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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Kinetics of Acid Hydrolysis of Acetylglucosamine

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Abstract—The kinetics of acid hydrolysis of *N*-acetylglucosamine at different temperatures and reagent concentrations was studied. A mathematical model of the hydrolysis was proposed. The rate constant and activation energy of deacetylation were calculated.

Utilization of large volumes of chitin-containing waste of crustaceans involves usually chemical hydrolysis of chitin and chitosan. Under these conditions, chitin is hydrolyzed to its monomers: glucosamine (GA) and acetylglucosamine (AGA). Complete depolymerization of chitin and chitosan is usually performed in an acidic solution at elevated temperatures [1]. Under these conditions, the glucoside bonds in the polysaccharide are ruptured to form the monomers. Deacetylation occurs in parallel with depolymerization. The deacetylated monomer is usually isolated in the form of its salt of the acid used for hydrolysis. The study of the mechanisms of acid hydrolysis of chitin and chitosan as influenced by the degree of deacetylation and molecular weight of the initial polysaccharide and hydrolysis conditions (temperature and acid concentration) is of both practical and theoretical interest.

Acid hydrolysis of chitin and chitosan was extensively studied [1–5]. However, the kinetics of this process was not understood and the rate constants of its elementary steps were not determined. Previously we suggested a mathematical model of acid deacetylation of chitin [6, 7]. We found that the chitin deacetylation is described by the first-order kinetic equation and the dependence of the reaction rate passes through a maximum at the hydrochloric acid concentration w_{HCl} = 29.8%.

The aim of this study was to estimate the rate constant and activation energy of AGA deacetylation and to determine the hydrolysis rate of the acetamide bond as influenced by the degree of polymerization of the polysaccharide.

EXPERIMENTAL

We used *N*-acetylglucosamine (AGA) prepared by acetylation of *D*-glucosamine with acetic anhydride by the reaction [8]

$$C_6H_{11}NO_5 + (CH_3CO)_2O \rightarrow C_8H_{15}NO_6 + CH_3COOH. \quad (1)$$

Acetylation was performed as follows. A 900-ml portion of AV-17-8 anion exchanger converted into the CO_3 form by treatment with 10% aqueous solution of sodium carbonate was placed into a flask equipped with a stirrer. A 900-ml portion of 0.38 M aqueous solution of *D*-glucosamine hydrochloride [75 g (0.46 mol) GA·HCl] and 90 ml of ethanol (w = 96%) were added at 0–5°C. Acetic anhydride (45 ml, 0.64 mol, w = 99%) was added in small portions at 0–5°C. The reaction mixture was stirred for 3 h at 0–5°C. The resin was filtered off, washed with 500 ml of distilled water, and regenerated.

The filtrate and wash waters were evaporated under reduced pressure (10–20 mm Hg) at 50–60°C to a viscous syrup containing crystals. Ethanol (75 ml, w = 96%) was added, and the resulting mixture was left to crystallize at 0–5°C for 12–15 h.

The crystals were filtered off, washed with 300 ml of acetone (chemically pure grade) to remove water, and dried in a vacuum. The *N*-acetylglucosamine yield was 73.5% of the theoretical yield corresponding to Eq. (1).

N-Acetylglucosamine was hydrolyzed in hydrochloric acid with a concentration from 10 to 37.2% at 40, 60, and 80°C. The hydrolyzate was neutralized first with 2.7 M NaOH and then with 0.1 M NaOH to pH 7.0, filtered through a Schott filter (pore diameter no larger than 10 μm, POR 10), and analyzed for AGA and GA content (M).

The AGA content was determined by the procedure described in [9]; the total AGA + GA content, by the procedure from [10]. The GA amount was calculated

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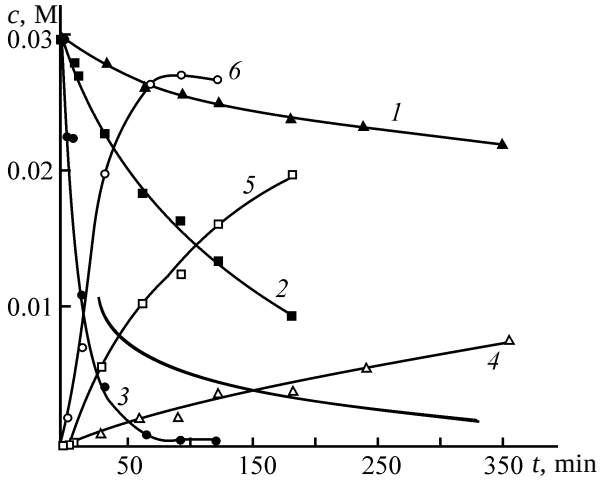

Fig. 1. Kinetic curves of AGA hydrolysis at (*1*) 313, (*2*) 333, and (*3*) 353 K and kinetic curves of GA formation at (*4*) 313, (*5*) 333, and (*6*) 353 K. c_{HCl} = 6.02 M (w_{HCl} = 20%). (*c*) concentration of AGA and GA and (*t*) hydrolysis time.

as the difference between the total AGA + GA amount and the AGA amount. The kinetic curves of AGA consumption and GA accumulation in 20% HCl at different temperatures are shown in Fig. 1. Hydrolysis of AGA is accelerated with increasing temperature. The major product of AGA hydrolysis is glucosamine:

$$C_8H_{15}NO_6 + H_2O \rightarrow C_6H_{11}NO_5 + CH_3COOH. \quad (2)$$

Analysis of the kinetic curves of AGA hydrolysis shows that the reaction can be described by a first-order kinetic equation. The rate constants of AGA deacetylation and GA formation at different temperatures were calculated by the first-order kinetic equation [11]

$$k = 1/t \ln(c_0/c), \quad (3)$$

where t is the reaction time (s^{-1}); c, current concentration of the reactant at time t (M); and c_0, initial concentration of the reactant (M).

