

Kinetics Stimulate Microwave Radiation Acylation Reaction of Diethylamine M-Toluic Acid in the Presence of Zn-B-P/Al₂O₃/Al Catalyst

P.A.Muradova, S.M.Zulfugarova, M.R.Efendiyev, N.V.Shakunova, E.M.Guseynova and Yu.N.Litvishkov
Institute of Catalysis and Inorganic Chemistry named after M.F.Nagiyev National Academy of Sciences of Azerbaijan,
AZ1143Baku.

ARTICLE INFO

Article history:

Received: 17 May 2016;

Received in revised form:

28 June 2016;

Accepted: 2 July 2016;

Keywords

M-toluic acid,
Diethylamine,
Acylation,
Diethylamide of m-toluic acid,
Microwave radiation,
A kinetic model.

ABSTRACT

In the article presents the results of a study of kinetic regularities stimulated by microwave electromagnetic radiation acylation of diethylamine m-toluic acid in the presence of intense microwave absorbing Zn-B-P/Al₂O₃/Al- catalyst. Mounted parallel series circuit of the target formation (N, N-diethyl-m-toluic acid) and the reaction byproducts and the observed kinetic model proposed transformations. With the use of optimization software for chemical engineering processes calculated the kinetic parameters of total and partial transformations of m-toluic acid and diethylamine.

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Introduction

Diethylamide m-toluic acid (DETA) belongs to a class of effective Insect repellent selective action against blood-sucking insects and lepidopteran destroyers materials and products [1]. The most common method of obtaining DEET is the acylation of dialcylamine chloride m-toluic acid derived its halogenation with thionyl chloride, fosgenom or phosphorus chlorides [2,3].

Noted method has a number of common deficiencies, such as the use of the step of preparing the acid chloride of m-toluic acid, highly toxic reagents, the periodicity of processes and low technical and economic processes indicators (output DETA does not exceed 80-85% of the commitments made by acid);

Earlier, we, as well as a number of other authors developed a more efficient way of direct heterogeneous catalytic acylation of diethylamine benzoic and m-toluic acids [4-7]. In particular, it was found that in the presence of a modified zinc oxide containing boron phosphate catalyst (Zn-B-P/Al₂O₃) reacting m-toluic acid and diethylamine proceeds with an acceptable yield for practical realization of the target diethyltoluamide.

Despite the obvious benefits of this process, precluding use as acylating agent an acid chloride of m-toluic acid, the latter due to the endothermic nature of the equilibrium reaction, a high-energy, and for the intensification requires the involvement of more effective as compared with traditional methods of energy, such as an ultrahigh frequency electromagnetic radiation (microwave) for which there is no need of preheating the feedstock and the desired reaction temperature is achieved by catalytic transformation of the charge absorbed energy of the electromagnetic field in the heat.

In this work presents the results of the study the kinetics of the reaction of acylation of diethylamine m-toluic acid in the presence of an active microwave absorbing Zn-B-P/Al₂O₃/Al- catalyst [8] under the influence of electromagnetic radiation microwave.

Experimental Part

In accordance with the picked up component composition optimal Zn-B-P/γ-Al₂O₃ catalyst acylation diethylamine, characterized by high activity and selectivity diethyltoluamide [4,5], to prepare samples of absorbing microwave radiation, Al/γ-Al₂O₃- carrier was used which impregnated (by incipient wetness) with aqueous solutions of boric acid, phosphoric acid and zinc nitrate appropriate concentrations, and after decanting the excess impregnating solution was subjected successively drying and calcination thermolysed in a microwave field.

The experiments on the conversion of m-toluic acid and diethylamine under the action of microwave radiation were carried out in a flow reactor at the facility, constructed on the basis of a multi brand microwave oven EM-G5593V (Panasonic) with a volume of 23L resonator. The operating frequency of the radiation generator - the magnetron was 2450 MHz, the maximum input power of 1200 watts. The temperature in the reaction zone is measured by remote non-contact infrared thermometer brand VA6520 c measuring range -50 ÷ 6000°C. To prevent overheating of the reactor, was placed in the oven cavity shunt capacitance circulating distilled water to reduce the output power. To facilitate dosing of the reaction mixture in the contact zone, the latter was fed to the head of the reactor in the form of a saturated aqueous solution of diethylammonium salt of m-toluic acid.

