KINETICS STUDY OF HYDRAZODICARBONAMIDE SYNTHESIS REACTION

In this study, the kinetics of hydrazodicarbonamide (HDCA) synthesis reaction were investigated. Hydrazodicarbonamide is prepared by reaction of urea and hydrazine in acidic medium. Synthesis of HDCA from urea and hydrazine is a two-step reaction. In the first step, semicarbazide is synthesized from the reaction of one mole of urea and one mole of hydrazine and in the second step, semicarbazide reacts with urea to produce hydrazodicarbonamide. By controlling the temperature and pH in the reaction, hydrazine concentration and the amount of produced hydrazodicarbonamide were measured and using this data, reaction rate constants were calculated. Based on this study, it was found that the semicarbazide formation reaction from hydrazine is the rate-limiting step. The rate of semicarbazide synthesis is \(-r_1 = 0.1396[NH_2NH_2]^{0.5810}\) and the rate of hydrazodicarbonamide synthesis is \(-r_2 = 0.7715[NH_2CONHCONH_2]^{0.8430}\).

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acidic conditions is the commercial process for HDCA production, so the kinetics of this reaction were the subject of this research study. Hydrazine sulfate and urea were used for synthesis of HDCA and determination of reaction rate constants. The HDCA synthesis reaction can be written as:

\[
H_2N-NH_2 + 2H_2N\overset{O}{\overset{NH}{\n}}H_2 \rightarrow H_2N-O-O-NH_2 + 2 NH_3
\]  

which is a two steps reaction. In the first step, an intermediate compound named semicarbazide is produced and in the second step, HDCA is produced as presented in Eqs. (2) and (3):

\[
\text{Step 1: } -r_1 = -\frac{d[NH_2NH_2]}{dt} = K_1[NH_2NH_2]_n
\]

\[
\text{Step 2: } -r_2 = -\frac{d[NH_2NHCONH_2]}{dt} = K_2[NH_2NHCONH_2]_m
\]

It is necessary to consider that temperature and pH have an influence on the type of product, e.g., if \(T < 30^\circ C\) and \(pH < 1\), hydrazine sulfate forms. If \(50^\circ C < T < 90^\circ C\) and \(7 < pH < 9\), semicarbazide forms and if \(85^\circ C < T < 95^\circ C\) and \(3 < pH < 6\), HDCA forms [20].

**EXPERIMENTAL**

Hydrazine sulfate, urea and sulfuric acid were purchased from Merck. The procedure for synthesis of HDCA is as follows: 0.1 mol hydrazine sulfate, 0.4 mol urea and 300 g water were mixed in the reactor. Then, the temperature was increased to 92-93 °C and kept constant during reaction period (1, 2, …, 9 h) by gentle heating. By gradual addition of sulfuric acid solution, the pH of the reaction mixture was kept constant during reaction. After that, the temperature was lowered rapidly to room temperature and the precipitated HDCA was separated from the mother liquor by filtration and was weighed after drying. The concentration of unreacted hydrazine in the mother liquor was measured by the iodometric method, in which iodine was used to oxidize the hydrazine and the amount of unreacted iodine was measured by sodium thiosulfate solution, using starch as indicator [21,22].

The reactor setup used for HDCA synthesis consisted of a three-way flask and a condenser attached to it. Sulfuric acid solution was added during the reaction from one connection, and the other connection of the flask was used for thermometer attachment.

It was assumed that hydrazine decomposition was negligible during synthesis reaction. The concentration of semicarbazide at the end of synthesis reaction period was calculated by mass balance through the hydrazine concentration and the weight of precipitated HDCA.

**RESULTS AND DISCUSSION**

Figures 1 and 2 represent hydrazine concentration and the weight of precipitated hydrazodicarbonamide versus time, while Figure 3 shows the calculated concentration of semicarbazide versus time.

Because the concentration of urea in the reaction mixture is high, it can be assumed that the concentration of urea in the reaction mixture is constant and the rate of reactions depend on the concentration of the other components (hydrazine and semicarbazide). That is, the method of excess is applicable. So the equations for rate of reactions can be written as follows:

\[
\text{Step 1: } -r_1 = -\frac{d[NH_2NH_2]}{dt} = K_1[NH_2NH_2]_n
\]

\[
\text{Step 2: } -r_2 = -\frac{d[NH_2NHCONH_2]}{dt} = K_2[NH_2NHCONH_2]_m
\]

where \(K_1\) and \(K_2\) are the reaction rate constants and \(n\) and \(m\) are the orders of the reaction rate equations.

**First step: reaction between urea and hydrazine**

From Eq. (3), the following relations can be derived:

\[
-r_1 = -\frac{d[NH_2NH_2]}{dt} = K_1[NH_2NH_2]_n
\]

where \(K_1\) and \(K_2\) are the reaction rate constants and \(n\) and \(m\) are the orders of the reaction rate equations.
\[ \ln \left( \frac{c_N}{c_{N_0}} \right) = -K_1 t \]. So, a plot of \( \ln \left( \frac{c_N}{c_{N_0}} \right) \) versus time (t) should result in a straight line if the order of reaction is unity.

From Figure 1 it can be found that the order of reaction (n) is a positive number and lower than unity. So, by using MATLAB software and optimization methods, optimum values for \( K_1 \) and n can be determined. For the optimum value of n, the graph of \( \left( \frac{c_N^{1-n} - c_{N_0}^{1-n}}{1-n} \right) = -K_1 t \) versus time is approximately linear with the slope of \( K_1 \) [23,24].

