	−2.90
b_{15}	−3.69	−3.46	−1.16	−6.51
b_{22xxx}	−13.42[a]	−12.96[a]	−1.14	−1.99
b_{23}	−6.31[a]	−0.25	−1.89	2.31
b_{24}	4.96[a]	−54.75	−0.37	−0.39
b_{25}	5.90[a]	10.07	1.34	−4.40
b_{33}	−0.12	0.62	−2.52[a]	−3.04
b_{34}	7.90[a]	11.16	2.05	−1.27
b_{35}	4.62[a]	9.49	0.31	−6.60
b_{44}	−7.11[a]	−9.73	−0.16	2.64
b_{45}	−11.27[a]	−5.68	−1.28	5.00
b_{55}	−1.17	−4.33	0.39	2.80
R	0.88	0.87	0.89	0.88
Δz_{max}	37.8	49.5	8.8	26.9

[a] Essential coefficient.

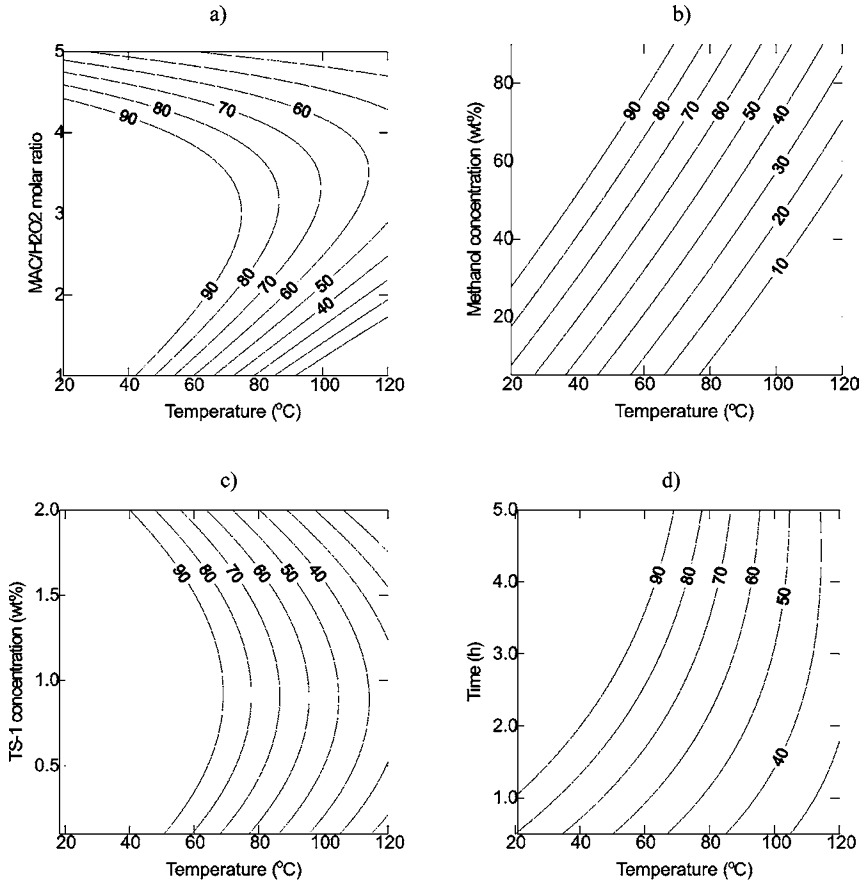

Figure 1. **Influence of parameters on the selectivity of transformation to MEP in relation to MAC consumed: (a) temperature and the MAC/H_2O_2 molar ratio, (b) temperature and methanol concentration, (c) temperature and TS-1 catalyst concentration, (d) temperature and reaction time. Constant parameters: the MAC/H_2O_2 molar ratio 2:1, methanol concentration 90 wt %, TS-1 catalyst concentration 1.0 wt %, reaction time 300 min.**

Table 5. **Maximum values of response functions z_1-z_4 and corresponding to them parameters**

function or parameter	unit	z_1 $S_{MEP/MAC}$	z_2 $S_{org/H2O2}$	z_3 C_{MAC}	z_4 C_{H2O2}
maximum value of function	(mol %)	100	100	65	77
parameter:					
temperature	(°C)	20	20	120	120
MAC/H_2O_2 molar ratio	(mol/mol)	2:1	2:1	1:1	1:1
methanol concentration	(wt %)	90	90	90	90
TS-1 catalyst concentration	(wt %)	1.0	2.0	2.0	2.0
time	(min)	300	170	300	300
values of functions z_1 and z_2 at parameters determining the maximum of functions z_3 and z_4	(mol %)	0	27	-	-
values of functions z_3 and z_4 at parameters determining the maximum of function z_1	(mol %)	-	-	37	100

170 min (Table 5). The influence of technological parameters on the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed is presented in Figure 2.

