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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Kinetic Model of Acylation of Diacetylethylenediamine

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Abstract—Descriptive kinetics of synthesis of tetraacetylethylenediamine by acylation of diacetylethylenediamine with acetic acid anhydride was examined. The apparent rate constants of the process were obtained, and a mathematical model adequately describing the process was constructed.

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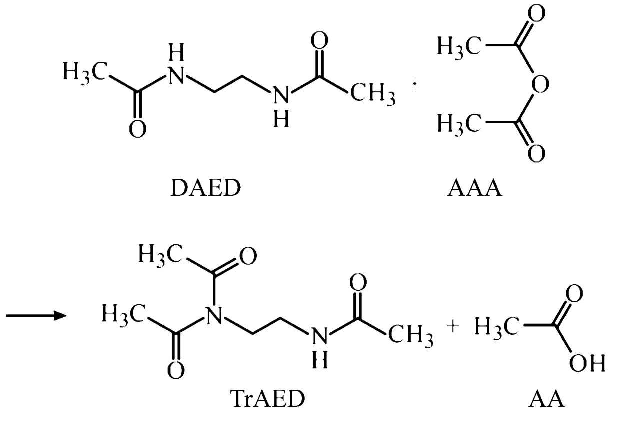
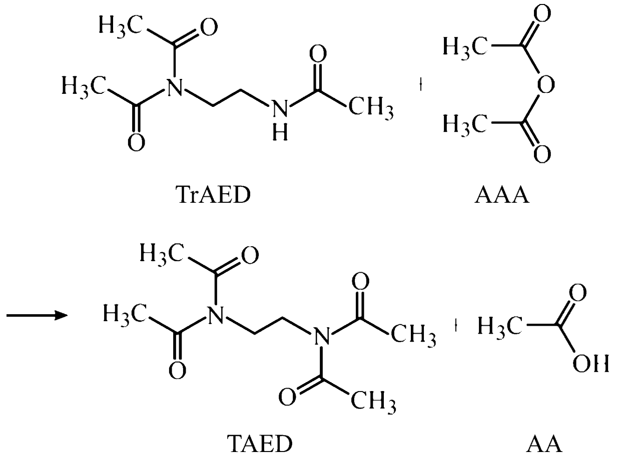
In recent years, the developmental efforts in detergent chemistry have been mainly focused on a search for, and preparation of new composite systems and additives to provide a highly efficient bleaching and removal of contaminations from fabrics at as low temperatures as possible. Among such additives is tetraacetylethylenediamine (TAED), a low-temperature peroxide bleaching activator [1, 2].

Tetraacetylethylenediamine is a typical representative of the class of polyacylated aliphatic diamines, which is produced by acylation of diacetylethylenediamine (DAED) with acetic acid anhydride (AAA). The procedures for preparation of TAED were described in detail in patents [3–5], the mechanism and kinetics of the process were disregarded. At the same time, it is known that acylation of DAED into TAED involves formation of an intermediate, triacetylethylenediamine (TrAED) [6]:





Hence, for simulating the commercial process of DAED acylation, we examined the macrokinetic relationships. To this end, we carried out a series of kinetic experiments with varied DAED : AAA molar ratio (1 : 6.5; 1 : 8.5; 1 : 17) and temperature (120 and 140°C).

EXPERIMENTAL

To study the formal-kinetic aspects of DAED acylation and TAED deacylation, we used a three-necked temperature-controlled flask equipped with a mechanical stirrer, thermometer, and reflux condenser. The structure of the reaction mass was analyzed by gas–liquid chromatography on a Kristall 2000 chromatograph with a flame-ionization detector and a 30 m × 0.53 mm CPS sil-5CB capillary column in the column-temperature-programming mode (initial temperature

100°C, 5 min; heating to 240°C at a rate of 12 deg min^{-1}; final temperature 240°C, 10 min) with nitrogen as carrier gas.

The necessary amount of AAA (or AA in the case of TAED deacetylation) was placed in the flask at room temperature and heated to the desired temperature, whereupon the calculated amount of DAED (or TAED) was introduced under agitation. The instant when mixing of the reactants was complete was taken as the reaction onset time.

