

Optimization of the Technological Parameters of 3-Chloro-3-methyl-1-butene Synthesis

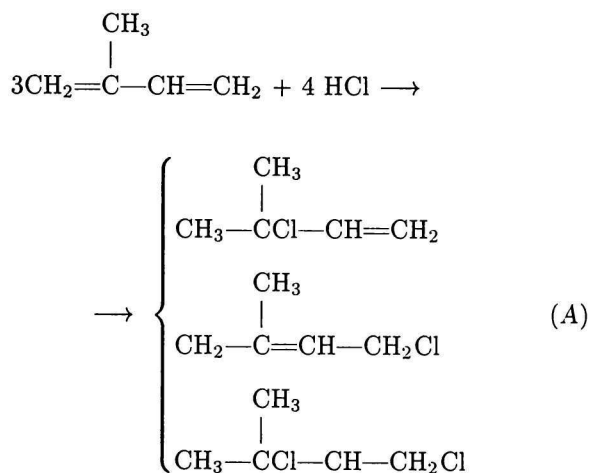
G. LEWANDOWSKI and E. MILCHERT

*Department of Organic Technology, Technical University of Szczecin,
PL-70322 Szczecin*

Received 28 May 1997

The isoprene hydrochlorination has been investigated in the presence of anhydrous diethyl ether, diethyl ether containing water, and in the presence of water and ammonium salt. Conditions of the highest selectivity of the transformation of isoprene to 3-chloro-3-methyl-1-butene in an isoprene—water system in the presence of didodecyldimethylammonium bromide have been established basing on statistical methods of the design of the experiments. The conditions are as follows: temperature -30°C , hydrogen chloride to isoprene mole ratio 0.45, hydrogen chloride flow rate 0.01 g min^{-1} (for 1 g of isoprene), water mass fraction (w) 5.0 mass %, didodecyldimethylammonium bromide $w = 0.2$ mass %. Also the conditions of the highest isoprene conversion were worked out and the isomerization of chloromethylbutene was investigated.

During the addition of hydrogen chloride to isoprene a mixture of 3-chloro-3-methyl-1-butene (3ch3m1b), 1-chloro-3-methyl-2-butene (1ch3m2b), and 1,3-dichloro-3-methylbutane (1,3dch3mb) is formed



Chloromethylbutenes are used mainly in production of odorizing agents for perfume industry [1–4] and auxiliary agents for plastics production [5].

3ch3m1b or its mixture with 1ch3m2b are used as alkylating and telomerizing agents for olefins [6–9]. The telomerization of chloromethylbutenes with isoprene results in formation of the mixture of chloro derivatives: $\text{C}_5\text{H}_9-(\text{C}_5\text{H}_8)_n-\text{Cl}$. From the practical point of view, terpene chlorides of geraniol, terpineol, linalol are of greatest importance considering the production of synthetic vitamin A. Lowering the temperature conduces the attainment of 3ch3m1b. Heating

of 3ch3m1b and the presence in the mixture of hydrogen chloride [10, 11] or chlorides of Ni, Cu, Bi, and Pd [8, 12, 13] causes its isomerization to 1ch3m2b.

Ultée [10] obtained 3ch3m1b by passing dry hydrogen chloride through the mixture of isoprene and anhydrous diethyl ether at the temperature of -15°C and mole ratio of hydrogen chloride to isoprene 0.66. The yields of 3ch3m1b and 1ch3m2b with respect to hydrogen chloride introduced were 66.7 % and 16.5 %, respectively.

Pocker *et al.* [11] obtained pure 3ch3m1b by gradual passing through 0.66 mol of hydrogen chloride with respect to equimolar amount of isoprene. The reaction was carried out in the presence of diethyl ether or nitromethane at the temperature -78°C .

Both methods are characterized by low reaction rates. In order to achieve a full conversion of hydrogen chloride, the reaction product was kept at the low temperature for 24–36 h.

The aim of this study was to find the best method of isoprene hydrochlorination towards 3ch3m1b, the determination of the most advantageous parameters of hydrochlorination and their influence on the results of the synthesis.

EXPERIMENTAL

The following materials were used: 2-methyl-1,3-butadiene (isoprene), pure, stabilized with 50 ppm 4-*tert*-butylpyrocatechol (Merck—Schuchardt, Germany); hydrogen chloride stored in a gas cylinder, pure (BASF, Germany); didodecyldimethylammonium bromide, pure (Fluka, Switzerland).