Analysis of the composition of the liquid component of the catalyzate carried gas chromatography (LCM-80 MD unit,

the 3-rd model, a flame ionization detector, column $l = 2.4$ m, $d = 3.0$ mm, separating the phase - Silicone is the SE-30 10% hezorsorbe AWHMD, fraction 0.35-0.5 mm internal standard - n-octyl alcohol. As for the phase separation of gaseous products - CO_2 and ethylene TGNM used for INZ-600).

Discussion of Results

In order to implement the process in a continuous flow of the reaction medium in the contact zone without preheating components was studied as a function of time for establishing a stationary temperature regime the power consumption of the magnetron, the molar ratio of m-toluic acid: diethylamin and conditional contact time $\tau(h) = \nu_{\text{e}} / \nu_{\text{n}}$, where ν_{n} (l / h) - hourly space velocity in the liquid phase, ν_{e} (l) - the amount of catalyst.

Temperature dependence of the contact zone of the reactor, in steady-state condition in the reaction system, the power of microwave radiation at different values of the conditional contact time (catalyst volume ratio of the charge amount supplied to the reactant mixture) is shown in Fig.1. It is seen that with increasing contact time contingent, for fixed values of power of the magnetron, a higher temperature is achieved in the contact zone of the reactor. Thus, with increasing the radiation power during the establishment of steady (temperature) state is significantly reduced.

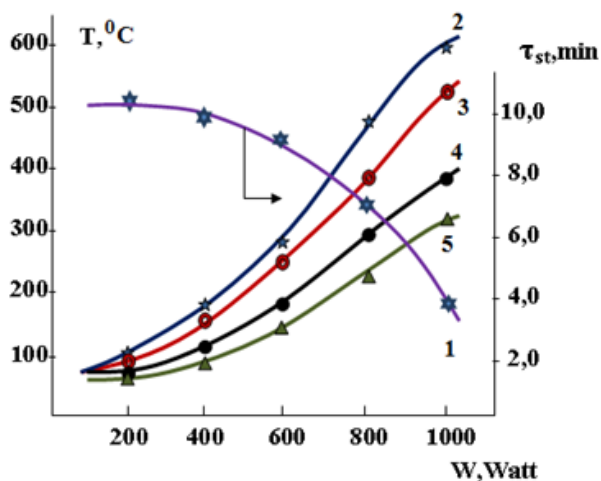
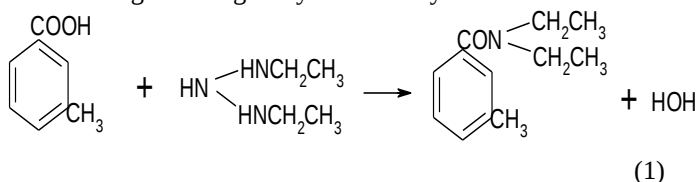


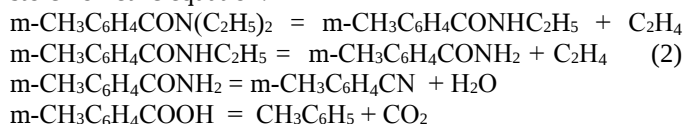
Fig 1. Temperature dependence of the steady-state mode and reaction time required to establish steady state (1) by acting on the power of the microwave radiation, the reaction system by varying the contact time of the conditioned. 1 – $\tau = 10$ sec; 2 – $\tau = 7$ sec; 3 – $\tau = 5$ sec; 4 – $\tau = 2$ sec., molar ratio $\text{CH}_3\text{C}_6\text{H}_4\text{COOH} : \text{HN}(\text{C}_2\text{H}_5)_2 : \text{H}_2\text{O} = 1:2:4$.

It is established that the variation in the studied range of microwave power, contact time and conditional molar ratio of m-toluic acid and diethylamine dominant direction converting m-toluic acid is the N-acylation of diethylamine to form the desired product N, N-diethyl m-toluic acid.