At regular intervals of time (15 or 30 min) during 6 h, the reaction mass was sampled and samples were placed in a cooled solvent (dioxane) used in an amount sufficient for terminating the reaction, and the reaction mass was analyzed by gas–liquid chromatography. Using test mixtures, we showed that no side reactions proceed under the chromatographic conditions. Each sample taken was subjected to at least three replicated measurements.

The derived concentration values were used for plotting the primary kinetic curves and calculating the apparent rate constant of the reaction.

The kinetic data were processed by the regression analysis procedure using Table Curve Windows V1.10 software.

Statistical processing of the measurements results was carried out by the least-squares and regression analysis procedures; the confidence interval (error corridor) was calculated under a homogeneous reproducibility condition [7].

Using the concentration values derived at different molar ratios of the reactants [DAED : AAA = 1 : (6.5–17)] and temperatures (120–140°C), we plotted the primary kinetic dependences $c = f(\tau)$, one of which is shown in Fig. 1.

An analysis of the processed experimental data (Figs. 2, 3) showed that the DAED acylation by acetic acid anhydride can be described by the pseudo-first order reaction model.

As can be seen from Fig. 3, the semilogarithmic anamorphoses are straight lines with breaks. This pattern indirectly evidences that the DAED acylation by acetic acid anhydride includes two stages. The first stage consists in the formation of TrAED, and the second, in the acylation of TrAED to TAED; the rate of the first stage exceeds that of the second stage.

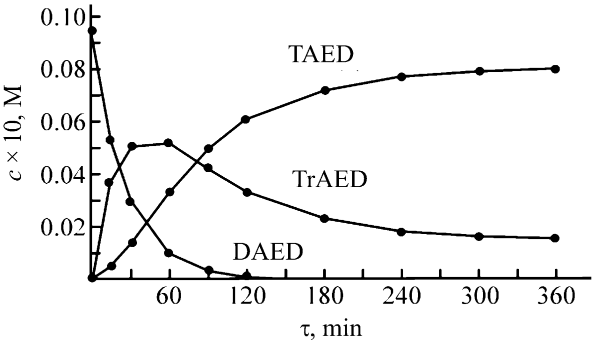


Fig. 1. Primary experimental curves of the DAED acylation by acetic acid anhydride at 140°C and initial molar ratio DAED : AAA = 1 : 8.5. (*c*) Concentration and (τ) time.

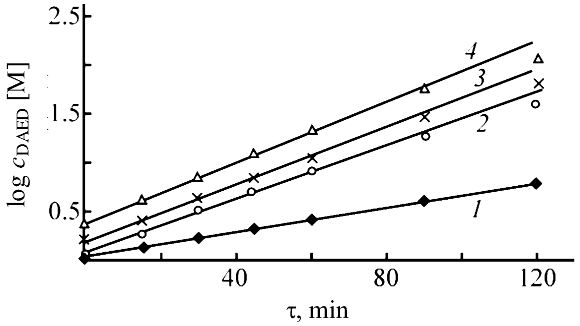


Fig. 2. Semilogarithmic plot of c_{DAED} vs. time τ. Initial molar ratio DAED : AAA, *T*, °C: (*1*) 1 : 8.5, 120; (*2*) 1 : 8.5, 140; (*3*) 1 : 6.5, 140; and (*4*) 1 : 17, 140; the same for Fig. 3.

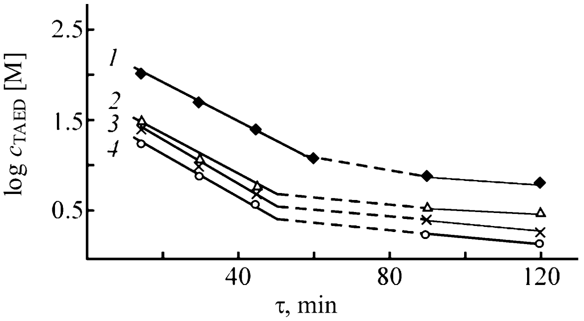


Fig. 3. Semilogarithmic plot of c_{TAED} vs. time τ.