Syntheses of chloromethylbutenes were carried out

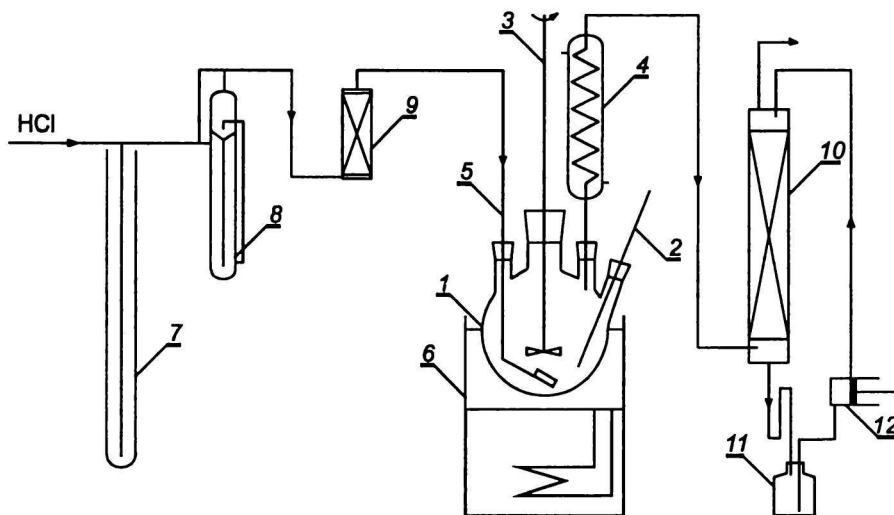


Fig. 1. Scheme of the apparatus for isoprene hydrochlorination. 1. Reactor, 2. thermometer, 3. paddle mixer, 4. reflux condenser (water—glycol; -25°C), 5. bubbler for hydrogen chloride, 6. thermostat, 7. liquid seal, 8. flow meter, 9. HCl drier, 10. scrubber, 11. container of 2 % soda lye, 12. pump.

on the apparatus shown in Fig. 1. Isoprene, water, and didodecyldimethylammonium bromide were introduced into a dry and clean reactor. The stirrer was turned on, the reactor placed in the thermostat at determined temperature for stabilization (about 10 min). Hydrogen chloride from steel cylinder equipped with needle valve flew under the surface of the liquid in the reactor. The moment of the introduction was assumed to be the beginning of the reaction. Waste gases from the reactor went to scrubber sprinkled with 2 % NaOH solution from container.

The amount of hydrogen chloride used was calculated on the basis of potentiometric determinations of chloride ions concentration in an aqueous layer and in refluxes from the scrubber of waste gases, and in the organic layer after the hydrolysis of chlorine bound in organic compounds.

Components of organic layer were determined by a gas chromatography method. The analyses were carried out using a Chrom 5 type gas chromatography with flame ionization detector (FID). A 1 m \times 3 mm stainless steel column packed with Chromosorb G DMCS AW 149—177 μm , coated with 5 mass % SE-30 was used. The temperature of the column was 30°C . The injection temperature was 40°C and the detection temperature was 50°C .

RESULTS AND DISCUSSION

Basing on the literature, the isoprene hydrochlorination was performed according to three different methods: in the presence of anhydrous diethyl ether, in the presence of water and diethyl ether, and in the presence of water and ammonium salt.

For each of the methods, the preliminary experiments were performed at boundary values of one pa-

rameter: temperature -30 — 20°C , hydrogen chloride to isoprene mole ratio 0.45—1.25, hydrogen chloride flow rate 0.002 — 0.01 g min^{-1} (for 1 g of isoprene), and the amount of the auxiliary agent 0—50 mass %. The rest of the parameters were settled at the average level for a given range.

The preliminary examinations showed that the highest yields of chloromethylbutenes were achieved in the isoprene—water system in the presence of didodecyldimethylammonium bromide. Simultaneously the reaction rate was ten times greater than in other methods. The separation and purifying of the product is simplified when a homogeneous solvent is not used.

On the basis of preliminary experiments results the essential reaction parameters (independent variables) and ranges of changes: temperature (Z_1) -30 — 20°C , hydrogen chloride to isoprene mole ratio (Z_2) 0.45—1.25, hydrogen chloride flow rate (Z_3) 0.002 — 0.010 g min^{-1} (for 1 g of isoprene), water mass fraction (Z_4) 5—20 mass % with respect to isoprene mass, ammonium salt mass fraction (Z_5) 0.2—1.0 mass % with respect to isoprene mass (Z_i — independent variables in natural form) were determined.

Experiments in the isoprene hydrochlorination were carried out according to rotatable uniform design of the second order, applying in its nucleus a fractional design of 2^{k-1} type with generating relation $x_5 = x_1 x_2 x_3 x_4$ (x_i — independent variables in a coded form) [14].

