Kinetics and mechanism of the methylation reactions of anilines with dimethylcarbonate

A.F. Mullayanova[1], Y.Y. Mayakova[2], K.F. Koledina[1,2], R.I. Khusnutdinov[2], A.N. Abdrahmanov[2]

[1]Ufa State Petroleum Technological University, Cosmonavtov street 1, Ufa, Russia, 450062

[2]Institute of Petrochemistry and Catalysis Russian Academy of Sciences, Prospect October 141, Ufa, Russia, 450075

Abstract. The paper investigates the mechanism of the reaction of methylation of primary anilines by the reagent "Green chemistry" dimethylcarbonate. The mathematical model of the description of change of concentration of substances which represents a problem of Cauchy is constructed. For temperature t=145^{0}C and speed constants are determined.

1. Introduction

Dimethylcarbonate (DMK) is one of the environmentally safe chemicals of "green chemistry". DMK is a substitute for toxic chemicals such as phosgene, dimethylsulfate and methylhalides, because it is weakly toxic compared to other carboxylic or alkylating agents [1].

According to [2], the direction of the reaction of primary aromatic anilines with dimethylcarbonate depends on the nature of the catalyst. In the presence of zeolite catalysts, N-methylation of primary anilines is observed.

$$2ArNH_2 + 2(CH_3O)_2CO(\rightarrow)ArNHCH_3 + [ArN(CH_3)_2 + CH]_3OH + 2CO_2 + H_2O(1)$$

So, under the conditions: 130-180 ^{0}C with high selectivity (92-97%), mono-N-methylated anilines ($ArNHCH_3$) are formed during the conversion of the starting anilines 72-93%. If there are electron-withdrawing substituent's in aniline molecules, the reaction rate decreases. At 130 ^{0}C, the degree of conversion of aniline ($ArNH_2$) and DMC ($(CH_3O)_2CO$) after 300 min is 76%, and after 195 min the conversion of aniline ($ArNH_2$) is 94% [3-5]. Also, it was found that the optimal reaction conditions is the ratio of aniline: DMK = 1:4 [2].

2. Mathematical model

On the basis of literary sources, experimental data, a detailed scheme of chemical transformations of reaction (1) in the form of elementary stages is proposed (Table 1).

On the basis of the law of mass action [6], the change in concentration of substances $x_j(t)$ participating in the reaction at any time moment t is described by a system of ordinary nonlinear

Table 1. Scheme of chemical transformations of the reaction of methylation of anilines with dimethylcarbonate

N	Stage	Speed reaction
1	$[FeHY]^+(\mathbf{x_7}) + (CH_3O)_2CO(\mathbf{x_2})(\rightarrow)[FeHY]^+[CO_2OCH_3]^-(\mathbf{x_8}) + [CH_3]^+(\mathbf{x_9})$	$r_1 = k_1x_2x_7$
2	$[FeHY]^+[CO_2OCH_3]^-(\mathbf{x_8})(\rightarrow)[FeHY]^+[CH_3O]^-(\mathbf{x_{10}}) + CO_2(\mathbf{x_6})$	$r_2 = k_2x_8$
3	$[ArNH]_2(\mathbf{x_1}) + [CH_3]^+(\mathbf{x_6})(\rightarrow)ArNHCH_3(\mathbf{x_3}) + H^+(\mathbf{x_{11}})$	$r_3 = k_3x_1x_9$
4	$[FeHY]^+[CH_3O]^-(\mathbf{x_{10}}) + H^+(\mathbf{x_{11}})(\rightarrow)[FeHY]^+(\mathbf{x_7}) + [CH]_3OH(\mathbf{x_5})$	$r_4 = k_4x_10x_11$
5	$ArNHCH_3(\mathbf{x_3}) + [CH_3]^+(\mathbf{x_9})(\rightarrow)ArN[CH_3]_2(\mathbf{x_4}) + H^+(\mathbf{x_{11}})$	$r_5 = k_5x_3x_9$

