

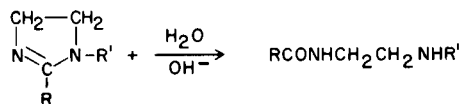
Department of Chemistry, The University of New Mexico

The Kinetics of the Hydrolysis of Some 2-Imidazolines

B. G. Harnsberger (1) and J. L. Riebsomer

A 1,2-disubstituted-2-imidazoline was hydrolyzed in aqueous solutions of varying pH . The rate of reaction approaches a maximum as the base concentration is increased. Salt effects and activation energies also seem to vary with pH .

Alkyl substituted 2-imidazolines are subject to base catalyzed hydrolysis wherein it appears that the initial reaction is an attack by hydroxide ion at the number two carbon of the ring. Subsequent reaction leads to ring fission and the formation of an amide.



Various ring substituents are known to exert a strong influence on the rate of this reaction (2), however the effect of varying base concentration has not been reported.

KINETIC STUDIES

Aqueous solutions of 1-hydroxyethyl-1,2-pentyl-2-imidazoline were used in all of these experiments. Previous experience with this compound had indicated that the rate of hydrolysis would be experimentally convenient, and the compound is quite soluble in water.

Progress of the hydrolysis was followed spectrophotometrically. *Pseudo* first-order kinetics were observed and half-lives and rate constants were determined graphically.

The effect of neutral salts on the rate of hydrolysis varies with the pH of the hydrolytic solution. In one series of experiments, run in 0.0025 molar sodium hydroxide of pH about 11.4, the addition of sodium perchlorate strongly inhibited the reaction. The half-life varied from 22.8 minutes at zero concentration of sodium perchlorate, to 81 minutes when the solution was one molar with respect to sodium perchlorate. In another series of experiments run in solutions of about pH 13.7, the half-life of the hydrolysis reaction was 25.5 minutes in 1 molar sodium perchlorate and 27 minutes in 0.2 molar sodium perchlorate.

The activation energy for the *pseudo* first-order hydrolysis also varies with pH . In a buffer solution of pH 12.45, the experimental activation energy was 16690 cal./g. mole. In buffer solutions of pH 11.25 the activation energy was 20200 cal./g. mole.

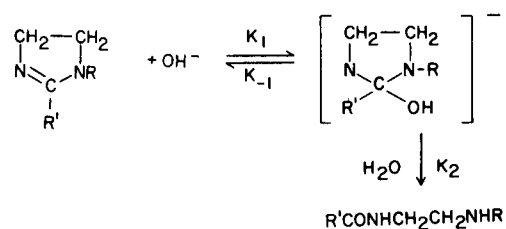
The effect of base concentration was studied in buffered one molar sodium perchlorate solutions.

The total salt concentration reached a maximum of about 1.5 moles per liter at high pH ; however the salt effect at low pH seems to be proportional to the square root of the salt concentration, and salt effects at higher pH seem to be negligible. It therefore did not seem likely that this variation in salt concentration would seriously affect the rate of reaction. Table I and Figure 1 show the data obtained in this series of reactions.

DISCUSSION

The variation of the rate of hydrolysis with the concentration of hydroxide ion is very unusual. Figure 1 shows that the rate of reaction approaches a maximum at high pH . It should also be mentioned that a maximum rate is observed in the hydrolysis of imidazolines in 95% ethanol. The data for this are qualitative, but the maximum does apparently exist.

According to Laidler (3), the observation of a maximum rate is evidence for specific basic catalysis, and there may be an equilibrium between the imidazoline and hydroxide ion to form a complex which subsequently reacts with water to give the observed products. These ideas are formulated in more concrete terms in the following reaction sequence:



The reaction between the imidazoline and hydroxide ion is fast and reversible while the reaction of the complex with water is rate controlling and irreversible under these conditions. With the assumption that the above reaction sequence is correct and that the salt of the imidazoline is not reactive (2), it is possible to formulate a theoretical rate equation that fits the observed variation of rate with base concentration.