Table 1 shows parameters influencing the course of isoprene hydrochlorination to 3ch3m1b. The values of these parameters are given in natural (Z_i) and coded (x_i) form on all levels resulting from the design of experiments. The selectivity of the transformation to 3ch3m1b with respect to isoprene used (Y_1) and isoprene conversion (Y_2) was assumed as response func-

Table 1. Independent Factors of the Plan

Level	Coded factor, x_i	Temperature, $Z_1/^\circ\text{C}$	HCl to isoprene mole ratio, Z_2	HCl flow rate, Z_3 (for 1 g of isoprene)/(g min ⁻¹)	Water mass fraction, $Z_4/\text{mass } \%$	Ammonium salt mass fraction, $Z_5/\text{mass } \%$
Basic	0	-5.0	0.85	0.006	12.50	0.6
Higher	+1	7.5	1.05	0.008	16.25	0.8
Lower	-1	-17.5	0.65	0.008	8.75	0.4
Star higher	+2	20.0	1.25	0.010	20.00	1.0
Star lower	-2	-30.0	0.45	0.002	5.00	0.2

x_i – independent factors in a coded form; Z_1 – Z_5 – independent factors in a natural form.

Table 2. Design Matrix and Experimental Results

Number of experiments	Temperature, x_1	HCl to isoprene mole ratio, x_2	HCl flow rate, x_3	Water mass fraction, x_4	Ammonium salt mass fraction, x_5	Selectivity, Y_1	Conversion, Y_2
1	1	1	1	1	1	13.8	92.2
2	-1	1	1	1	-1	33.2	81.5
3	1	-1	1	1	-1	16.3	41.9
4	-1	-1	1	1	1	33.1	57.4
5	1	1	-1	1	-1	20.1	88.6
6	-1	1	-1	1	1	25.2	85.1
7	1	-1	-1	1	1	15.3	53.3
8	-1	-1	-1	1	-1	33.0	48.1
9	1	1	1	-1	-1	17.4	90.8
10	-1	1	1	-1	1	34.2	86.4
11	1	-1	1	-1	1	18.8	64.2
12	-1	-1	1	-1	-1	42.0	51.1
13	1	1	-1	-1	1	12.5	97.6
14	-1	1	-1	-1	-1	30.5	90.1
15	1	-1	-1	-1	-1	16.3	56.9
16	-1	-1	-1	-1	1	34.0	64.9
17	-2	0	0	0	0	39.5	73.1
18	2	0	0	0	0	16.8	78.8
19	0	-2	0	0	0	26.1	39.9
20	0	2	0	0	0	16.7	97.8
21	0	0	-2	0	0	17.2	77.2
22	0	0	2	0	0	24.4	74.2
23	0	0	0	-2	0	30.1	76.8
24	0	0	0	2	0	23.7	67.4
25	0	0	0	0	-2	24.5	64.0
26	0	0	0	0	2	18.7	76.3
27	0	0	0	0	0	22.1	73.0
28	0	0	0	0	0	22.4	75.2
29	0	0	0	0	0	20.0	76.9
30	0	0	0	0	0	22.0	75.2
31	0	0	0	0	0	22.7	73.7
32	0	0	0	0	0	20.8	76.6

x_1 – x_5 – independent factors in a coded form; Y_1 – selectivity of the transformation of isoprene to 3ch3m1b/mole %; Y_2 – conversion of isoprene/mole %.

tions characterizing the hydrochlorination process.

The experiments were carried out basing on the design matrix shown in Table 2. In the last two columns there are experimental values of response functions (Y_1 and Y_2) in particular design systems.

An influence of independent factors (x_1 – x_5) of isoprene hydrochlorination on the value of response functions Y_1 and Y_2 is presented as the regression equation in the form of a polynomial of the second order

$$y^* = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i < j}^k b_{ij} x_i x_j + \sum_{i=1}^k b_{ii} x_i^2 \quad (1)$$

where y^* is the independent variable, one of response functions: Y_1 , Y_2 ; b_0 , b_i , b_{ij} , b_{ii} are the regression equation coefficients ($i, j = 1, \dots, k$); x_i , x_j are the independent factors in coded form ($i, j = 1, \dots, k$); and k is the number of factors in the experiment design ($k = 5$).