The charts showing the influence of temperature and the molar ratio as well as the influence of temperature and time (Figure 2a and d) demonstrate that the function $S_{org/H2O2}$ has the maximum value (100 mol %) over a wide range of examined parameters. However, this range becomes narrower due to the interactions among the respective parameters: methanol concentration, temperature and catalyst concentration, and temperature. From Figure 2b, the results show that it is beneficial to run the process at the methanol concentration above 60 wt %. In this case the selectivity of transformation to organic compounds is limited to the selectivity of the sum of MEC and 1-chloro-2-methylpropane-2,3-diol. Under these technological parameters the remaining compounds (methallyl alcohol, 2-methylacrolein) are formed either in trace amounts or not at all (Scheme 1). An increase in the catalyst concentration over the range 0.1−0.9 wt % at a constant temperature causes an increase of the value of function $S_{org/H2O2}$ (Figure 2c). The hydration of MAC to 1-chloro-2-methylpropane-2,3-diol simultaneously proceeds. From the point of view of this function, the influence of temperature is insignificant. The function $S_{org/H2O2}$ achieves a constant value for the catalyst concentrations above 0.9 wt % over the whole range of studied temperatures. The highest value of this function was achieved in the temperature

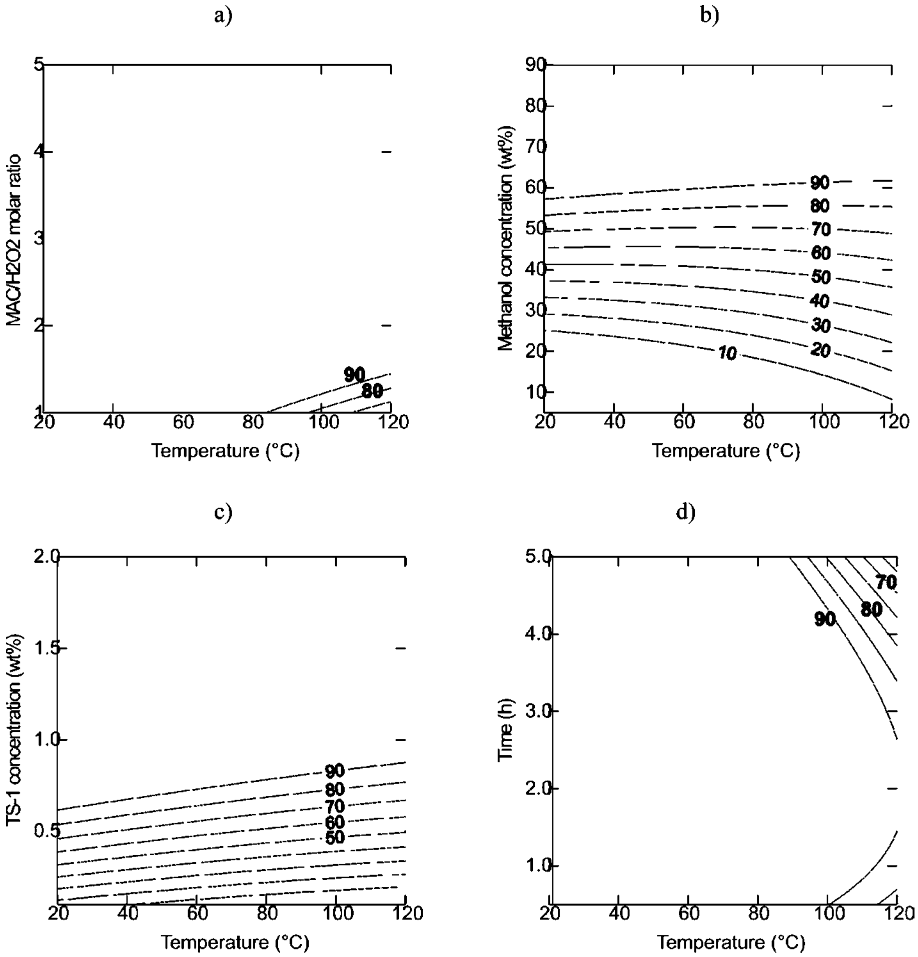

Figure 2. **Influence of parameters on the selectivity of transformation to organic compounds in relation to hydrogen peroxide consumed: (a) temperature and MAC/H_2O_2 molar ratio, (b) temperature and methanol concentration, (c) temperature and TS-1 catalyst concentration, (d) temperature and reaction time. Constant parameters: MAC/H_2O_2 molar ratio 2:1, methanol concentration 90 wt %, TS-1 catalyst concentration 2.0 wt %, reaction time 170 min.**

