Kinetics and mechanism of alkaline hydrolysis of urea and sodium cyanate

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The kinetics of hydrolysis of urea has been studied in 0.5 to 3.0 mol dm^{-3} sodium hydroxide solution at different temperatures. Urea hydrolysis follows an irreversible first order consecutive reaction path:

$$\text{urea} \xrightarrow[-NH_3]{k_{1obs}} \text{cyanate} \xrightarrow{k_{2obs}} NH_3 + CO_2$$

The variation of k_{1obs} with [alkali] is linear. at $[OH^-]=5.0$ to 1.5 mol dm^{-3}, thereafter a sharp increase in the reaction rate is observed for first step hydrolysis of urea. The second step rate constant (k_{2obs}) is found to be independent of [alkali]. Hydrolysis of urea in alkaline medium follows an elemination-addition mechanism. The reaction does not proceed through the formation and decomposition of tetrahedral intermediate. Sodium cyanate hydrolysis obeys an irreversible pseudo-first order kinetics. $[OH^-]$ has no significant effect on the rate constants. The following rate equations have been derived for the two step hydrolysis of urea.

$$k_{1obs} = k_0 + \frac{k_1[OH^-](k_4 + k_3[OH^-])}{k_{-1} + k_4 + k_3[OH^-]}$$

$$k_{2obs} = k_2 K_h$$

On the basis of observed data, probable mechanisms have been proposed.

Agriculture and biological importance of urea is well known. Hydrolysis of urea[1] occurs in acidic, neutral and alkaline media and in the presence of enzyme urease giving ammonia and carbondioxide. The hydrolysis of urea has been studied by Lynn[2] in 1.0 M to 2.0 M sodium hydroxide solution, who showed that the basic ureolysis is a simple pseudo-first order reaction. The concentration of ammonia was estimated after a time sufficient to allow the hydrolysis of any cyanate which

formed during the hydrolysis of urea. Though the mechanism had been given, neither rate determining step had been defined nor rate expression had been given. The alkaline hydrolysis of urea was not a simple first order reaction and required much more kinetic studies. Therefore, the kinetics of the reaction has been studied in alkaline medium with the aim to establish the consecutive nature as well as mechanism of two step hydrolysis of urea. The rate constants of the consecutive steps have been calculated using Swain equation[3]. In support of the mechanism of ureolysis, basic hydrolysis of cyante was also described in the note.

Experimental

Urea (BDH), sodium cyanate (Fluka) and sodium nitrate (E. Merck) were used as such. The stock solution of carbonate free sodium hydroxide (E. Merck) at about 17 mol dm^{-3} was prepared and diluted to the required concentrations using doubly distilled water. All other reagents were of reagent grade. Nessler's reagent was prepared by literature method.

Hydrolysis of urea was carried out under two different conditions.

(i) Estimation of ammonia—A two-necked flask containing sodium hydroxide and potassium nitrate (used to maintain the ionic strength) was thermostatted in an oil bath whose temperature was maintained within $\pm 0.1°C$. Urea solution was then added and the evolved ammonia was flushed out by passing a continuous current of nitrogen gas and was absorbed in hydrochloric acid and then estimated at regular time intervals spectrophotometrically by nesslerization[4].

(ii) Estimation of unreacted [urea]—The concentration of urea was estimated by taking out aliquots at regular time intervals, neutralising it with standard acid solution after cooling, adding 4.0 ml of 50% H_2SO_4 and 2.0 ml of working diacetyl monoxime solution in reaction after heating for ten minutes in boiling water bath and measuring the absorbance of the developed pink colour at 500 nm. Concentration of unreacted urea was estimated from standard plot of absorbance versus urea solutions of known concentrations ranging from 5.0×10^{-6} mol dm^{-3} to 35.0×10^{-6} mol dm^{-3}. This carbamido diacetyl reaction does not give any colour with cyanate or ammonium ions.

Table 1—Activation parameters for the hydrolysis of urea and sodium cyanate

Reaction	$\Delta G^{\neq}$ (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$-\Delta S^{\neq}$ (K^{-1} J mol^{-1})	E_a (kJ mol^{-1})	ln A (s^{-1})
urea $\xrightarrow{k_{1obs}}$ +|NCŌ	112.38	60.72	142.31	63.73	9.44
	(110.00)	(56.86)	(146.39)	(59.58)	(8.94)
NCŌ $\xrightarrow{k_{2obs}}$ NH$_3$	108.01	52.53	153.41	55.34	8.09
	(108.32)	(49.67)	(161.57)	(52.68)	(7.11)

$\Delta G^{\neq}$ calculated at 363K. Parantheses values are for the estimation of urea concentration and sodium cyanate hydrolysis respectively.