Table 3. Significant Regression Coefficients in Natural Form and Statistical Parameters

Selectivity of the transformation of isoprene to 1ch3m2b, Y_1				Conversion of isoprene, Y_2			
Coefficient		Statistical parameters		Coefficient		Statistical parameters	
b_0	42.74	S_{rep}^2	1.12	b_0	-42.37	S_{rep}^2	2.33
b_1	-0.85	f_{rep}	5	b_1	-0.56	f_{rep}	5
b_2	-17.97	S_{adeq}^2	3.38	b_2	165.52	S_{adeq}^2	4.24
b_3	2244.16	f_{adeq}	18	b_3	-2189.58	f_{adeq}	18
b_4	-2.63	F	3.01	b_4	-0.72	F	1.82
b_5	-7.03	$F(\alpha)$	4.65	b_5	79.81	$F(\alpha)$	4.65
b_{12}	0.40	$R(\alpha)$	0.98	b_{12}	0.78	$R(\alpha)$	0.99
b_{13}	-40.05			b_{13}	—		
b_{14}	0.02			b_{14}	—		
b_{24}	0.92			b_{24}	1.56		
b_{25}	—			b_{25}	-49.59		
b_{34}	-136.33			b_{34}	—		
b_{35}	—			b_{35}	2775.00		
b_{11}	0.01			b_{11}	—		
b_{22}	—			b_{22}	-40.13		
b_{44}	0.10			b_{44}	-0.06		
b_{55}	—			b_{55}	-31.94		

Table 4. Optimum Values of Independent Variables of the Regression Function (Y_1 , Y_2)

Variables	$Y_1 \text{ max} = 80.0 \text{ mole \%}$	$Y_2 \text{ max} = 100 \text{ mole \%}$
Temperature, $Z_1 / ^\circ\text{C}$	-30.0	20.0
HCl to isoprene mole ratio, Z_2	0.45	1.05
HCl flow rate, Z_3 (for 1 g of isoprene)/(g min ⁻¹)	0.010	0.002
Water mass fraction, Z_4 /mass %	5.0	8.1
Ammonium salt mass fraction, Z_5 /mass %	0.2	0.5

The transition from the system of independent factors in natural form to coded form was performed by linear transformation of variables

$$x_i = (Z_i - Z_{i0})/\Delta Z \quad (2)$$

where x_i is the coded variable value in the point of the experiment design ($i = 1, \dots, k$); Z_i is the natural variable value in the point of the experiment design ($i = 1, \dots, k$); Z_{i0} is the natural variable value in the central point of the experiment design ($i = 1, \dots, k$); and ΔZ_i is the step value along the Z_i axis (natural).

The coefficients of the regression equation were calculated applying the method of the least squares.

Having calculated the coefficients a statistical analysis of the regression equations was performed [15]. For each of the equations the repeatability variance S_{rep}^2 and critical values of t -Student test were calculated and compared with the table value [16]. For $f_{\text{rep}} = 5$ and the significance level $\alpha = 0.05$ it is 2.571. After the elimination of insignificant coefficients the values of the significant coefficients of regression equations were recalculated. The adequacy variances S_{adeq}^2 and values of the F quotient of the Fisher—Snedocor test were determined. For Y_1 function this value is 3.01 and for Y_2 1.62. The critical value $F(\alpha)$ read

from the tables [17] for $\alpha = 0.05$, $f_{\text{rep}} = 5$, $f_{\text{adeq}} = 18$ is $F(\alpha) = 4.65$. For both functions $F < F(\alpha)$. Thus the functions adequately describe the results of the experiment.

The coefficients of the regression equations in natural form and the results of the statistical analysis are shown in Table 3.

Due to a great number of independent variables ($k = 5$) the optimization of the regression equations was performed numerically applying the Gauss—Siedel and Hook—Jeeves methods [17]. Both methods gave identical optimum values of independent variables values for a given regression function.

Table 4 shows the maximum values of response functions (Y_1 , Y_2) and corresponding values of independent variables (in natural form). The comparison indicates that achieving the maximum selectivity of the transformation to 3ch3m1b with simultaneous maximum isoprene conversion is not possible.

On the basis of the regression equations and with the use of Surfer 5.01 computer program, the lines of the same values of both response functions in two-dimensional coordinate system (isolines) have been plotted.

An analysis of Y_1 function and its graphical illustration (Figs. 2—4) showed that it depends on all in-

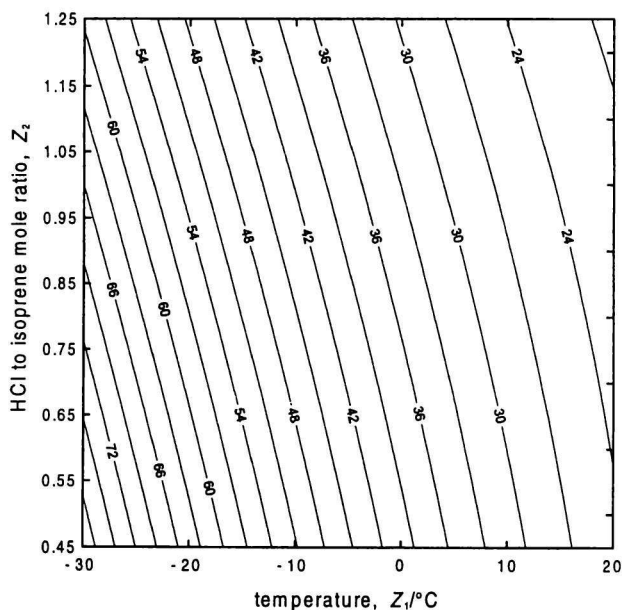


Fig. 2. The influence of the temperature and HCl to isoprene mole ratio on the transformation of isoprene to 3ch3m1b selectivity; HCl flow rate 0.01 g min^{-1} (for 1 g of isoprene), water $w = 5.0$ mass %, ammonium salt $w = 0.2$ mass %.