range 20−100 °C, which is interesting from the technological point of view. Therefore, it is advantageous to run the process at temperature 20 °C, and the catalyst concentrations should be at least 0.7 wt %.

The investigations of the influence of parameters on the course of function $S_{org/H2O2}$ indicate that this function achieves its maximum (100 mol %) for the following parameters: temperature 20 °C, the molar ratio of MAC/H_2O_2 = 1:1, methanol concentration at least 60 wt %, TS-1 concentration above 0.7 wt %, and reaction time at least 30 min.

3.3. Influence of Process Parameters on the Conversions of Methallyl Chloride (C_{MAC}) and Hydrogen Peroxide (C_{H2O2}). To graphically present the influence of technological parameters on the conversion functions C_{MAC} and C_{H2O2} (Figure 3a−e), the general regression equation was reduced to a function of a single independent variable (parameter). The values of the conversion function in this case were calculated during the changes of one parameter with the remaining parameters kept constant and simultaneously allowing the maximum of the function (Table 5) to be achieved. The functions of conversions of methallyl chloride (C_{MAC}) and hydrogen peroxide (C_{H2O2}) do not have such a significant importance as do the selectivities, $S_{MEP/MAC}$ and $S_{org/H2O2}$. However, knowledge of the values of conversions is necessary for the technological parameters to determine the highest selectivities.

Figure 3a shows that the conversion of methallyl chloride and hydrogen peroxide increases along with temperature elevation. At 120 °C both functions of conversion C_{MAC} and C_{H2O2} achieve the maximum value of 65 and 77 mol %, respectively. A decrease of epoxidation temperature to 20 °C is not advantageous in this case. This causes a decrease of the values of examined functions to 25 mol % for C_{MAC} and to 10 mol % for C_{H2O2}. However, from the point of view of the selectivity of transformation described by the functions z_1 and z_2, the most advantageous temperature is 20 °C. The achievement of high selectivities of transformation, described by the functions $S_{MEP/MAC}$ and $S_{org/H2O2}$, is more important for the course of the process than the possibility of obtaining high conversions of methallyl chloride and hydrogen peroxide. A decrease of the selectivity of transformation to MEP in relation to both MEC and H_2O_2 at higher temperatures is caused by the side reactions such as the hydrolysis of MEC to methallyl alcohol, the formation of dimethallyl ether, and the oxidation to 2-methylacrolein. The 1-chloro-2-methylpropane-2,3-diol formed in the process can cause the elution of titanium from the crystalline structure of silica. This leads to a decrease of the catalyst activity in the consecutive cycles