differential equations (SONDE) (2):

$$\begin{cases} \frac{dx_1}{dt} = -r_3, \\ \frac{dx_2}{dt} = -r_1, \\ \frac{dx_3}{dt} = r_3 - r_5, \\ \frac{dx_4}{dt} = r_5, \\ \frac{dx_5}{dt} = r_4, \\ \frac{dx_6}{dt} = r_2, \\ \frac{dx_7}{dt} = -r_1 + r_4, \\ \frac{dx_8}{dt} = r_1 - r_2, \\ \frac{dx_9}{dt} = r_1 - r_3 - r_5, \\ \frac{dx_{10}}{dt} = r_2 - r_4, \\ \frac{dx_{11}}{dt} = r_3 - r_4 + r_5. \end{cases} \quad (2)$$

with initial data $\mathrm{x_1}(0) = \mathrm{x_1^0}, \mathrm{x_2}(0) = \mathrm{x_2^0}, \mathrm{x_5}(0) = \mathrm{x_5^0}, \mathrm{x_i}(0) = 0, \mathrm{i} = 3, 4, 6 - 11$, where r_j - speed reaction, $mol/l * min$, which are calculated by the Arrhenius equation $\mathrm{k} = \mathrm{k_0 e}^{-\frac{\mathrm{E}}{\mathrm{RT}}}$,
where k_i - reaction rate constants,k_0 - preexponential factor (its dimension coincides with the dimension k_i); R - gas constant equal to 8,3144 $J/mol * K$, T - temperature, ; E - activation energy,J/mol.
The initial reagents are aniline and dimethylcarbonate, and the final products are methylaniline ($x_3 = ArNHCH_3$) and dimethylaniline ($x_4 = ArN(CH_3)_2$). During the chemical experiment, a change in the concentration of the reacting substances with time is observed, depending on the initial concentrations of the starting materials, temperature and other parameters.
To find the kinetic parameters, the direct and inverse kinetic problems were solved.

The direct problem - the problem of calculating the composition of a multicomponent reactive mixture and the reaction rate when solving SONDE (2) with known parameters is a tough problem; therefore, the Rosenbrock method of the third order of accuracy was used [7].
The mathematical inverse problem is to determine such a set of velocities k_i so that the solution of the ODE system (2) is as close as possible to the experimental data [8]. The parameters of the kinetic equations were determined from the condition for achieving the optimization criterion using a genetic algorithm.

$$\sum_{i=1}^{L}\sum_{j=1}^{M}(x_{ij}^{p}-x_{ij}^{e})^{2}\rightarrow min \qquad (3)$$

where and x_{ij}^{p}, x_{ij}^{e} - experimental and calculated concentrations of substances ,L - the number of measurement points in time of the observed substances during the reaction, M - amount of substances.

3. Result

As a result of mathematical processing of experimental data in Matlab710, the kinetic constants of the corresponding stages were found (Table 2). Graphs were compared comparing the calculation and experiment of the measured substances (Fig. 1 - 3). For the reaction of primary aromatic amines with dimethylcarbonate, the measured substances are x_1 (consumed), x_3 (formed) and x_4 (formed).

Table 2. Kinetic constants of the rate of the reaction of methylation of amines with dimethylcarbonate at $T = 145^0C$

Legend	k_j
k1, $[l/(mol*min)]$	0,2428
k2, $[1/min]$	0,5477
k3, $[l/(mol*min)]$	3,9628
k4, $[l/(mol*min)]$	10,0441
k5, $[l/(mol*min)]$	2,5089

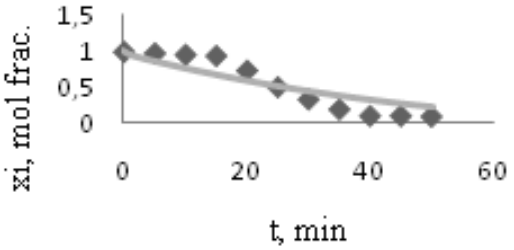

Figure 1. Graph of changes in aniline concentration ($x_1 = ArNH_2$) versus time.