Hydrolysis of sodium cyanate in alkaline medium was also carried out under similar conditions as those for urea hydrolysis (estimation of ammonia).

Results and discussion

The basic hydrolysis of urea follows a two step reaction paths.

$$\text{Urea} \xrightarrow{k_1} \text{NH}_3 + \text{B}$$

$$\text{B} \xrightarrow{k_2} \text{NH}_3 + \text{CO}_2$$
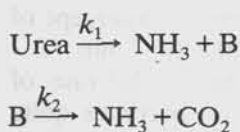
where B stands for cyanate. For this reaction, the concentration of ammonia is related with time by Eq. (1).

$$[\text{NH}_3] = A_0 \left[2 - \left(\frac{k_1 - 2k_2}{k_1 - k_2} \right) e^{-k_1 t} \right.$$

$$\left. - \left[\frac{k_1}{k_1 - k_2} \right] e^{-k_2 t} \right] \qquad \ldots (1)$$

where k_1 and k_2 are the pseudo-first order rate constant and A_0 is the initial concentration of urea.

On making of substitution,

$$\phi = [\text{NH}_3]/A_0 - 2; \quad \theta = k_1 t \text{ and } \rho = k_2/k_1$$

Eq. (1) converts to Eq. (2).

$$\phi(\rho - 1) = e^{-\rho\theta} - (2\rho - 1) e^{-\theta} \qquad \ldots (2)$$

Equation (2) can be solved[3] if the value of θ is guessed since the value of θ and the error, ε, can be closely approximated from Eq. (4)

$$\theta = \theta_0 + \varepsilon \qquad \ldots (3)$$

$$\varepsilon = \frac{\phi(\rho - 1) + (2\rho - 1) e^{-\theta_0} - e^{-\rho\theta_0}}{(2\rho - 1) e^{-\theta_0} - \rho e^{-\rho\theta_0}} \qquad \ldots (4)$$

We have determined values of ϕ using Eqs (3) and (4) using computer program (FORTRAN IV) at a given ρ and at different time intervals from the value of $[\text{NH}_3]$ for a given set of reactions. The ratios of consecutives values of θ i.e., θ_1/θ_2, θ_2/θ_3, θ_3/θ_4.... along the corresponding ratio of time $(t_1/t_2, t_2/t_3, t_3/t_4....)$ were calculated. Moreover the various trial values of ρ were introduced and the best value of ρ was selected at which the difference between the sum of squares of ratios of θ and sum of squares of ratios of time was found to be minimum.

The effect of $[\text{OH}^-]$ on hydrolysis of urea was studied by carrying out a series of kinetic runs within the $[\text{OH}^-]$ range of 0.5 mol dm^{-3} to 3.0 mol dm^{-3} at 363 K. The reaction rate was found to be linear at low $[\text{OH}^-]$ (0.5-1.5 mol dm^{-3}) and a sharp increase in the reaction rate was also observed at high $[\text{OH}^-]$. From these results it is clear that the variation of k_{1obs} with [alkali] obeys Eq. (5).

$$k_{1obs} = B_1 + B_2 k_1 [\text{OH}^-] \qquad \ldots (5)$$

where B_1 and B_2 are the empirical constants. The rate constants of second step hydrolysis (k_{2obs}) was found to be independent of [alkali].

The rate constants were found insensitive to ionic strength. Studies were carried out at different temperatures and activation parameters, evaluated using Arrhenius and Eyring equations with linear least squares techniques, are given in Table 1.

The rate of the non-enzymatic degradation of urea in aqueous medium was independent of pH between 2.0 and 12.0. The reaction rate decreased below pH 2.0 and increased above

Scheme 1 (Step 1)

Scheme 2 (Step 2)

pH 12.0. It has been demonstrated that at pH 7, 13 and 14 the hydrolysis of urea is an elimination reaction which gives ammonia and cyanic acid. The fall off reaction rate below pH 2.0 is due to the protonation of urea and the dependence of rate on $[OH^-]$ above pH 12.0 is ascribed to base catalysis of the elimination reaction.

The mechanisms consistent with the observed results for both the steps of hydrolysis of urea have been given in Schemes 1 and 2.

The usual mechanism of alkaline hydrolysis of amides[2] that involves acyl oxygen fission by the addition of hydroxide ion to the carbonyl carbon to form tetrahedral intermediate followed by its decomposition to give products (ammonia and CO_2) may be applied for urea hydrolysis. But the mechanism does not suitably explain the formation of cyanate ion from tetrahedral intermediate. The mechanism presented in Scheme 1 has been adequately supported by a variety of models[5,6] explaining cyanate formation as a stable intermediate. The mechanism for the second step hydrolysis of urea (cyanate hydrolysis) involved addition of water molecule to cyanate ion as rate determining step. The carbamic acid formed as an addition product is unstable and readily decomposes to ammonia and carbon dioxide. Therefore, complete hydrolysis of urea in alkaline medium occurs by an elimination-addition mechanism.