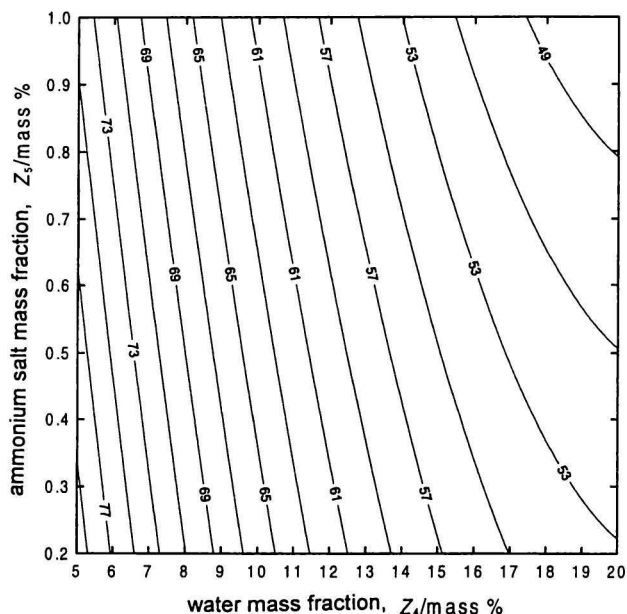


Fig. 4. The influence of water and ammonium salt mass fraction on the transformation of isoprene to 3ch3m1b selectivity; temperature -30°C , HCl to isoprene mole ratio 0.45, HCl flow rate 0.01 g min^{-1} (for 1 g of isoprene).

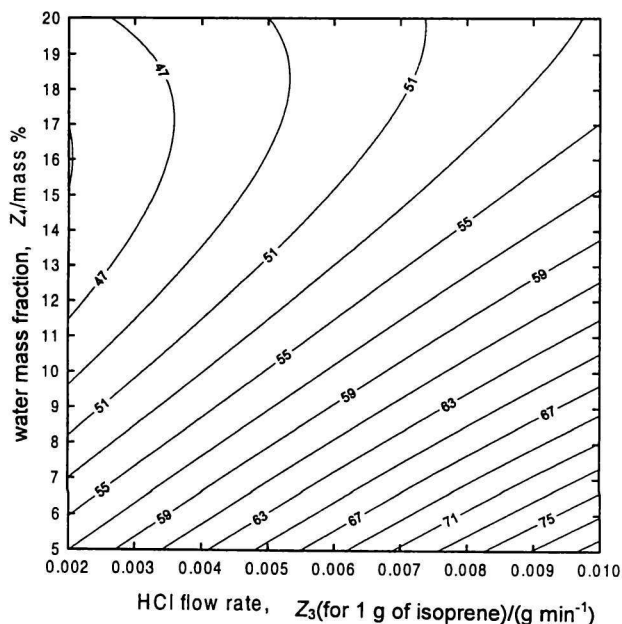


Fig. 3. The influence of HCl flow rate and water mass fraction on the transformation of isoprene to 3ch3m1b selectivity; temperature -30°C , HCl to isoprene mole ratio 0.45, ammonium salt $w = 0.2$ mass %.

vestigated independent factors of the design.

The course of the isolines (Fig. 2) shows that the selectivity of the transformation of isoprene to 3ch3m1b depends considerably on the temperature. At the optimum other parameters of the reaction the lowering of the temperature from 20°C to -30°C

causes the increase of the transformation selectivity from 24.7 to 80.0 mole %. That is the highest increase among the investigated reaction parameters.

The lowering of hydrogen chloride to isoprene mole ratio results in an increase in selectivity of transformation of isoprene to 3ch3m1b (Fig. 2) from 59.6 to 80.0 mole %.

Similar changes of selectivity are caused by increasing the rate of introducing hydrogen chloride or lowering the water concentration (Figs. 3 and 4), respectively, from 56.9 or 53.2 to 80.0 mole %.

Much lower is the influence of changes in concentration of ammonium salt. At the fixed other reaction parameters (Fig. 4) the change of ammonium salt mass fraction from 1.0 to 0.2 mass % results in the increase of the selectivity of the transformation of isoprene to 3ch3m1b from 74.4 to 80.0 mole %.