Analysis of the primary experimental curves (Fig. 1) suggests that the stage of acylation of TrAED to TAED is reversible, and chemical equilibrium is eventually attained in the acylation reaction. Our experiments were carried out under nearly industrial conditions, for which reason we used 97% acetic acid anhydride. In the experiments carried out under a 8.5-fold molar excess of acetic acid anhydride over DAED, the molar ratio of the components of the DAED : AAA : AA reaction system at the initial instant of time was 1 : 8.5 : 0.4 mole, respectively. After the equilibrium was established in the system, the molar ratio of the components of the reaction mixture TrAED : TAED : AAA : AA was 0.2 : 0.8 : 6.7 : 2.2. This can

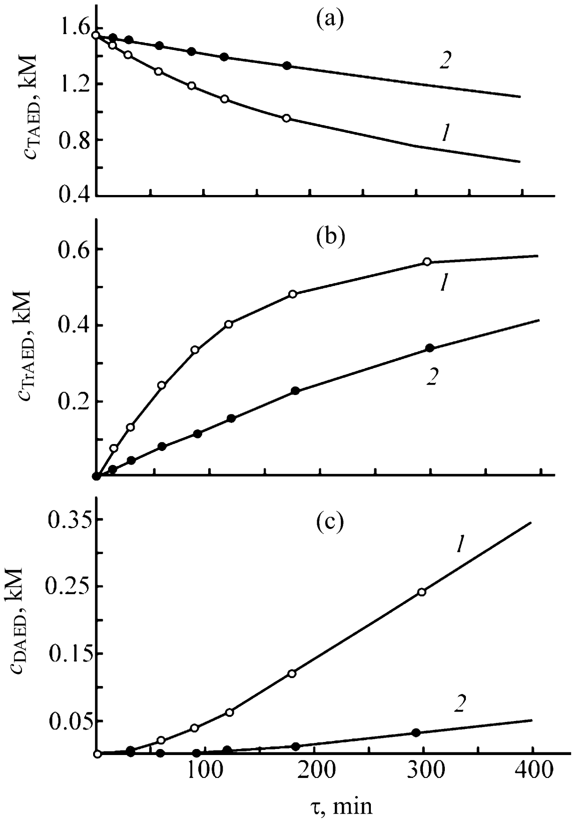


Fig. 4. Variation of the concentration c of (a) TAED, (b) TrAED, and (c) DAED with time τ. T, °C : (*1*) 125 and (*2*) 110.

be attributed to occurrence of a reverse reaction between the TAED acylation product and acetic acid formed during the reaction.

The reversibility of the reaction in the case of TrAED acylation by acetic acid anhydride was confirmed experimentally by the appearance of the peak of acetic acid anhydride in the chromatogram recorded for the reaction of TAED with acetic acid.

Thus, the DAED acylation by acetic acid anhydride is a two-stage process; the second stage of acylation of TrAED to TAED is reversible, which is responsible for the not very high (≤84%) yield of the reaction product, TAED. Naturally, each of the stages includes a series of chemical transformations. Therefore, it is expedient to describe the kinetics in terms of the concentration and yield of the target product, using the known dependences for two first-order reactions of the type

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \underset{k_3}{\overset{k_2}{\rightleftarrows}} \mathrm{C}.$$

The variation of the concentration of the substances can be described by the dependences [8]

$$a_0 = c_\mathrm{A} + c_\mathrm{B} + c_\mathrm{C},$$

$$c_\mathrm{A} = a_0 e^{-k_1 t},$$

$$c_\mathrm{B} = c_{\mathrm{B}\infty} + (k_2 + k_3 - k_1)^{-1}\{a_0(k_1 - k_3)\mathrm{e}^{-k_1 t} - [k_2 c_{\mathrm{B}\infty} - c_{\mathrm{C}\infty}(k_3 - k_1)]e^{-(k_2 + k_3)t}\},$$

$$c_\mathrm{C} = c_{\mathrm{C}\infty} - (k_2 + k_3 - k_1)^{-1} \times \{a_0 k_2 \mathrm{e}^{-k_1 t} - [k_2 c_{\mathrm{B}\infty} - c_{\mathrm{C}\infty}(k_3 - k_1)]e^{-(k_2 + k_3)t}\},$$

where a_0 is the initial concentration of substance A, M; c_A, c_B, c_C, running concentrations of the initial, intermediate, and final compounds, respectively, M; and $c_{\mathrm{B}\infty}$, $c_{\mathrm{C}\infty}$, equilibrium concentrations of the intermediate and final compounds, respectively, M.