Formation of products including monoethyltoluamida, m-toluamide, m-tolunitrile and indicates the occurrence of toluene along with target acylation diethylamine:



adverse reactions consecutive elimination of ethylene molecules diethyl toluamide and toluamide dehydration and decarboxylation of m-toluic acid, described by the following stoichiometric equation:



The reduced the formation of byproducts sequence indicates the presence in the gaseous portion catalyze respective equations given stoichiometric amounts of ethylene and carbon dioxide fixed by chromatography.

By varying the magnetron power ranging of 600-800 W, is established that an increase in reaction temperature achieved by absorption of the catalyst and the charge energy transforming microwave radiation, a target is observed intensification and side reactions of m-toluic acid (Fig.2).

It was established that fixed parameters in the microwave radiation to increase the contact time of the conditioned in high conversion of m-toluic acid), a sharp increase in the rate of formation monoethyltoluamida, toluamide, and tolunitrile (Fig.3), which corresponds to successive transformations of m-toluic acid described by the stoichiometric equation (2). Practical toluene constancy same production rate changes in a wide range conversion of m-toluic acid (10-80%) indicates the presence of a parallel route decarboxylation m-toluic acid in toluene.

To determine the functional dependence of the observed values of the conversion rates m-toluic acid and diethylamine, as well as accumulation of reaction products in stationary conditions the partial pressure of the reagents have been implemented by a series of experiments conditional variation in contact time range of 2.0 - 10.0 .. in the temperature range 250 – 450°C and molar ratios: $\text{CH}_3\text{C}_6\text{H}_4\text{COOH} : \text{HN}(\text{C}_2\text{H}_5)_2 : \text{H}_2\text{O} = 1:2:4$.

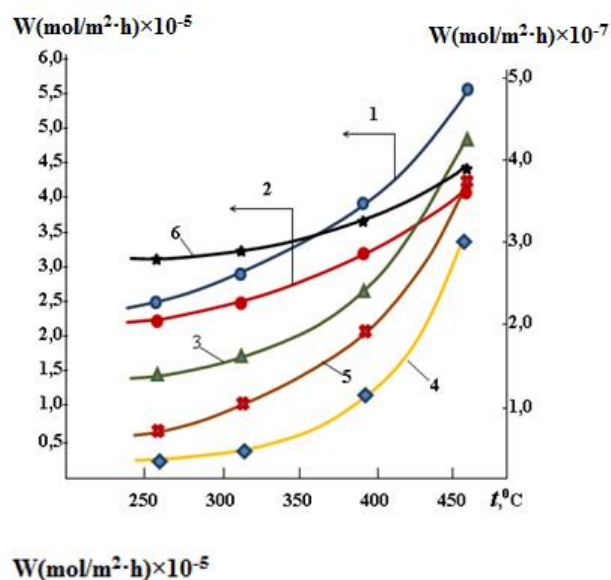


Fig 2. The dependence of the rate of the overall transformation of m-toluic acid (1), Education DETA (2), monoethyltoluamida (3), toluamide (4), tolunitrile (5) and toluene (6) the reaction temperature achieved by absorbing a catalyst for energy-ogy microwave corresponding to the radiation power. Conditional contact time of 5 seconds. molar ratio $\text{CH}_3\text{C}_6\text{H}_4\text{COOH} : \text{HN}(\text{C}_2\text{H}_5)_2 : \text{H}_2\text{O} = 1:3:2$.

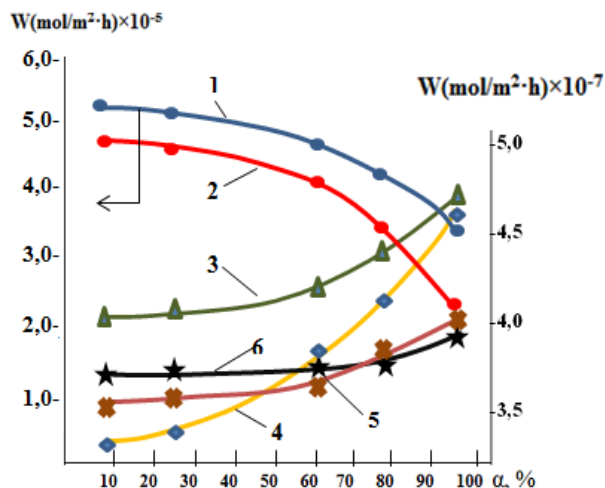


Fig 3. The velocity of the total conversion of m-toluic acid (1) and DETA formation (2) monoethyltoluamide (3) toluamide (4), tolunitrile (5), and toluene (6) on the degree of conversion of m-toluic acid. Magnetron power of 800 watts. Molar ratio $\text{CH}_3\text{C}_6\text{H}_4\text{COOH} : \text{HN}(\text{C}_2\text{H}_5)_2 : \text{H}_2\text{O} = 1:3:2$.

