

# Selective Chlorination of Acetone in the Gas Phase

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The aim of this paper is to describe the principal chemical reactions by an appropriate kinetic model, and to determine parameters of this model by means of kinetic data obtained in a continuous isothermal stirred reactor. The reactions of chlorination of acetone are very fast. Chlorine reacts completely, its outflow concentration is equal to zero and is not dependent on the temperature and the inlet acetone/chlorine mole ratio. Maximum selectivity is reached for low temperature, below 55 °C, a higher temperature causes a decrease in the selectivity. Also a high acetone/chlorine mole ratio maximizes the selectivity of the process, the optimal ratio is ranging from 10 to 15. A further increase in this value does not influence the selectivity, on the contrary, it causes a decrease in both conversion and yield of acetone. In practice it means that there is a large amount of unreacted acetone in the outlet flow from the reactor, which has to be recycled back into the reactor after separation of the reaction products.

Monochloroacetone has been utilized in the pharmaceutical industry and in the manufacture of fine chemicals as alkylating agent for the production of dyes, pigments, drugs, and insecticides employed in the agriculture. Chlorination of acetone to monochloroacetone in the gas phase is a consecutive reaction, it means that simultaneously a further chlorination to 1,1-dichloroacetone and 1,3-dichloroacetone proceeds. Due to the fact that the products of chlorination are very reactive, also further reactions proceed yielding products which cannot be readily identified. This reaction produces also hydrogen chloride as by-product, which catalyzes the dimerization of acetone to 4-methyl-3-penten-2-one (mesityl oxide). To derive a complex reaction network involving all partial reactions and by-products is practically impossible. This would necessitate gathering of much experimental data and a very detailed analysis of reaction products (the best way would be *on line*), since various condensation reactions take place during their storage. Therefore, in determining kinetic parameters, we had to derive a very simple kinetic scheme including only reactions yielding analyzed products [1, 2]. Furthermore, we had to take into account the formation of only one derivative of dichloroacetone, because in the analysis the above-mentioned two derivatives could not be distinguished.

Chlorination of acetone is a very fast reaction.

Chlorine charged into the reactor reacts practically quantitatively, its concentration at the outlet from the reactor is zero, regardless the ratio of reactants charged into the reactor and the reaction temperature. In this case the potential extinction of chlorine by chemical reactions can be higher than its addition into the reactor by the inlet flow.

The aim of this work is:

- to describe the principal two chemical reactions by an appropriate kinetic model. The model has to describe the evaluation of the principal components in the reaction mixture depending on the conditions in the reactor. The parameters of the model have been determined by fitting the experimental data obtained from laboratory glass-made reactor,
- using the kinetic model and experimental data to propose the design of the industrial reactor and optimal working conditions maximizing the selectivity of the process to desired product.

## EXPERIMENTAL

Experimental measurements of the kinetics of chlorination of acetone to monochloroacetone (MCA) were carried out in the enterprise Novácke chemické závody, a.s., Nováky. The experimental apparatus is schematically drawn in Fig. 1. The reactor made of glass had a volume of 0.5 dm<sup>3</sup>. Experiments were carried out

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at atmospheric pressure. The temperature in the reactor was adjusted by the temperature of inlet gases and measured continuously by a thermocouple. Acetone was charged into the reactor continuously in the gas phase and in the required ratio with regard to the charged chlorine. The reaction mixture was stirred only by gases flowing through inlet jets. After reaching a steady state in the reactor condensed products were withdrawn and analyzed by gas chromatography. We analyzed only the products MCA and DCA. Other by-products like HCl, or unreacted acetone were not analyzed quantitatively. The outlet concentration of chlorine was always zero. In the analysis of DCA we did not distinguish between derivatives 1,1-DCA and 1,3-DCA, which were considered to be one product.

Experimental data represent three sets of data (Table 1):

– 1st set: the temperature in the reactor was 59 °C, at the inlet into the reactor various mole ratios of acetone and chlorine were used and their molar flow rates were adjusted. We analyzed the required product MCA and the unrequired product DCA. Other components were not analyzed in the system.

– 2nd set: the temperature in the reactor was 65 °C, otherwise as in the 1st set.

– 3rd set: the inlet chlorine/acetone ratio was approximately constant, only the temperature in the re-