The results of these calculations are presented in Table 1.

Table 1. Rate constants of AGA hydrolysis and GA formation. c_{HCl} = 6.02 M (w_{HCl} = 20%)

T, K	AGA		GA	
	k, s^{-1}	$\ln k$	k, s^{-1}	$\ln k$
313	0.00129	–6.653	0.00079	–7.143
333	0.00804	–4.824	0.00638	–5.055
353	0.0544	–2.912	0.0369	–3.301

Table 2. Rate constants of deacetylation of chitin and AGA at T = 353 K

Compound	w_{HCl}, %	c_{HCl}, M	k, s^{-1}
Chitin	35.8	11.57	0.0523
	29.8	9.38	0.0558
AGA	20	6.02	0.0544
	37.2	12.08	0.0428

The rate constants of AGA deacetylation were compared with the rate constant of acid deacetylation of chitin, determined in our previous study [6]. The rate constants of chitin deacetylation at 353 K, calculated by Eq. 3, are presented in Table 2.

As seen from Table 2, the rate constants of deacetylation of AGA and chitin at 353 K are of the same order. These results suggest that the rate constant of deacetylation of chitin and oligomeric and monomeric products of its acid hydrolysis is independent of the molecular weight.

The activation energy of hydrolysis of the acetamide bond was calculated from the temperature dependence of the rate constant by the Arrhenius equation [11]:

$$k = Ae^{-E_a/RT}. \quad (4)$$

The activation energy is 85.7 kJ mol^{-1}.

The calculations were performed on the assumption that the AGA deacetylation is described by the first-order kinetic equation and the true (second) reaction order is reduced owing to large excess of hydrochloric acid [11]. Since the rate of chitin deacetylation depends on the hydrochloric acid concentration [6], we studied the similar dependence for AGA.

The dependence of the rate constant of AGA deacetylation at T = 353 K on the hydrochloric acid concentration is shown in Fig. 3.

The dependence of the rate constant of chitin deacetylation on the hydrochloric acid concentration is similar [6]: it passes through a maximum at the hydrochloric acid concentration of 9 M (w = 29%) and then decreases with a further increase in c_{HCl}.

Since the acid is involved in the catalytic reaction, its concentration should enter into the pseudo-first-order rate constant $k = k'c_{HCl}$. However, the sharp ac-

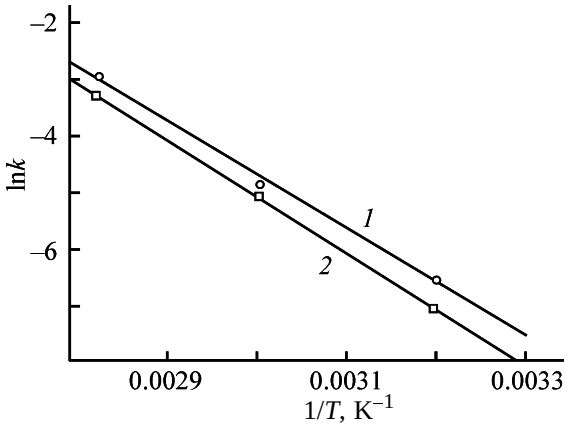

Fig. 2. Logarithms of rate constants ln*k* of (*1*) AGA hydrolysis and (*2*) GA formation as functions of 1/*T*.

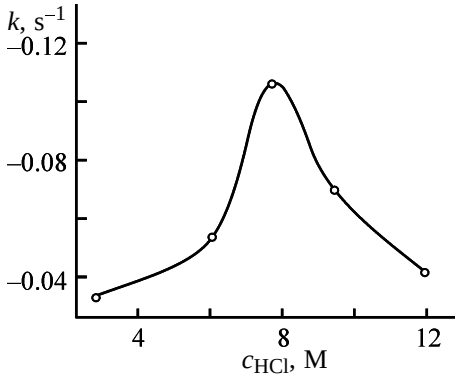

Fig. 3. Rate constant *k* of AGA deacetylation at 353 K as a function of the hydrochloric acid concentration c_{HCl}.

celeration of the reaction in 9 M HCl (Fig. 3) is difficult to explain.

The fact that the dependence for acid hydrolysis of chitin is similar additionally confirms that the mechanism of acid deacetylation of the monomeric and polymeric species is the same.

CONCLUSIONS

(1) The rate constant of acid hydrolysis of acetamide bonds in chitin is similar to that in its oligomers and *N*-acetylglucosamine.

(2) The dependence of the rate of *N*-acetylglucosamine deacetylation on the hydrochloric acid concentration passes through a maximum at $c_{HCl} \sim 8$ M ($w_{HCl} = 26\%$).

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