According postulated scheme converting m-toluic acid and diethylamine in the studied conditions, the reaction can be described by four independent (basic) routes (Table 1). Derivation of the equations of speeds on basic routes as a function of the partial pressures of the reactants, was carried out in accordance with the algorithm proposed by M.I.Temkin [9], wherein the reaction rate of the N_i - route can be represented by the following equation:

$$r^{Ni} = \frac{r_{S_1} \cdot r_{S_2} \cdots r_{S_m} - r_{-S_1} \cdot r_{-S_2} \cdots r_{-S_m}}{\sigma_{S_1} \cdot r_{S_2} \cdots r_{S_m} + r_{-S_1} \cdot \sigma_{S_2} r_{S_3} \cdots r_{S_m} + \cdots + r_{S_1} \cdot r_{-S_2} \cdots r_{-S_{m-1}} \cdot \sigma_{S_m}}$$

where $r_{S_1-S_m}$ and $r_{-S_1-S_m}$ - the speed stages constituting the route under consideration in the forward and backward direction; $\sigma_{S_1} - \sigma_{S_m}$ - stoichiometry of the respective stages.

From the expression for the effective rate constant of the reaction at the appropriate route:

$$k_{\text{eff}}^{N_i} = \sigma_i \cdot k_{N_i} \cdot K_i \quad (4)$$

where: k_{N_i} - the rate constant of the rate-limiting step in the route of N_i ; K_i - adsorption equilibrium constant of i - component; σ_i - stoichiometric coefficients for the reaction routes on the basis of the above matrix (Table 1), and

assumptions about the type Langmuir adsorption isotherms of the reaction components, the equation for the observed consumption rates of formation and accumulation of key reaction components diethylamine N-acylation of m-toluic acid in the presence of Zn-B-P/ Al_2O_3 /Al- catalyst can be represented as:

$$-W_{MTA}^{\Sigma} = \frac{k_{EFF}^1 \cdot P_{MTA} \cdot P_{DEA}}{1 + K_{MTA} \cdot P_{MTA} + K_{DEA} \cdot P_{DEA}} + \frac{k_{EFF}^5 \cdot P_{MTA}}{1 + K_{MTA} \cdot P_{MTA}}$$

$$W_{DETA} = \frac{k_{EFF}^1 \cdot P_{MTA} \cdot P_{DEA}}{1 + K_{MTA} \cdot P_{MTA} + K_{DEA} \cdot P_{DEA}} - \frac{k_{EFF}^2 \cdot P_{DETA}}{1 + K_{DETA} \cdot P_{DETA}} \quad (5)$$

$$W_{META} = \frac{k_{EFF}^2 \cdot P_{DETA}}{1 + K_{DETA} \cdot P_{DETA}} - \frac{k_{EFF}^3 \cdot P_{META}}{1 + K_{META} \cdot P_{META}};$$

$$W_{TA} = \frac{k_{EFF}^3 \cdot P_{META}}{1 + K_{META} \cdot P_{META}} - \frac{k_{EFF}^4 \cdot P_{TA}}{1 + K_{TA} \cdot P_{TA}}$$

$$W_{TN} = \frac{k_{EFF}^4 \cdot P_{TA}}{1 + K_{TA} \cdot P_{TA}}; \quad W_{TOL} = \frac{k_{EFF}^5 \cdot P_{MTA}}{1 + K_{MTA} \cdot P_{MTA}}$$

where: W_{MTA}^{Σ} - overall conversion rate of m-toluic acid, W_{DETA} - overall conversion rate of m-toluic acid, W_{META} - monoethanolamide rate of accumulation of m-toluic acid, W_{TA} - The rate of accumulation of m-toluamide, W_{TN} - rate of m-tolunitrile, W_{TOL} - the rate of formation of toluene.