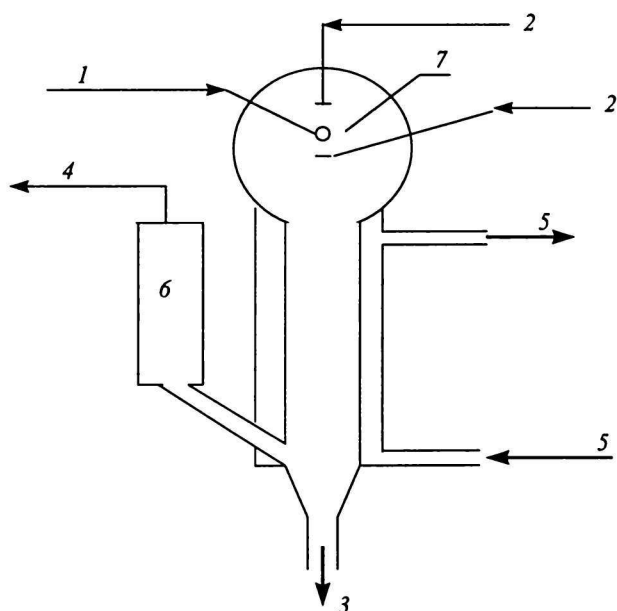


Fig. 1. Scheme of the laboratory reactor for chlorination of acetone in the gas phase. 1. Inlet of chlorine, 2. inlet of gaseous acetone, 3. collecting tank for the product, 4. outlet of hydrogen chloride, 5, 6. cooling, 7. thermocouple.

Table 1. Experimental Data from Kinetic Measurement of Acetone Chlorination in the Laboratory Reactor

Run	$\theta_R$ °C	Inlet flows		Product			
		$F_{O1}$ mol h <sup>-1</sup>	$F_{O2}$ mol h <sup>-1</sup>	Mole ratio		Mole ratio	
				$F_{O1}$	$F_{O2}$	$F_2$	$F_4$
Set 1							
1	59	22.2	1.37	16.2	1	1	0.5
2	59	22.2	1.75	12.7	1	1	0.56
3	59	22.2	2.09	10.6	1	1	0.62
4	59	22.2	2.37	9.4	1	1	0.65
5	59	22.2	2.61	8.5	1	1	0.71
6	59	3.26	0.56	5.8	1	1	0.85
Set 2							
7	65	16.64	1.20	13.9	1	1	0.56
8	65	16.64	1.59	10.5	1	1	0.82
9	65	16.64	2.09	8.0	1	1	1.14
10	65	6.84	0.89	7.72	1	1	1.61
11	65	16.64	2.37	7.0	1	1	1.69
12	65	3.58	0.82	4.37	1	1	2.39
13	65	3.03	0.90	3.39	1	1	2.38
Set 3							
14	58	3.26	0.56	5.82	1	1	0.85
15	62	3.26	0.56	5.82	1	1	1.04
16	63	3.26	0.56	5.82	1	1	1.09
17	64	3.67	0.56	6.55	1	1	1.18
18	65	3.67	0.56	6.55	1	1	1.19
19	65.5	3.67	0.56	6.55	1	1	1.12

Table 2. Denotation of the Compounds

Compound	Abbreviation	Number
Acetone	Ac	1
Chlorine	Cl <sub>2</sub>	2
Chloroacetone	MCA	3
Dichloroacetone	DCA	4
Hydrogen chloride	HCl	5

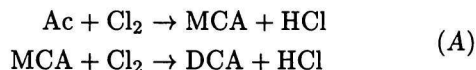
actor was changed within the range 58–65.5°C.

In all cases the inlet mole ratio of reactants, their inlet molar flow rate, and the temperature in the reactor are known.

## THEORETICAL

### Reaction Scheme

In the simplified kinetic scheme only two reactions,  $N_R = 2$ , will be considered



The number of components is being considered to be  $N_C = 5$ , and individual components given in the further text will be denoted according to Table 2.

Let us define a matrix of stoichiometric coefficients  $\mathbf{A}_\nu$ , having a dimension ( $N_R \times N_C$ ) the elements of which are the stoichiometric coefficients of the reaction scheme (A),  $\nu_{ji}$ , where the first index indicates the reaction and the second one the component. Thus, matrix  $\mathbf{A}_\nu$  has the following form

$$\mathbf{A}_\nu = \begin{pmatrix} -1 & -1 & 1 & 0 & 1 \\ 0 & -1 & -1 & 1 & 1 \end{pmatrix} \quad (1)$$

### Kinetic Model

The rate of the  $j$ -th reaction is defined by

$$r_{Vj} = \frac{1}{V_R} \cdot \frac{dn_i}{\nu_{ji} dt} \quad (2)$$

and the rate equation for the  $j$ -th reaction will be considered in the following form

$$r_{Vj} = k_{vj\infty} \exp\left(\frac{-E_j}{RT}\right) \prod_{i=1}^{N_C} C_i^{a_{ji}} \quad (3)$$

in which  $k_{vj\infty}$  is the frequency factor of the rate constant of the  $j$ -th reaction,  $E_j$  is activation energy of the  $j$ -th reaction, and  $a_{ji}$  is the partial order of the  $i$ -th component in the  $j$ -th reaction. Parameters  $k_{vj\infty}$ ,  $E_j$ ,  $a_{ji}$  for  $j = 1, \dots, N_R$  and  $i = 1, \dots, N_C$  are parameters of the rate equations which must be determined

on the basis of experimental data. In the majority of cases occurring in the practice partial orders of reaction products are equal to zero.