Analysis of the plots suggests that these dependences cannot adequately describe the experimental data. This is apparently due to the occurrence of a more complex process that cannot be described by dependences for first-order reactions.

For more detailed description of the acylation process, we performed a set of kinetic experiments on TAED deacylation by acetic acid at temperatures of 110–125°C under a significant excess of acetic acid (TAED : AA = 1 : 7). Figure 4 presents the primary experimental curves for the upper and lower limits of the temperature range examined.

A kinetic description of the DAED acylation by acetic acid anhydride is a mathematically complex procedure. Hence, we applied a special software, namely, DesK-Pro software available from Khiminform Private Company [9], used for construction of descriptive kinetic models and reactor modeling.

Descriptive kinetic models are suitable for reactions proceeding in batch, semicontinuous, or continuous reactors operating under various heating conditions and for simulation and optimization of processes.

The construction of these models requires that the initial hypothesis about the chemical nature of the reactions should be formulated, experimental data on the concentration responses be available, and basic properties of substances (thermal capacity and density as functions of temperature and molecular weight) be known.

Descriptive concentration models describe the reaction mechanism in detail. These models are based on the generalized law of mass action (GLMA) which states that the rate of a stage is proportional to the product of the concentrations raised to arbitrary powers (orders). A special case of the law of mass action is the exact law of mass action (ELMA), in which the orders coincide with the stoichiometric coefficients.

A multi-stage reaction is described by the stoichiometric scheme

$$\sum_{i=1}^{N}(\beta_{ji}-\nu_{ji})A_{ji}=0; \quad j=1,\ldots,M, \tag{1}$$

where the rate of *j*th stage is set by the expression

$$r_j = k_j \prod_{(i)} [\mathrm{A}_{ji}]^{\nu_{ji}} \quad \text{for GLMA and}$$

$$r_j = k_j \prod_{(i)} [\mathrm{A}_{ji}]^{n_{ji}} \quad \text{for ELMA;}$$

$$j = 1, \ldots, M, \tag{2}$$

and the rate at which the concentration of *i*th component changes is described by the equation

$$\frac{\mathrm{d}[\mathrm{A}_i]}{\mathrm{d}t} = \sum_{(j)}(\beta_{ji}-\nu_{ji})r_j, \tag{3}$$

where ν, β are stoichiometric coefficients; *r*, rate of a stage, $\mathrm{mol\,m^{-3}\,s^{-1}}$; *k*, rate constant of the stage, $k(T) = k_0\exp(-E/RT)$; k_0, pre-exponential coefficient; *E*, activation energy, $\mathrm{kJ\ mol^{-1}}$; *R*, gas constant, $\mathrm{J\ mol^{-1}\ K^{-1}}$; [A], concentration of substance A, $\mathrm{mol\,m^{-3}}$; and *t*, time, s.

The model is supplemented by the appropriate initial conditions and observation model, a set of equations relating the rates of stages to the observed responses (concentration, heat or gas evolution, etc.) :

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \sum_{(j)} Q_j^{\infty} r_j;$$

$$\frac{\mathrm{d}G}{\mathrm{d}t} = \sum_{(j)} G_j^{\infty} r_j;$$

$$[A_{ji}], \tag{4}$$

where *Q* is the specific heat evolution, $\mathrm{kJ\ mol^{-1}}$; Q^{∞}, specific heat effect of a stage, $\mathrm{kJ\ mol^{-1}}$; and G^{∞}, specific final gas evolution in the stage, $\mathrm{mol\ mol^{-1}}$.

A specific feature of complex kinetic models is that they are substantially nonlinear in the parameters. Hence, the general approach to solving the inverse kinetic problem (estimating the model parameters) is based on nonlinear optimization.