TABLE I

Pseudo First-order Rate Constants for the
Hydrolysis of 1-Hydroxyethyl-2-pentyl-2-imidazoline
In Solutions of Varying pH.

pH	OH ⁻ concentration moles x 10 ⁵ /l.	K x 10 ⁵ /minute
9.10	1.26	1.82
10.30	19.9	28.7
10.66	45.7	78.4
10.91	81.3	160
11.15	141	334
11.25	178	460
11.70	513	513
12.15	1440	1740
12.40	2510	2080
12.45	2820	2330
12.67	4680	2430
12.99	9770	2630
13.60	39800	2720
13.70	56200	2540

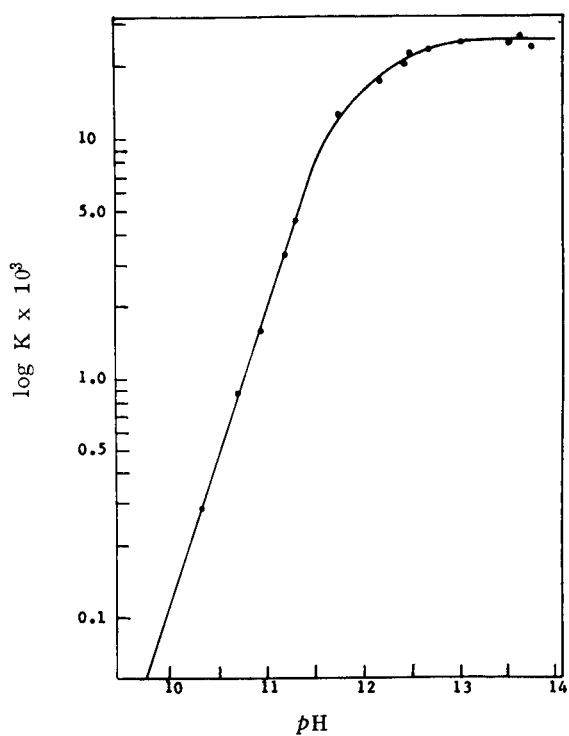


Figure 1

Semi-logarithmic plot of rate constants against pH for the hydrolysis of 1-hydroxyethyl-2-pentyl-2-imidazoline at 25.6°.

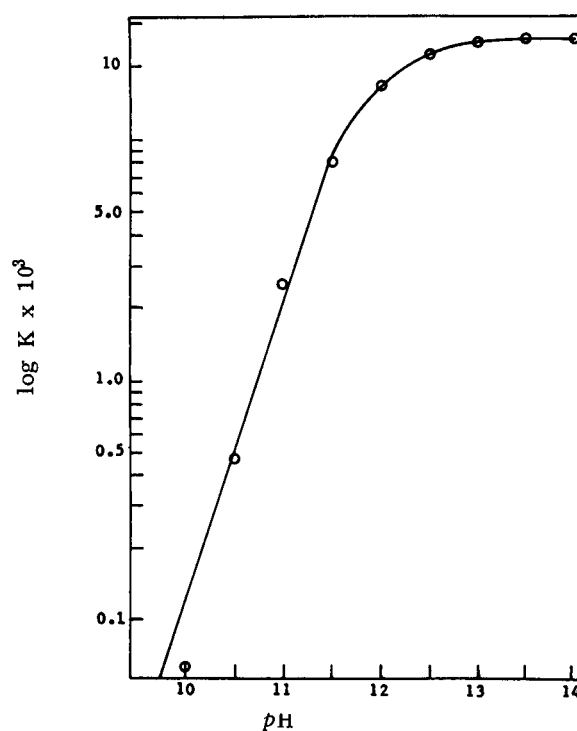


Figure 2

Calculated rate constants from equation X compared with the experimental rate versus pH curve for the hydrolysis of 1-hydroxyethyl-2-pentyl-2-imidazoline.

Let I be an imidazoline and;

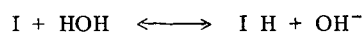
I H the imidazoline salt;

I OH⁻ the imidazoline complex with hydroxide ion;

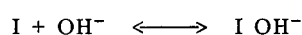
C a prefix denoting the concentration of a reactant;

f the activity coefficient of a reactant.