In our case, *i.e.* chlorination of acetone to MCA and DCA, both reactions will be considered to be of the zero order also with respect to chlorine. This assumption is possible due to the fact that the rate of reaction is very high and chlorine charged into the reactor does react practically quantitatively, its conversion is 100%, *i.e.* at the outlet of the reactor the concentration of chlorine is zero. It means, the rate of chemical reactions calculated from eqn (3), assuming nonzero reaction order with respect to chlorine, would be zero.

If the potential rate of consumption of the  $k$ -th reactant (in our case chlorine,  $k = 2$ ) given by the rate eqn (3) is higher than its addition into the reactor  $F_{0k}$ , *i.e.*

$$F_{0k} \leq \left| V_R \sum_{i=1}^{N_R} \nu_{jk} r_j \right| \quad (4)$$

then the outlet concentration of the reactant  $k$  is zero. In this case it does not have sense to speak about the rate of chemical reaction, but only about the rates of formation of components,  $w_i$ , which are proportional to the inlet flow of the  $k$ -th reactant and stoichiometric ratio of the rate of extinction of this reactant by the  $j$ -th reaction to the overall rate of its extinction by all reactions, *i.e.*

$$w_i = \sum_{j=1}^{N_R} \nu_{ji} \Xi_j \quad (5)$$

where

$$\Xi_j = r_j \quad (6)$$

for  $\nu_{jk} = 0$  and

$$\Xi_j = \frac{F_{0k}}{V_R} \frac{\nu_{jk} r_j}{\sum_{n=1}^{N_R} \nu_{nk} r_n} \quad (7)$$

if  $\nu_{jk} < 0$ .

The estimation of the rate of formation of components necessitates the knowledge of the value of chemical reactions according to relation (3). Since in all kinetic measurements (Tables 1–3), which are available, the concentration of chlorine at the outlet from the reactor is zero, one cannot determine parameters of real rate equations from the measured data. We can determine only the rates of formation of individual components, which are similarly as the rates of chemical reactions, a function of temperature and concentrations of individual components in the system.

Therefore, we will consider the rates of formation of components according to the relations (5) and (7), in which, however, the values of real reaction rates  $r_{Vj}$  will not be involved, only functions  $\xi_{Vj}$ , which are dependent on the temperature and concentration of

**Table 3.** The Values of Kinetic Parameters Obtained by Comparison of the Theoretical Results with Experimental Data

$\kappa_{v1\infty}/(\text{mol}^b \text{ m}^c \text{ h}^{-1})$ , $b = 1 - \alpha_{11}$ ; $c = 3\alpha_{11} - 3$	$0.195 \times 10^{-14}$
$\kappa_{v2\infty}/(\text{mol}^b \text{ m}^c \text{ h}^{-1})$ , $b = 1 - \alpha_{23}$ ; $c = 3\alpha_{23} - 3$	$0.2032 \times 10^{-3}$
$\varepsilon_1/(\text{J mol}^{-1})$	5 312
$\varepsilon_2/(\text{J mol}^{-1})$	69 350
$\alpha_{11}$	0.9802
$\alpha_{23}$	0.5648
$\delta_{\text{MCA}}/\%$	8.61
$\delta_{\text{DCA}}/\%$	4.03

reactants in the  $j$ -th reaction and formally coincident with eqn (3), *i.e.*

$$\xi_{V1} = \kappa_{v1\infty} \exp\left(-\frac{\varepsilon_1}{RT}\right) C_1^{\alpha_{11}} \quad (8)$$

$$\xi_{V2} = \kappa_{v2\infty} \exp\left(-\frac{\varepsilon_2}{RT}\right) C_3^{\alpha_{23}} \quad (9)$$

Thus, we must determine parameters involved in eqns (9, 10). We would like to point out that parameters  $\kappa_{v\infty}$ ,  $\varepsilon$ , and  $\alpha$  are not the real kinetic parameters of reaction rates, *e.g.* reaction rate constants, activation energies, and orders of reactions.

### Reactor Model

Let us denote the inlet and the outlet molar flow rates of the  $i$ -th component ( $i = 1, \dots, 5$ )  $F_{0i}$  and  $F_i$ , respectively, and the outlet mole ratio MCA/DCA by the symbol  $p$ , *i.e.*

$$p = \frac{F_3}{F_4} \quad (10)$$

If we know the molar flow rate of chlorine at the inlet into the reactor,  $F_{02}$ , and reacting of chlorine is supposed to proceed quantitatively ( $F_2 = 0$ ), then the molar flow rates of products MCA and DCA at the outlet of the reactor will take the following form

$$F_4 = \frac{F_{02}}{p + 2} \quad (11)$$

and

$$F_3 = pF_4 \quad (12)$$

The outlet flow rate of acetone,  $F_1$ , results from the balance

$$F_1 = F_{01} - (F_3 + F_4) \quad (13)$$

Thus, for the degree of conversion of acetone

$$x_1 = \frac{F_{01} - F_1}{F_{01}} \quad (14)$$

The molar flow rate of HCl at the outlet of the reactor,  $F_5$ , must be equal to the molar flow rate of chlorine at the inlet of the reactor, *i.e.*