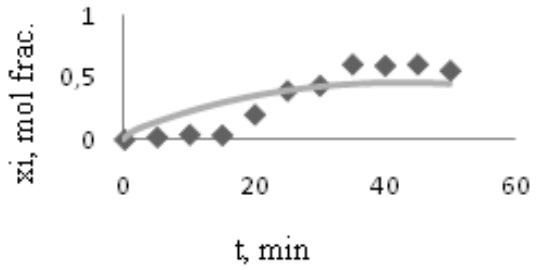

Figure 2. Graph of changes in methylaniline concentration ($x_3 = ArNHCH_3$) versus time.

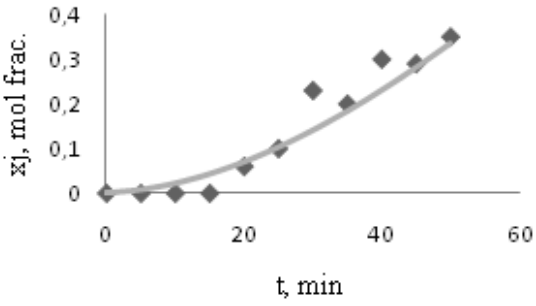

Figure 3. Graph of changes in dimethylaniline concentration ($x_4 = ArN(CH_3)_2$ versus time.

It can be seen that the compliance of the experimental data with the calculated values is not satisfactory for all reactions (aniline, methylaniline). Therefore, it was proposed to conduct additional field experiments with a view to detailing the stages. Also, for optimal control of planning new field chemical experiments without additional costs, it is necessary to investigate the temperature dependence of the reaction.

4. References

[1] Ariko, F. Dimethylcarbonate - a modern ”green” reagent and solvent / F. Ariko, P. Tundo Chemistry advances. – 2010. – Vol. 6. – P. 532.

[2] Ardieva, S. Aniline methylation reaction with dimethyl carbonate under the effect of granulated zeolite na-y without a binder / S.I. Ardieva, N.A. Chadneva, Y.Y. Mayakova, R.I. Khusnutdinov // Materials of the IXAll-Russian Scientific Internet Conference, 2015. – P. 5-6.

[3] Selva, M. Selective mono-N-methylation of primary aromatic amines by dimethyl carbonate over faujasite X- and Y-type zeolites / M. Selva, A. Bomben, P. Tundo // Journal Chem. Soc. Perkin Trans. – 1997. – Vol. 245. – P. 21-23.

[4] Onaka, M. N-alkylation of aniline derivatives by use of potassium cation-exchanged Y-type zeolite / M. Onaka, K. Ishikawa, Y. Izumi // J. Chem. Soc., Chem. Commun. – 2011. – P. 1202-1203.

[5] Izumi, Y. Organic syntheses using aluminosilicates. Advances in catalysis / Y. Izumi, M. Onaka. – 2009. – Vol. 249. – P. 38.

[6] Guldberg, A. The law of the masses / A. Guldberg, P. Vaage, 1867.
[7] Alshin, A. Rosenbrock Schemes with Complex Coefficients for Rigid and Differential-Algebraic Systems / A.B. Alshin, E.A. Alshina, N.N. Kalitkin, A.B. Koryagina // Zh. Vychisl. Math and mat. Phys., 2006. – P. 1392-1414.
[8] Koledina, K. Information system for constructing a kinetic model of a catalytic reaction, planning an economically optimal chemical experiment / K.F. Koledina, S.N. Koledin, I.M. Gubaidullin, R.R. Safin, I.V. Akhmetov // Control systems and information technology. – 2015. – Vol. 61(3). – P. 79-84.

Acknowledgment
The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the research project No. 18-37-00015.