The analysis of the regression function and its graphical illustration (Figs. 2–4) shows that the biggest influence on the value of the selectivity of the transformation of isoprene to 3ch3m1b is exerted by the temperature. Much lower is the influence of reagents mole ratio, hydrogen chloride flow rate, and water concentration. The lowest is the influence of ammonium salt concentration.

In the control experiments, in the point of the highest selectivity of the 3ch3m1b synthesis (Table 4), the average transformation selectivities were as follows ($x/\text{mole } \%$): 3ch3m1b 80.5 ± 5.6 ; 1ch3m2b 16.9 ± 6.5 ; 1,3dch3mb 2.3 ± 0.9 . The isoprene conversion was (23.0 ± 7.7) mole %.

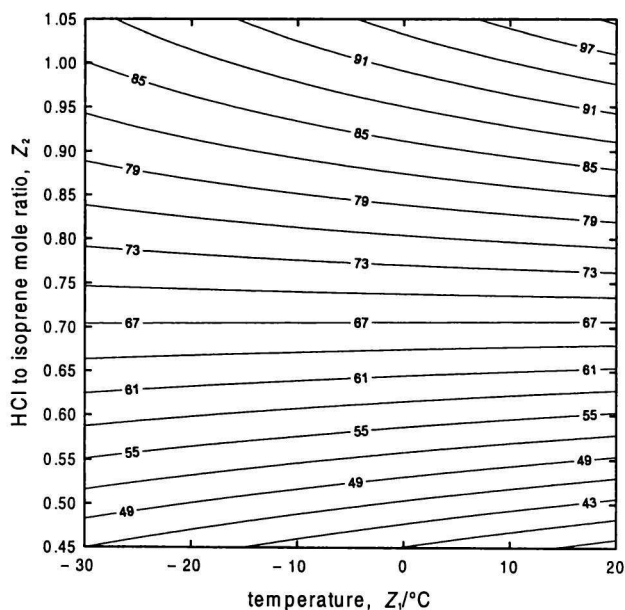


Fig. 5. The influence of the temperature and HCl to isoprene mole ratio on the conversion of isoprene; HCl flow rate 0.002 g min^{-1} (for 1 g of isoprene), water $w = 8.1 \text{ mass } \%$, ammonium salt $w = 0.5 \text{ mass } \%$.

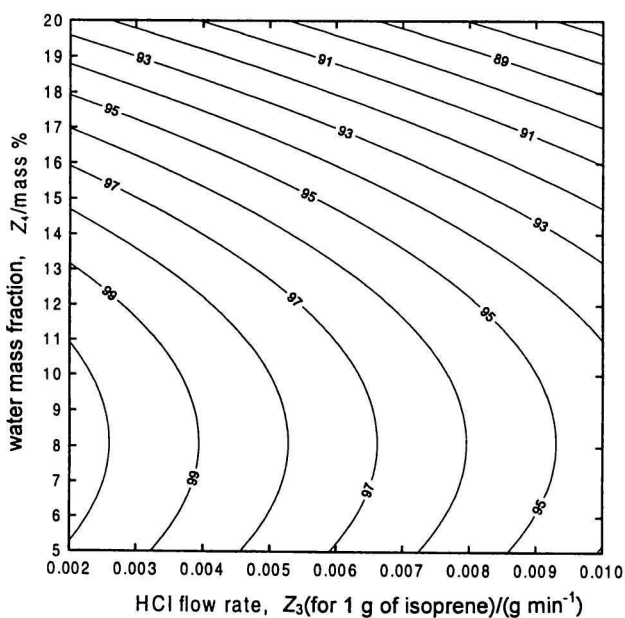


Fig. 6. The influence of HCl flow rate and water mass fraction on the conversion of isoprene; temperature 20°C , HCl to isoprene mole ratio 1.05, ammonium salt $w = 0.5 \text{ mass } \%$.

The analysis of isoprene conversion function Y_2 pointed out that the increase of process temperature and hydrogen chloride to isoprene mole ratio, and the decrease in hydrogen chloride flow rate result in the increase of isoprene conversion (Figs. 5–7).