$$F_5 = F_{02} \quad (15)$$

The volume flow rate at the inlet of the reactor,  $Q_0$ , is given by the equation of the state of ideal gas

$$Q_0 = \frac{F_0 RT}{P} \quad (16)$$

in which

$$F_0 = \sum_{i=1}^{N_C} F_{0i} \quad (17)$$

Because the overall amount of moles in the reactor is not changed by chemical reactions,

$$\sum_{j=1}^{N_R} \sum_{i=1}^{N_C} \nu_{ji} = 0 \quad (18)$$

the overall molar flow rates at the inlet and outlet of the reactor are equal. Thus, if we consider an isothermal regime in the reactor also the inlet and outlet volume flow rates are equal.

Assuming constant pressure, constant temperature, and perfect stirring in the reactor, the mathematical model of the reactor under steady-state conditions consists of material balances for individual components, *i.e.*

$$Q_0 C_{0i} + V_R w_i = Q C_i \quad (19)$$

where  $i = 1, \dots, N_C$ . Values  $w_i$  will be determined by eqns (5–9) and the equality  $Q_0 = Q$  will be assumed.

Eqns (19) represent a system of nonlinear algebraic equations (NAE), by solution of which and for given values  $Q_0$ ,  $C_{0i}$  ( $i = 1, \dots, N_C$ ),  $T_R$ , and  $V_R$  one gets the concentration values for all components at the outlet of the reactor.

In calculating the selectivity the following relationship [3] is used

$$\sigma = \frac{F_3 - F_{03}}{\nu_{13}} \frac{\nu_{11}}{F_1 - F_{01}} \quad (20)$$

and for the yield of acetone the equation

$$\eta = \frac{F_3 - F_{03}}{\nu_{13}} \cdot \frac{(-\nu_{11})}{F_{01}} \quad (21)$$

is applied.

### Estimation of Kinetic Parameters

Parameters of eqns (8) and (9) for the reaction system (A) have been determined by comparison of the predicted and measured concentrations of components using the nonlinear regression method, *i.e.* by the estimation of the minimum of the objective function

$$F(\kappa_{v1\infty}, \kappa_{v2\infty}, \varepsilon_1, \varepsilon_2, \alpha_{11}, \alpha_{23}) = \sum_{k=1}^{N_{\text{exp}}} \sum_{i=3,4} \left( \frac{C_{ik,\text{exp}} - C_{ik,\text{calc}}}{C_{ik,\text{exp}}} \right)^2 = \min \quad (22)$$

in which  $C_{ik,\text{exp}}$  represents the experimentally determined concentration of the  $i$ -th component at the outlet of the reactor in the  $k$ -th experiment,  $C_{ik,\text{calc}}$  represents the concentration of the  $i$ -th component at the outlet of the reactor under conditions of the  $k$ -th experiment determined by calculation solving model equations describing the reactor.

The minimum of the objective function (16) will be determined by a suitable method of multiparametric optimization (*e.g.* by the simplex method).

### RESULTS AND DISCUSSION

Values of parameters in the minimum of the objective function (22) are listed in Table 3. The relative errors given in this table are computed by the relation

$$\delta = \frac{\sum_{k=1}^{N_{\text{exp}}} \left| \left( \frac{C_{ik,\text{exp}} - C_{ik,\text{calc}}}{C_{ik,\text{exp}}} \right) \right|}{N_{\text{exp}}} 100 \% \quad (23)$$

The comparison of measured and calculated concentrations of MCA and DCA is depicted in Figs. 2 and 3. The agreement between these concentrations at the outlet of the reactor is good, which is documented also by the values of relative errors  $\delta$  – 8.66 % and 4.03 % for MCA and DCA, respectively.

It follows from the values of “activation energies”  $\varepsilon_1$  and  $\varepsilon_2$  (Table 3) that the rate of the second reaction (consecutive chlorination of MCA to DCA) increases faster with increasing temperature than the rate of the first reaction. The ratio of constants  $\kappa_{v2}/\kappa_{v1}$  against temperature is plotted in Fig. 4. It is obvious that an increase in temperature has a negative influence on the selectivity of the chlorination process yielding MCA. Therefore, the maximum of the process selectivity could be obtained at the lowest possible temperature, at which acetone is at given pressure in the gaseous phase.