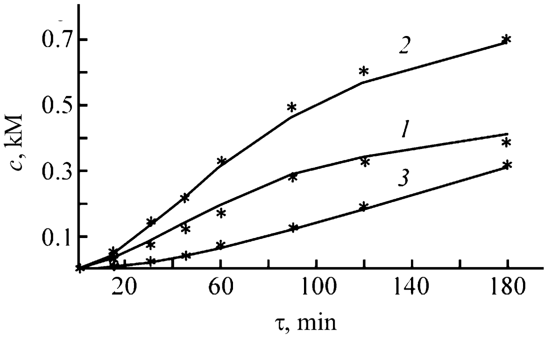


Fig. 5. Variation of the TAED concentration *c* with time τ. (*Line*) DesK-Pro program model and (*points*) experimental data. Initial molar ratio DAED : AAA, *T*, °C : (*1*) 1 : 17, 140; (*2*) 1 : 8.5, 140; and (*3*) 1 : 8.5, 120.

To solve the inverse problem means to find the kinetic parameters that best fit the experimental data. For this purpose, a certain measure of residuals between the experimental and simulated responses is minimized. Most of nonlinear optimization algorithms are based on the least-squares procedure which utilizes to this end the sum of the squared residuals. The parameter vector $\mathbf{P}_\mathrm{r}$ is estimated by minimization of the target function SS :

$$\mathrm{SS}(\mathbf{P}) = \frac{1}{2}\sum_{(i)}\left(\frac{Y_{\mathrm{exp}}(t_i)-Y_{\mathrm{sim}}(\mathbf{P},t_i)}{\varepsilon_i}\right)^2 \rightarrow \min = \mathrm{SS}(\mathbf{P}_\mathrm{r}), \tag{5}$$

where SS(**P**) is the weighted sum of the squared residuals; *i*, experimental point number; *e*, experimental error at the point; and Y_{exp} and Y_{sim}, experimental and calculated responses, respectively.

The condition for the minimum SS is set by a system of the nonlinear algebraic equations

$$\frac{\partial SS(\mathbf{P})}{\partial P_j} = 0; \quad j = 1,\ldots,L, \tag{6}$$

where P_j is *j*th component of the parameter vector.

The target function is extended by inclusion of the data derived from several multi-response experiments. Simultaneous processing of the results of several experiments and responses of varied physical nature allows use of different kind of information on the reaction and provides more adequate resulting kinetics.

A primary program processing of the experimental data (Fig. 5) showed that synthesis of TAED is satisfactorily described by the model of two successive

Rate constants and activation energies of the DAED acylation reaction

Stage no.	Activation energy E, kJ mol^{-1}	Pre-exponent, l mol^{-1} s^{-1}	Rate constants $k \times 10^{-5}$	
			120°C	140°C
1	62.3	6.02×10^3	3.2	8.1
2	87.1	2.92×10^6	0.2	1.3
3	103.3	1.69×10^8	0.8	2.8
4	112.9	2.46×10^9	0.3	1.5

reversible second-order bimolecular reactions in accordance with the general scheme.

$$\mathrm{DAED} + \mathrm{AAA} \underset{k_3}{\overset{k_1}{\rightleftarrows}} \mathrm{TrAED} + \mathrm{AA},$$

$$\mathrm{TrAED} + \mathrm{AAA} \underset{k_4}{\overset{k_2}{\rightleftarrows}} \mathrm{TAED} + \mathrm{AA}.$$

The rate constants and activation energies are listed in the table.

CONCLUSIONS

(1) Diacetylethylenediamine is acylated by acetic acid anhydride in two stages.

(2) Tetraacetylethylenediamine is deacylated by acetic acid to diacetylethylenediamine via a triacetylethylenediamine intermediate. Hence, the acylation of diacetylethylenediamine is described by successive reversible second-order equations.

(3) The formal kinetics of acylation of diacetylethylenediamine by acetic acid anhydride was examined, which allowed determination of the activation energies and the functional temperature dependences of the apparent rate constants of the reaction k_1–k_4 for two successive reversible stages of the process.

(4) The kinetic data obtained allow construction of an adequate mathematical model for industrial apparatus.

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