The temperature appears to have a relatively low

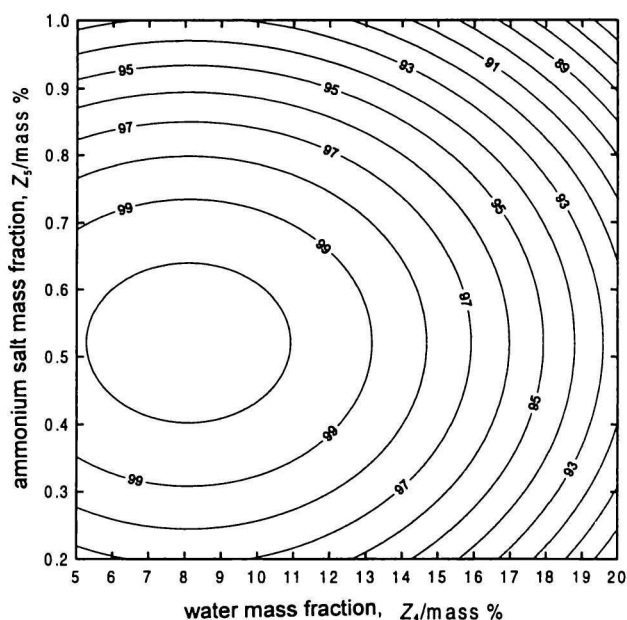


Fig. 7. The influence of water and ammonium salt mass fraction on the conversion of isoprene; temperature 20°C , HCl to isoprene mole ratio 1.05, HCl flow rate 0.002 g min^{-1} (for 1 g of isoprene).

influence on the isoprene conversion (Fig. 5). For example, at hydrogen chloride to isoprene mole ratio equal to 0.72 the isoprene conversion does not depend on the temperature over the whole range of its changes. At the established optimum remaining parameters of the reaction, the change in temperature from -30°C to 20°C causes the increase in the isoprene conversion from 87.2 to 100 mole %.

The greatest influence on the isoprene conversion is observed when changing the mole ratio of hydrogen chloride to isoprene. Its increase from 0.45 to 1.05 at the established optimum remaining parameters of the reaction causes the increase of the conversion from 35.8 to 100.0 mole % (Fig. 5). The total isoprene conversion is achieved at hydrogen chloride to isoprene mole ratio equal to 1.04. Due to the lack of physical sense of response surface at mole ratios above 1.05, the analysis was restricted to this value.

The hydrogen chloride flow rate exerts only very little influence on the isoprene conversion. The change in flow rate from 0.01 to 0.002 g min^{-1} (for 1 g of isoprene) at the established other reaction parameters, results in the conversion increase from 94.5 to 100.0 mole % (Fig. 6). The course of the isoline of the isoprene conversion at the hydrogen chloride flow rate similar to changes in hydrogen chloride to isoprene mole ratio is of linear character.

As for concentrations of water and ammonium salt (Fig. 7) the conversion isolines show distinct maxima: for water w between 5.2–11.0 mass % and for ammonium salt w between 0.4–0.64 mass %. Over the wide range of changes around the optimum point the

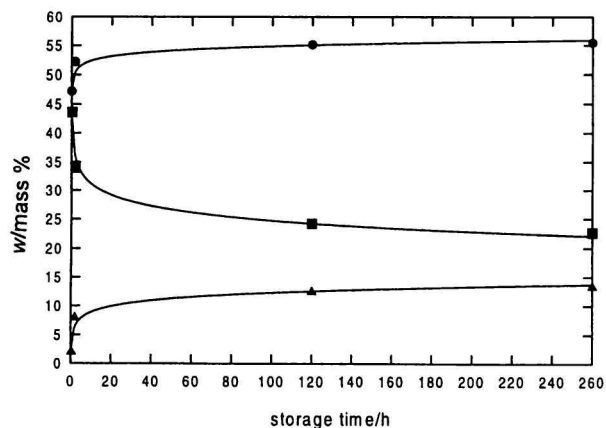


Fig. 8. The influence of the storage time on the product of isoprene hydrochlorination. ● 1ch3m2b, ■ 3ch3m1b, ▲ 1,3dch3mb.

isoprene conversion reaches the value close to the maximum.

Considering the investigated parameters of the hydrochlorination reaction it can be seen that the biggest changes in conversion are caused by changes in the mole ratio of hydrogen chloride to isoprene. The influence of other parameters is rather inconsiderable and can be presented in a decreasing series: hydrogen chloride to isoprene mole ratio \gg temperature $>$ water concentration $>$ hydrogen chloride flow rate $>$ ammonium salt concentration.

The experimental selectivities of the transformations of isoprene to the main reaction products in the point of maximum conversion (Table 4) are as follows ($x/\text{mole } \%$): 1ch3m2b 80.0 ± 4.5 ; 3ch3m1b 12.9 ± 3.7 ; 1,3dch3mb 6.4 ± 0.5 .

Also the examinations of the reaction mixture composition during storing the product at room temperature were performed. The initial composition of the mixture was as follows ($w/\text{mass } \%$): isoprene 5.1; 3ch3m1b 43.6; 1ch3m2b 47.1; 1,3dch3mb 2.0; hydrogen chloride 1.4; unidentified compounds 0.2; water 0.7. The changes in chloromethylbutenes and 1,3dch3mb content *vs.* time are shown in Fig. 8.