The process can be qualitatively characterized by three quantities: degree of conversion of acetone  $x_1$ , selectivity of the process for the desired product (MCA)  $\sigma$ , and yield of acetone with regard to the required product  $\eta$ . These values are influenced by the temperature and the acetone/chlorine ratio. The comparison

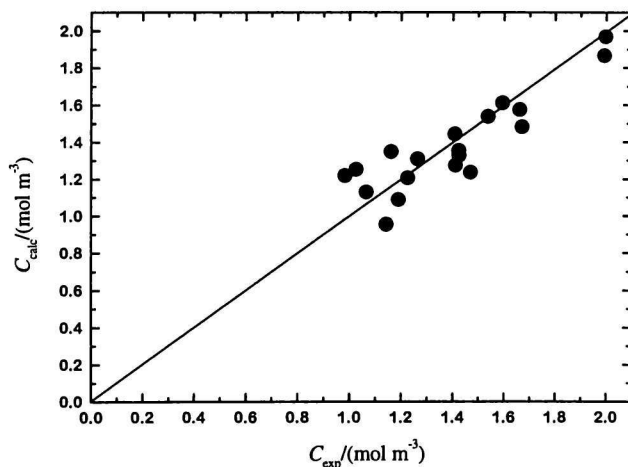


Fig. 2. Comparison of experimental and calculated outlet concentrations of MCA from the reactor.

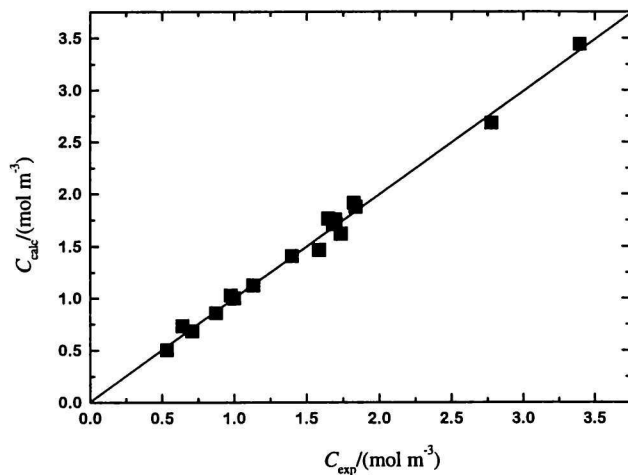


Fig. 3. Comparison of experimental and calculated outlet concentrations of DCA from the reactor.

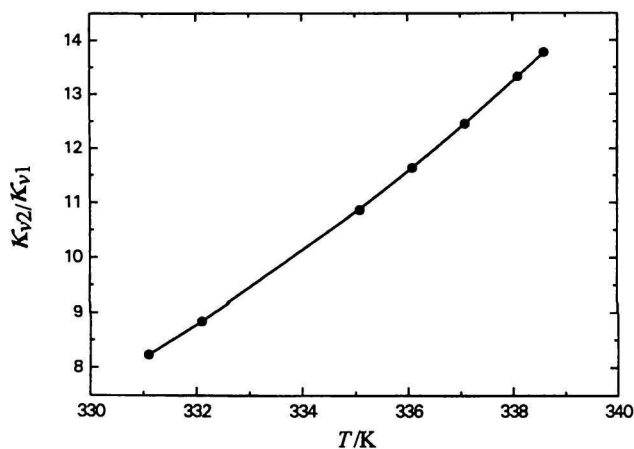
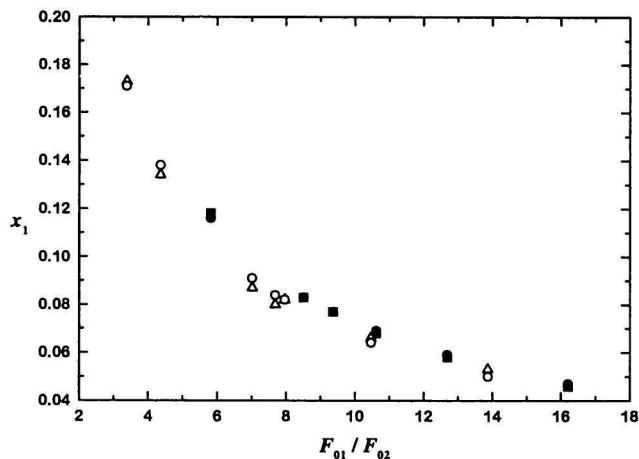
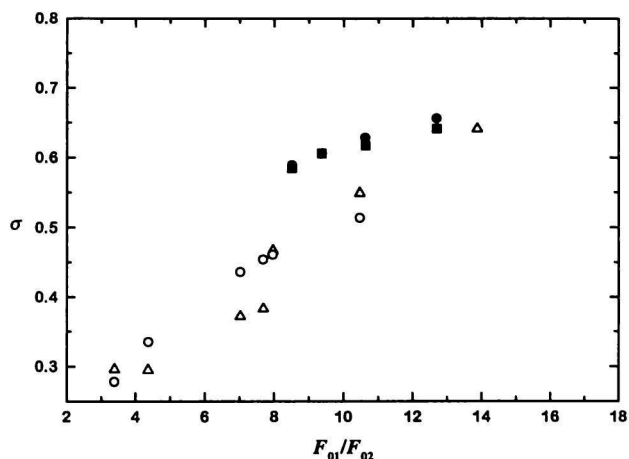