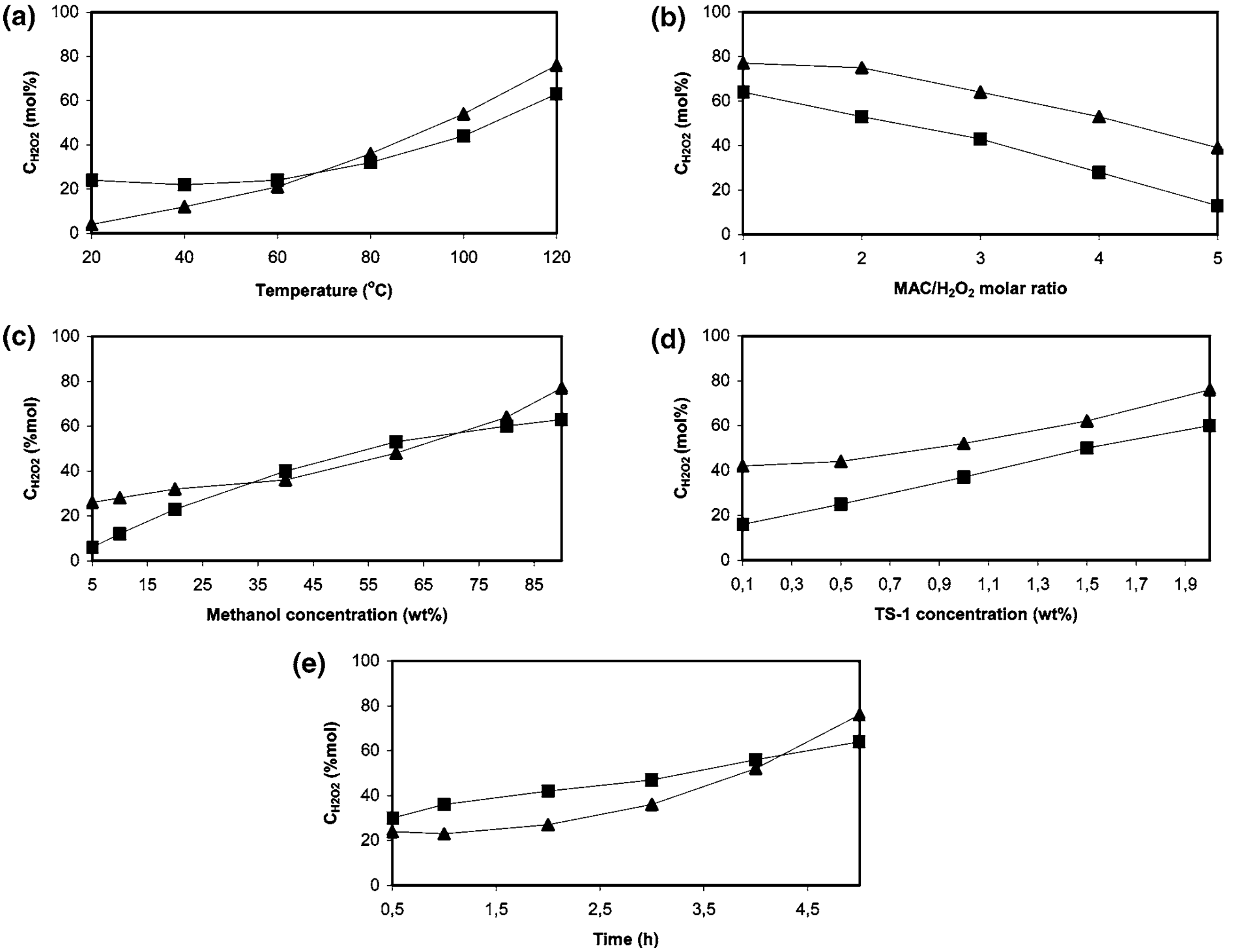

Figure 3. **(a) Influence of temperature on the conversion of methallyl chloride C_{MAC} (■) and hydrogen peroxide C_{H2O2} (▲). Constant parameters: MAC/H_2O_2 molar ratio 1:1, methanol concentration 90 wt %, TS-1 concentration 2.0 wt %, reaction time 300 min. (b) Influence of the MAC/H_2O_2 molar ratio on the conversion of methallyl chloride C_{MAC} (■) and hydrogen peroxide C_{H2O2} (▲). Constant parameters: temperature 20 °C, methanol concentration 90 wt %, TS-1 concentration 2.0 wt %, reaction time 300 min. (c) Influence of methanol concentration on the conversion of methallyl chloride C_{MAC} (■) and hydrogen peroxide C_{H2O2} (▲). Constant parameters: temperature 20 °C, MAC/H_2O_2 molar ratio 1:1, TS-1 concentration 2,0 wt %, reaction time 300 min. (d) Influence of TS-1 catalyst concentration on the conversion of methallyl chloride C_{MAC} (■) and hydrogen peroxide C_{H2O2} (▲). Constant parameters: temperature 20 °C, MAC/H_2O_2 molar ratio 1:1, methanol concentration 90 wt %, reaction time 300 min. (e) Influence of reaction time on the conversion of methallyl chloride C_{MAC} (■) and hydrogen peroxide C_{H2O2} (▲) Constant parameters: temperature 20 °C, MAC/H_2O_2 molar ratio 1:1, methanol concentration 90 wt %, TS-1 concentration 2.0 wt %.**

of the epoxidation. Such a catalyst, after the regeneration and reuse, does not allow the same technological parameters of the synthesis to be maintained.[27−29] Another problem is associated with the formation of polymers, which cause clogging of the inlets of the catalyst pores. In such a case the regeneration of catalyst by the calcinations at 550 °C becomes necessary. A relatively low conversion of methallyl chloride at 20 °C (25 mol %) means that any unreacted MEC should be recovered by the distillation and recycled.