The greatest changes in the composition are observed up to 120 h. The mass fraction of 3ch3m1b lowers to 33.9 mass %, and of 1ch3m2b increases to 52.1 mass % after 2 h storage. After 120 h of storing the mass fraction of 3ch3m1b decreases to 24.2 and that of 1ch3m2b grows to 55.1 mass %. The further storage causes only inconsiderable changes in chloromethylbutenes concentrations (to 1 mass %). The 1,3dch3mb mass fraction after 120 h storage increases to 12.45 mass % and inconsiderably increases during the further storing. Also the increase of the concentration of unidentified compounds, probably products of oligomerization, telomerization or chloromethylbutenes hydration has been observed.

CONCLUSION

The most effective synthesis of 3-chloro-3-methyl-1-butene from isoprene and hydrogen chloride proceeds in the following conditions: temperature -30°C , hydrogen chloride to isoprene mole ratio 0.45, hydrogen chloride flow rate 0.010 g min^{-1} (for 1 g of isoprene), water $w = 5.0 \text{ mass } \%$, ammonium salt $w = 0.2 \text{ mass } \%$. In such conditions the maximum selectivity of the transformation to 3ch3m1b is 80.5 mole %, and the selectivities of the transformation of isoprene to 1ch3m2b and 1,3dch3mb are 16.9 and 2.3 mole %, respectively, at the isoprene conversion equal to 23.0 mole %.

The rise of temperature increases the rate of isomerization of the formerly formed 3ch3m1b to 1ch3m2b and therefore influences the selectivity of the transformation of isoprene to 3ch3m1b.

A recirculation of considerable amounts of isoprene to the synthesis reactor must be taken into consideration in the realization of the technological process. Its separation from 3ch3m1b will require distillation columns of high efficiency. It is of great importance to maintain precise parameters of the process, especially temperature, because the satisfactory selectivity of the transformation to 3ch3m1b is achieved in relatively narrow ranges of their changes.

During the storage 3ch3m1b isomerizes to 1ch3m2b. Also the hydrochlorination of the second double bond occurs resulting in formation of 1,3dch3mb and products of oligomerization or telomerization.

REFERENCES

- Eur.* 444 742 (1991), Shell International Research Maatschappij, B. V. (Inv.: Kramer, P. A. and Wullink-Schelvis, A. M.).
- Ind.* 161 321 (1987), Council of Scientific and Industrial Research Indian, *Chem. Abstr.* 110, 23344U.
- Min'kovskii, M. M., Cherkarevt, V. G., and Korostel'eva, I., *Pishch. Prom.* (Moscow) 9, 49 (1988).
- Eur.* 24 306 (1981), L. Givaudan & CIE Société Anonyme. (Inv.: Gonzabach, H. U. and Ochsner, P. A.).
- U.S.* 2382031 (1945), United Gas Improvement Comp. (Inv.: Soday, F. J.).
- Petrov, A. A., Razumova, N. A., and Genusov, M. L., *Zh. Obshch. Khim.* 28, 1128 (1958).
- Petrov, A. A., Bal'yan, Kh. V., Kheruze, Yu. I., Shvarts, E. Yu., and Cherenkova, L. L., *Zh. Obshch. Khim.* 28, 1435 (1958).
- Brit.* 1123149 (1968), Mitsubishi Petrochemical Company Ltd.
- Fr.* 1548516 (1968), Société des Usines Chimiques Rhône-Poulenc.
- Ultée, A. J., *Rec. Trav. Chim. Pays-Bas* 68, 125 (1949).
- Pocker, Y., Stevens, K. D., and Champoux, J. J., *J. Am. Chem. Soc.* 91, 4199 (1969).
- Eur.* 132 543 (1985), Union Camp Corporation. (Inv.:

- Mitchell, P. W. P., McElligott, L. T. and Sasser, D. E.).
13. *Eur.* 132 545 (1985), Union Camp Corporation. (Inv.: Mitchell, P. W. P. and McElligott, L. T.).
 14. Achnazarowa, S. L., and Kafarow, W. W., *Optymalizacja eksperymentu w chemii i technologii chemicznej*. Wydawnictwo Naukowo-Techniczne, Warszawa, 1982.
 15. Polański, Z., *Współczesne metody badań doświadczalnych*. Wiedza Powszechna, Warszawa, 1978.
 16. Zieliński, R., *Tablice statystyczne*. Państwowe Wydawnictwo Naukowe, Warszawa, 1972.
 17. Findeisen, W., Szymanowski, I., and Wierzbicki, A., *Teoria i metody obliczeniowe optymalizacji*. Państwowe Wydawnictwo Naukowe, Warszawa, 1980.