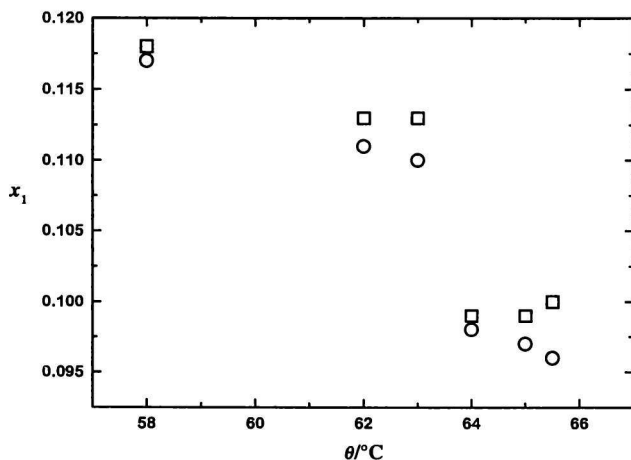
Fig. 4. Temperature dependence of the ratio of constants  $\kappa_{v2}/\kappa_{v1}$ .



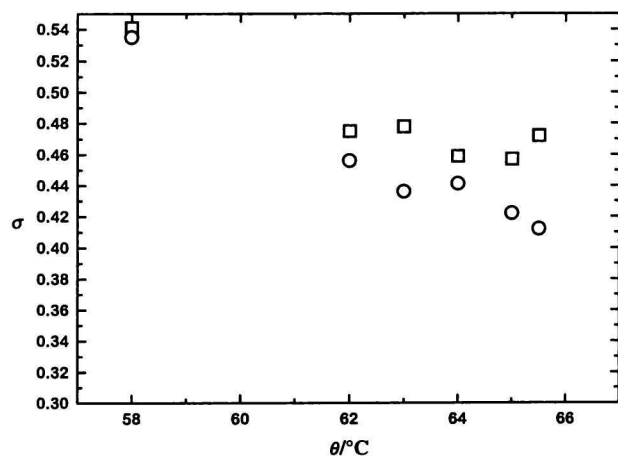
**Fig. 5.** Dependence of the degree of conversion of acetone on the acetone/chlorine mole ratio at the inlet of the reactor for experimental conditions given in Table 1, set 1 and 2. Comparison of experimentally measured and calculated values; exp  $\theta = 59^\circ\text{C}$  (■), calc  $\theta = 59^\circ\text{C}$  (●), exp  $\theta = 65^\circ\text{C}$  (Δ), calc  $\theta = 65^\circ\text{C}$  (○).



**Fig. 7.** Dependence of selectivity of chlorination to MCA on the mole ratio acetone/chlorine at the inlet of the reactor for experimental conditions given in Table 1, set 1 and 2. Comparison of experimentally measured and calculated values; exp  $\theta = 59^\circ\text{C}$  (■), calc  $\theta = 59^\circ\text{C}$  (●), exp  $\theta = 65^\circ\text{C}$  (Δ), calc  $\theta = 65^\circ\text{C}$  (○).



**Fig. 6.** Temperature dependence of the degree of conversion of acetone in the reactor for experimental conditions given in Table 1, set 3. Comparison of experimentally measured and predicted values; exp (□), calc (○).



**Fig. 8.** Temperature dependence of selectivity in the reactor for experimental conditions given in Table 1, set 3. Comparison of experimentally measured and calculated values; exp (□), calc (○).

of experimental and predicted values of the above-mentioned quantities *vs.* mole ratio acetone/chlorine is depicted in Figs. 5, 7, and 9. Figs. 6, 8, and 10 display the comparison of experimental and predicted values of the same quantities *vs.* temperature. From Figs. 5–10 a very good agreement between calculated and measured values is apparent.

An increase in temperature has a very negative influence on the selectivity of the process. In Fig. 11 is given the dependence of the selectivity of chlorination for MCA on the acetone/chlorine mole ratio ( $F_{01}/F_{02}$ ) at the inlet of the reactor for temperatures from  $50^\circ\text{C}$  to  $70^\circ\text{C}$ . It is obvious that the maximal selectivity is

achieved at lower temperatures. In addition, we can see that the optimal ratio  $F_{01}/F_{02}$  is ranging from 10 to 15. A further increase of this ratio does not cause a significant increase in the selectivity, on the contrary, a significant decrease in the degree of conversion and yield of acetone occurs. Practically it means that a large amount of unreacted acetone is released from the reactor. After separation of the reaction products, this acetone should be recycled back into the reactor (Figs. 5 and 9). A low value of the ratio  $F_{01}/F_{02}$  results in a significant decrease in the selectivity, as can be seen in Figs. 6–11.