The calculation based on optimization methods of MATLAB software shows that the optimum values for \( K_1 \) and n are 0.1396 and 0.5810, respectively. The value of \( R^2 \) (coefficient of determination) for optimization is 0.9918. In Figure 4, the concentration of hydrazine versus time is shown for both the experimental...
data and the optimization results, which shows good fitting between these two sets of data.

The rate equation for the first reaction is:

$$-r_1 = K_1[\text{NH}_2\text{NH}_2]^n = 0.1396[\text{NH}_2\text{NH}_2]^{0.5810}$$  \(5\)

**Second step: reaction between semicarbazide and urea**

Because semicarbazide is an intermediate compound, its concentration depends on the rate of both reactions (semicarbazide synthesis reaction and HDCA synthesis reaction). Based on the concentration-time diagrams for hydrazine and semicarbazide (Figures 1 and 3), it is obvious that the first reaction is the rate limiting step and rate of second reaction is higher than the first one. The change of semicarbazide concentration with time in the reaction mixture can be given as:
\[
\frac{dc_S}{dt} = K_2c_{S0}^m - K_2c_S^m \tag{6}
\]

which is a parametric differential equation and by solving this equation, optimum values for \(K_2\) and \(m\) can be obtained. Using optimization methods of MATLAB software, the optimum values of \(K_2\) and \(m\) were determined which are 0.7715 and 0.8430, respectively. The value of \(R^2\) (coefficient of determination) for optimization is 0.5912. In Figure 5, the concentration of semicarbazide versus time is shown for both the experimental data and the optimization results, which shows relatively good fitting between these two sets of data.

So, the rate equation for the second reaction (hydrazodicarbonamide formation reaction) is:

\[-r_2 = K_2[NH_2NHCONH_2]^m = 0.7715[NH_2NHCONH_2]^{0.8430} \tag{7}\]

and the change of semicarbazide concentration with time can be calculated from:

\[
\frac{d[NH_2NHCONH_2]}{dt} = 0.1396[NH_2NH_2]^{0.5810} - 0.7715[NH_2NHCONH_2]^{0.8430} \tag{8}\]

**CONCLUSIONS**

Studying the kinetics of a chemical reaction allows for more accurate reactor design. The study of the hydrazodicarbonamide formation reaction from urea and hydrazine shows that this reaction is a two-step reaction and each step has its own rate equation.

The plots of hydrazine concentration and semicarbazide concentration versus time show that the rate of semicarbazide synthesis reaction (reaction of urea with hydrazine) is lower than the rate of hydrazodicarbonamide synthesis reaction (reaction of semicarbazide with urea). In the plot of hydrazine concentration versus time and at \(t = 1\) h, there is a sudden change in the decreasing trend of hydrazine concentration versus time which is due to an increase in semicarbazide concentration in the reaction mixture. This change shows that the first reaction is more sensitive to semicarbazide concentration. This confirms the conclusion that the rate of semicarbazide formation reaction is lower than the hydrazodicarbonamide formation reaction and the former reaction is the rate limiting step for hydrazodicarbonamide synthesis reaction.

The semicarbazide synthesis reaction has the following rate equation:

\[-r_1 = 0.1396[NH_2NH_2]^{0.5810}\]

and the hydrazodicarbonamide synthesis reaction has the following rate equation:

\[-r_2 = 0.7715[NH_2NHCONH_2]^{0.8430}\]

**Nomenclature**

- \(c_n\) hydrazine concentration in reaction media
- \(c_S\) semicarbazide concentration in reaction media
- \(K_1\) semicarbazide synthesis reaction rate constant

![Figure 5. Comparison of the experimental data and optimization result for semicarbazide concentration.](image-url)
$K_z$ hydrazodicarbonamide synthesis reaction rate constant

$m$ order of hydrazodicarbonamide synthesis reaction rate equation

$n$ order of semicarbazide synthesis reaction rate equation.

REFERENCES


Proučavanje kinetike reakcije sinteze hidrazodikarbonamida

U ovom radu je ispitivana kinetika sinteze reakcije hidrazodikarbonamida (HDCA). Hidrazodikarbonamid se priprema reakcijom uree i hidrazina u kiseloj sredini. Sinteza HDCA iz uree i hidrazina se odigrava u dva stupnja. U prvom stupnju, reakcijom jednog mola uree i jednog mola hidrazina nastaje semikarbazid, koji u drugom stupnju reaguje sa ureom gradeći hidrazodikarbonamid. Kontrolom temperature i pH reakcije, merene su koncentracije hidrazina i količina nastalog hidrazodikarbonamida. Korišćenjem ovih podataka određene su konstante brzine reakcija. Na osnovu ovog istraživanja, utvrđeno je da je prvi stupanj formiranja semikarbazida limitirajući stupanj brzine reakcije. Brzina formiranja semikarbazida je \( r_1 = 0.1396[NH_2NH_2]^{0.5810} \), a brzina formiranja hidrazodikarbonamida je \( r_2 = 0.7715[NH_2NHCONH_2]^{0.3430} \).

Ključne reči: hidrazodikarbonamid, azodikarbonamid, semikarbazid, sinteza, kinetika.