On the basis of the proposed mechanism rate Eqs 6 and 7 have been derived for the two step hydrolysis of urea

$$k_{1obs} = k_0 + \frac{k_1[OH^-](k_4 + k_3[OH^-])}{k_{-1} + k_4 + k_3[OH^-]} \qquad \ldots (6)$$

and

$$k_{2obs} = k_2 K_h \qquad \ldots (7)$$

Equation (6) is similar to Eq. (5) with

$$B_1 = k_0$$

and

$$B_2 = \frac{(k_4 + k_3[OH^-])}{k_{-1} + k_4 + k_3[OH^-]}.$$

These equations indicate that rate constant (k_{1obs}) for the first step hydrolysis of urea is dependent on $[OH^-]$ and k_{2obs} (second step hydrolysis) is independent of $[OH^-]$ and confirm the observed results and proposed mechanism. At low $[OH^-]$ the rate of formation of dianionic species (c) is very slow and the reactive intermediate (b) is directly converted into the products. There, $k_4 > k_3$ $[OH^-]$ and Eq. (6) reduces to

$$k_{1obs} = k_0 + \frac{k_1 k_4[OH^-]}{k_{-1} + k_4} \qquad \ldots (8)$$

The value of k_0 obtained from the intercept of the plot of k_{obs} versus $[OH^-]$ is 2.0×10^{-4} min^{-1}.

At high $[OH^-]$ (> 1.5 mol dm^{-3}) the rate of formation of dianionic species (c) becomes quite fast in comparison to the decomposition of (b) to the products. This is quite resonable to suppose because the existence of a dianionic intermediate has been observed only in strong alkaline medium. Therefore, $k_3[OH^-] > k_4$ and k_0 can also be neglected at higher $[OH^-]$. Equation (6) which reduces to Eq. (9) may be rearranged as Eq. (10).

$$k_{1obs} = \frac{k_1 k_3[OH^-]^2}{k_{-1} + k_3[OH^-]} \qquad \ldots (9)$$

$$\frac{[OH^-]}{k_{1obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_3[OH^-]} \qquad \ldots (10)$$

According to Eq. (10) the plots of $[OH^-]/k_{1obs}$ versus $1/[OH^-]$ should be linear. This has been found to be the case. k_1 calculated from the intercept of such a plot is 9.52×10^{-4} min^{-1}. Deviations from the linearity are observed at lower and higher $[OH^-]$ in conformity with the suggested mechanism.

The hydrolysis of urea was studied separately by estimating unreacted urea to confirm the kinetic observations for the first step of the reaction. The pseudo-first order rate constants were calculated by varying initial [urea], temperature and $[OH^-]$. Thermodynamic parameters are given in

Table 2—Concentration dependence of k_{1obs} and k_{2obs} for hydrolysis of urea and sodium cyanate

[NaOH] = 1.00 mol dm^{-3}, μ = 0.05 mol dm^{-3}, temp. = 363K

| [A_0] mol dm^{-3} | Ureolysis | | Sodium cyanate hydrolysis |
	$10^4 \, k_{1obs}$ (min^{-1})	$10^3 \, k_{2obs}$ (min^{-1})	$10^3 \, k_{obs}$ (min^{-1})
0.002	6.08 ± 0.01	3.28 ± 10.02	2.15 ± 0.02
0.004	6.42 ± 0.01	2.18 ± 10.02	2.17 ± 0.02
0.006	5.13 ± 0.02	2.62 ± 10.01	2.15 ± 0.03
0.008	5.05 ± 0.04	2.12 ± 10.02	1.92 ± 0.04
0.010	5.43 ± 0.01	2.06 ± 10.01	2.00 ± 0.02
0.012	5.41 ± 0.02	2.14 ± 10.03	2.03 ± 0.01

Table 1. The experimental data fit the empirical Eq. (6) which was found for first step of ureolysis by estimating ammonia.

To confirm the mechanism of second step hydrolysis of urea, kinetics of hydrolysis of sodium cyanate was also carried out under the indentical conditions as those for urea hydrolysis (estimation of ammonia). These results are compiled in Tables 1 and 2. This study provides an additional support to the observed kinetic data of second step of the ureolysis. Hydrolysis of sodium cyanate follows a simple pseudo-first order reaction kinetics. The observed rate constants were found in close agreement with k_{2obs} obtained from ureolysis (Table 2). The rate constants were found to be independent of [alkali] concentration. Rate Eq. (7) has been derived on the basis of mechanism for the second step of ureolysis. Sufficiently large negative value of the entropy of activation indicates that the transition state involved in the critical rate-determining step is more polar than the reaction state.

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