Fig. 12 shows the influence of space time defined as

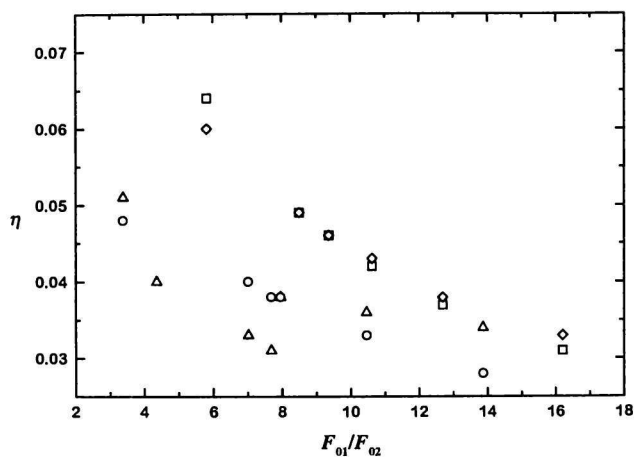


Fig. 9. Dependence of the yield of acetone calculated on MCA on acetone/chlorine mole ratio at the inlet of the reactor for experimental conditions given in Table 1, set 1 and 2. Comparison of experimentally measured and calculated values; exp  $\theta = 59^\circ\text{C}$  ( $\square$ ), calc  $\theta = 59^\circ\text{C}$  ( $\diamond$ ), exp  $\theta = 65^\circ\text{C}$  ( $\Delta$ ), calc  $\theta = 65^\circ\text{C}$  ( $\circ$ ).

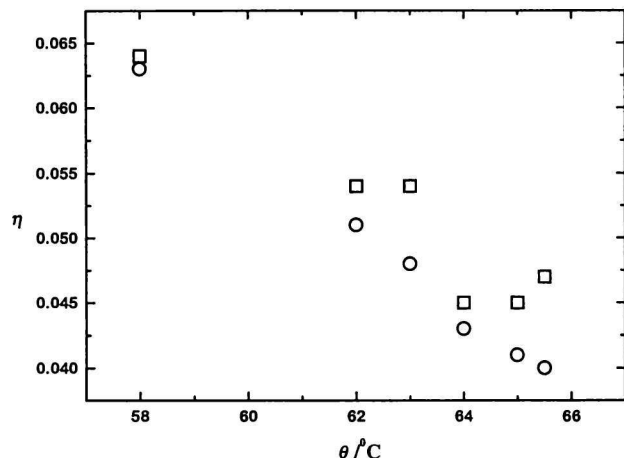


Fig. 10. Temperature dependence of the yield of acetone for experimental conditions given in Table 1, set 3. Comparison of experimentally measured and calculated values; exp ( $\square$ ), calc ( $\circ$ ).

the ratio of the reactor volume to the overall volume flow rate through the reactor, *i.e.*

$$\tau = \frac{V_R}{Q_0} \quad (24)$$

for two values of temperature, 55°C and 65°C and two various values  $F_{01}/F_{02}$ . Due to the fact that the reactions proceed instantaneously and chlorine reacts quantitatively, the influence of the reactor volume is already at very low values of space time (practically 1 s) negligible. This confirms also the preceding conclusions that the overall result of the process is rather influenced by the temperature and the mole ratio of reactants than by the size of the reactor.

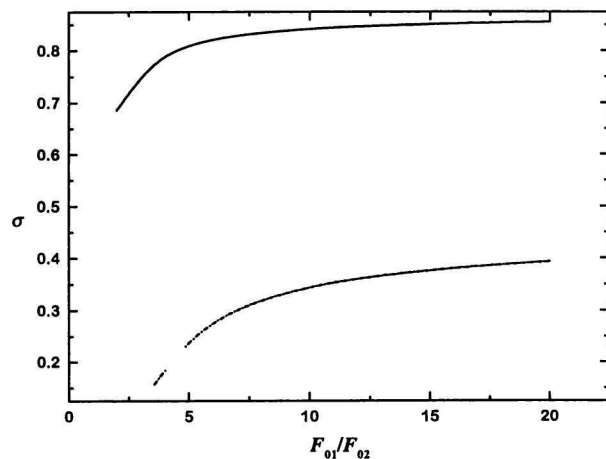


Fig. 11. Dependence of the selectivity of chlorination for MCA on acetone/chlorine mole ratio for various values of temperature;  $\theta = 50^\circ\text{C}$  (—),  $\theta = 55^\circ\text{C}$  (---),  $\theta = 60^\circ\text{C}$  (· · · · ·),  $\theta = 65^\circ\text{C}$  (— · — · —),  $\theta = 70^\circ\text{C}$  (- · - · -).