The influence of the MAC/H_2O_2 molar ratio on the course of the functions C_{MAC} and C_{H2O2} is shown in Figure 3b. The equimolar ratio of MAC/H_2O_2 was found to be the most advantageous for both examined functions. At this molar ratio the functions C_{MAC} and C_{H2O2} achieve the maximum values 65 and 77 mol %, respectively. Moreover, the MAC/H_2O_2 equimolar ratio is beneficial from the viewpoint of the selectivities: $S_{MEP/MAC}$ and $S_{org/H2O2}$. The course of conversion of each reagent indicates that a change of the MAC/H_2O_2 molar ratio influences in a similar way the increase or decrease of the rate of the same reactions.

Figure 3c shows that the conversions of both reagents increase as the methanol concentration is increased. To achieve high conversion of both methallyl chloride and hydrogen peroxide the most advantageous concentration of methanol should amount 90 wt %. Moreover, the functions of the selectivities of transformation to MEP ($S_{MEP/MAC}$) and to organic compounds ($S_{org/H2O2}$) at this methanol concentration achieve the highest values. Therefore, the best solution is to run the process at the methanol concentration of 90 wt

---

(27) Davies, L.; McMorn, P.; Bethell, D.; Bulman Page, P. C., King, F.; Hancock, F. E.; Hutching, G. J. *Chem. Commun.* **2000**, 1807.

(28) van der Waal, J. C.; van Bekkum, H. *J. Mol. Catal. A: Chem.* **1997**, *124*, 137.

(29) Adam, W.; Corma, A.; Reddy, T. J.; Renz, M. *J. Org. Chem.* **1997**, *62*, 3631.

% at temperature 20 °C, and at the equimolar ratio of the reagents. In addition, the temperature 20 °C limits the solvolysis of the epoxide ring by methanol and the side reactions shown in Scheme 1. Methanol used in the process can be easily recovered by a single distillation and recycled.

Elevation of TS-1 catalyst concentration from 0.1 to 2.0 wt % causes an increase of the values of both functions (Figure 3d). The functions C_{MAC} and C_{H2O2} achieve the maximum values 64 and 77 mol %, respectively. The catalyst concentration equal to 2.0 wt % is also advantageous to achieve the maximum of functions $S_{MEP/MAC}$ and $S_{org/H2O2}$.

The studies of the influence of reaction time (Figure 3e) on the conversions of methallyl chloride and hydrogen peroxide demonstrate that the process proceeded most effectively for the longest reaction time (300 min). Moreover, this reaction time allows the highest values of functions $S_{MEP/MAC}$ and $S_{org/H2O2}$ to be achieved. The time of the process duration equal to 300 min ensures the maximum value for each examined function.

Conclusions

On the basis of the courses of all the functions describing the process, it was found that the most advantageous technological parameters are as follows: temperature 20 °C, the equimolar ratio of MAC/H_2O_2, methanol concentration in the reaction mixture 90 wt %, TS-1 catalyst concentration about 2.0 wt %, and reaction time 300 min. At these parameters the selectivity of transformation to 2-methylepichlorohydrin in relation to methallyl chloride amounted to 79 mol %, whereas the selectivity for organic compounds in relation to hydrogen peroxide was 100 mol %. In this case the conversions of methallyl chloride and hydrogen peroxide amounted to 56 mol % and 100 mol %, respectively. The elaborated conditions allows limiting the quantity of byproducts formed in the process, particularly 1-chloro-2-methylpropane-2,3-diol and polymers. Moreover, the catalyst activity can be maintained at a constant level, because the elution of titanium from the crystalline structure of the catalyst does not proceed and clogging of the pores by polymers is limited. The elaborated parameters allow the process to be run under relatively mild conditions. Although a low temperature permits the operation of the process under the pressureless conditions, the autoclave was used to maintain methallyl chloride in the liquid phase. The solvent used in the process and unreacted MAC can be subjected to distillation and recycled to the autoclave.

Incomplete conversion of hydrogen peroxide was sometimes found in this process. Residual hydrogen peroxide should be decomposed before separation of 2-methylepichlorhydrin by fractional distillation. Decomposition of hydrogen peroxide can be carried out by using reducing agents such as sodium sulphate(IV), iron(II) salts, or suitable salts of other transition metals. Activated carbon, pumice, or porous glass can also be used for this purpose.

Received for review February 21, 2006.

OP0600411