Parameter estimation system of kinetic equations (7) on the assumption of the Arrhenius dependence values of the effective rate constants and constants of adsorption equilibrium of temperature:

$$k_{EFF}^i = k_0^i \exp\left(-\frac{E_{EFF}^i}{RT}\right)$$

$$K_i = K_0^i \exp\left(\frac{Q_i}{RT}\right) \quad (6)$$

where: k_0^i and K_0^i pre-exponential factors of the reaction constants and constants of adsorption equilibrium; E_{EFF}^i and Q_i - the apparent activation energy values of the observed reactions and heat of adsorption components, carried out on the PC in Windows 7 c using optimization methods "rolling admission" and Powell [10,11].

As a criterion of optimization function applies standard deviations between the experimentally observed and calculated according to equations proposed kinetic model (5) the values of conversion rate and accumulation of the key components of the reaction:

Table 1. Matrix coefficients stoichiometric basis routes final conversion of toluene in the acylation reaction N-diethylamine m-toluic acid.

Route	The reaction components									
	$\text{C}_8\text{H}_8\text{O}_2$	$\text{C}_4\text{H}_{11}\text{N}$	$\text{C}_{12}\text{H}_{17}\text{ON}$	$\text{C}_{10}\text{H}_{13}\text{ON}$	$\text{C}_8\text{H}_9\text{ON}$	$\text{C}_8\text{H}_7\text{N}$	C_7H_8	C_2H_4	CO_2	H_2O
N_1	-1	-1	1	0	0	0	0	0	0	1
N_2	0	0	-1	1	0	0	0	1	0	0
N_3	0	0	0	-1	1	0	0	1	0	0
N_4	0	0	0	0	-1	1	0	0	0	1
N_5	-1	0	0	0	0	0	1	0	1	0

$$F = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{W_{ij}^{\text{exp}} - W_{ij}^{\text{settl}}}{W_{ij}^{\text{exp}}} \right]^2 \quad (7)$$

Results of calculation of the kinetic parameters of the model are given in Table 2.

Table 2. The results of calculation of the kinetic parameters of the model.

Constants	Dimension	lgk ₀	E kJ/mol	Q kJ/mol
k_{EFF}^1	$\frac{mol}{m^2 \cdot h \cdot atm^2}$	8,485	108,7	-
k_{EFF}^2	$\frac{mol}{m^2 \cdot h \cdot atm^2}$	9,245	112,4	-
k_{EFF}^3	$\frac{mol}{m^2 \cdot h \cdot atm^2}$	10,126	121,5	-
k_{EFF}^4	$\frac{mol}{m^2 \cdot h \cdot atm^2}$	11,218	132,8	-
k_{EFF}^5	$\frac{mol}{m^2 \cdot h \cdot atm^2}$	11,432	133,7	-
K_{MTA}	atm^{-1}	-1,233	-	42,2
K_{DETA}	atm^{-1}	-1,456	-	38,6
K_{META}	atm^{-1}	-1,376	-	47,3
K_{TA}	atm^{-1}	-1,543	-	36,2

It is shown that in a minimum of (7), standard deviations calculated by the proposed kinetic model (5) the velocity values of the reactions experienced by their value does not exceed respectively: the total rate for the conversion of m-toluic acid - 5% savings rate diethylamide m- toluic acid - 7%; the rate of accumulation monoethylamine m-toluic acid - 8%, the rate of accumulation toluamide - 8%, the rate of formation of the nitrile of m-toluic acid - 11%, the rate of formation of toluene - 10%, which is within the experimental error with the analytical control composition catalyze.

Conclusion

From these results, it is seen that the reaction in the stimulating effect of the microwave radiation favorably reaction occurring in the conventional heating as the value achieved by the conversion of the starting components (95.3 vs. 90.5%), with a relatively smaller contact time, and consequently, lower catalyst loading, and a lack of need to preheat raw materials before being fed into the contact zone.

Consequently, the developed kinetic model adequately describes the experimental data in the range studied varying the reaction conditions, and can be used for mathematical modeling of the process and calculations of structural elements of the reaction vessel with a microwave heating source.

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