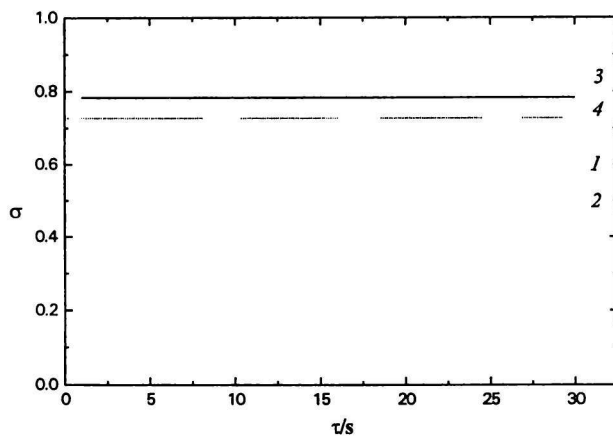


Fig. 12. Dependence of the selectivity of chlorination on space time;  $F_1/F_2 = 5, \theta = 55^\circ\text{C}$  (1),  $F_1/F_2 = 5, \theta = 65^\circ\text{C}$  (2),  $F_1/F_2 = 15, \theta = 55^\circ\text{C}$  (3),  $F_1/F_2 = 15, \theta = 65^\circ\text{C}$  (4).

## CONCLUSION

We can conclude that the kinetic model proposed in accordance with the kinetic scheme (A) along with the reactor model describe the reaction system and the behaviour of the reactor for the chlorination of the acetone in the gas phase very well. From the analysis of the obtained results following conclusions could be made:

Maximum selectivity ( $\sigma$ ) is reached for low temperatures, below 55°C. A higher temperature causes a decrease in the selectivity. Also a high acetone/chlorine mole ratio maximizes the selectivity of the process, the optimal ratio is ranging from 10 to 15. A further increase in this value does not influence the selectivity, on the contrary, it causes a decrease in both conversion



and yield of acetone. In practice it means that there is a large amount of unconverted acetone in the outlet flow from the reactor, which has to be recycled back into the reactor after separation of the reaction products. In designing a reactor for the MCA production, the above-mentioned requirements (low temperature, high acetone/chlorine mole ratio, recycling of unconverted acetone) have to be taken into account.

The chlorination of acetone in the gas phase is described by very simple kinetic model, together with very simple model of reactor. Despite this, the agreement between experimental and predicted values is very good. A larger set of data and particularly a complex analysis of the reaction mixture at the outlet of the reactor would enable to derive a more complex reaction scheme. For instance, an advanced reaction scheme extended by the reaction of formation of mesityl oxide would enable to distinguish the reactions of formation of 1,1-DCA and 1,3-DCA and a more precise estimation of parameters.

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## SYMBOLS

$A_\nu$	matrix of stoichiometric coefficients	
$a_{ji}$	order of the $i$ -th component in the $j$ -th reaction	
$C$	molar concentration	$\text{mol m}^{-3}$
DCA	dichloroacetone	
$E$	activation energy	$\text{J mol}^{-1}$
$F$	molar flow rate at the outlet of the reactor	$\text{mol h}^{-1}$
$F_0$	molar flow rate at the inlet of the reactor	$\text{mol h}^{-1}$
$k_\nu$	rate constant, its dimension depends on the form of the rate equation	
$k_{\nu\infty}$	frequency factor, its dimension depends on the form of the rate equation	
MCA	monochloroacetone	
$N_C$	number of components	
$N_{\text{exp}}$	number of experiments	

$N_R$	number of reactions	
$P$	pressure	Pa
$p$	outlet mole ratio MCA : DCA	
$Q$	volume flow rate at the outlet of the reactor	$\text{m}^3 \text{h}^{-1}$
$Q_0$	volume flow rate at the inlet of the reactor	$\text{m}^3 \text{h}^{-1}$
$R$	universal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
$r_{Vj}$	rate of the $j$ -th reaction	$\text{mol m}^{-3} \text{h}^{-1}$
$T$	temperature	K
$T_R$	temperature in the reactor	K
$t$	time	h
$V_R$	reactor volume	m
$w_i$	rate of formation of the $i$ -th component	$\text{mol m}^{-3} \text{h}^{-1}$
$x$	degree of conversion	

## Greek Letters

$\delta$	relative error defined by eqn (23)	
$\eta$	yield of acetone, defined by eqn (21)	
$\nu_{ji}$	stoichiometric coefficient of the $i$ -th component in the $j$ -th reaction	
$\xi$	function defined by eqns (8, 9)	
$\Xi$	rate of extinction of chlorine by the $j$ -th reaction, defined by eqn (7)	$\text{mol m}^{-3} \text{h}^{-1}$
$\sigma$	selectivity of chlorination of acetone defined by eqn (20)	
$\tau$	space time	h

## REFERENCES

1. Astarita, G. and Ocone, R., *Chem. Eng. Sci.* 47, 2135 (1992).
2. Markoš, J., Pisu, M., and Morbidelli, M., *METECC 94: Methods and Techniques in Computational Chemistry*. (Clementi, E., Editor.) Vol. C, Chapter 5, pp. 167–245. STEFF, Cagliari, 1994.
3. Froment, G. F. and Bischof, K. B., *Chemical Reactor Analysis and Design*. Wiley, New York, 1990.