The previously outlined reactions may then be formulated as:



$$(I) \quad K \text{ ionization} = K_i = \frac{C_{IH} C_{OH^-} f_{IH} f_{OH^-}}{C_I f_I}$$



$$(II) \quad K \text{ equilibrium} = K_{eq} = \frac{C_{IOH^-}}{C_I C_{OH^-}} \times \frac{f_{IOH^-}}{f_I f_{OH^-}}$$

The reaction was followed by measuring the absorbance of portions of the reaction mixture at known intervals. The measured absorbance was apparently a function of the total concentration of all species of unreacted imidazoline since the extinction coefficient is the same in either acidic or basic solution. If we define C_{It} as this concentration of unreacted imidazoline, then:

$$(III) \quad C_{It} = C_{IH} + C_I + C_{IOH^-}$$

If it is assumed that the reaction of the complex, IOH⁻, with water is rate controlling, then:

$$(IV) \quad \text{rate} = K_2 C_{IOH^-} C_{H_2O}$$

Omitting the activity coefficient from equations (I) and (II), and substituting the modified equation (I) and equation (II) into (III) gives:

$$(V) \quad C_{It} = C_I + \frac{K_i C_I}{C_{OH^-}} + K_{eq} C_I C_{OH^-}$$

$$(VI) \quad C_I = \frac{C_{It} C_{OH^-}}{C_{OH^-} + K_{eq} (C_{OH^-})^2 + K_i}$$

Substituting equation (VI) into equation (II) and rearranging gives:

$$(VII) \quad C_{IOH^-} = \frac{K_{eq} C_{It} (C_{OH^-})^2}{C_{OH^-} + K_{eq} (C_{OH^-})^2 + K_i}$$

Finally, substituting equation (VII) into equation (IV) gives:

$$(VIII) \quad \text{rate} = \frac{K_2 K_{eq} C_{It} (C_{OH^-})^2 C_{H_2O}}{C_{OH^-} + K_{eq} (C_{OH^-})^2 + K_i}$$

Since C_{OH^-} and C_{H_2O} were constant in any one run, the observed rate is *pseudo* first-order and:

$$(IX) \quad \text{rate} = K \text{ observed} C_{It}$$

$$(X) \quad K \text{ observed} = \frac{K_2 K_{eq} (C_{OH^-})^2}{K_i + C_{OH^-} (K_{eq} C_{OH^-} + 1)}$$

The value of K_i was experimentally found to be approximately 6×10^{-4} . A value of $K_{eq} = 164$ was found by determining the concentration of hydroxide ion when the observed rate was at a maximum and at one-half maximum. The value of K_2 was then found to be 0.0276/minute by substituting values of K observed, K_i , and K_{eq} into equation (X). Figure 2 shows the relation between the observed rate constant and the calculated rate constant. The semi-logarithmic plot is used because of the wide variation in the rate constant and the concentration of hydroxide ion. It is apparent that equation (X) does give a good approximation of the observed rate constant over much of the pH range considered.

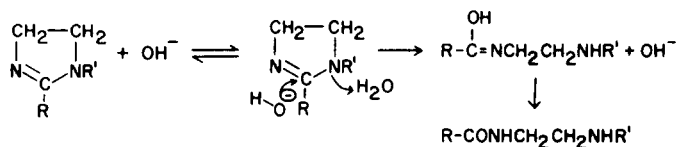
Equation (X) may be written to include the activity coefficients from equation (I). The modified equation is:

$$(XI) \quad K \text{ observed} = \frac{K_2 K_{eq} (C_{OH^-})^2}{\frac{K_i f_I}{f_{OH^-} f_{IH}} + C_{OH^-} (K_{eq} C_{OH^-} + 1)}$$

Equation (XI) appears to explain the negative salt effect at low pH and the absence of salt effects at high pH. At low pH, the term $C_{OH^-} (K_{eq} C_{OH^-} + 1)$ becomes small compared to the term $K_i f_I / f_{OH^-} f_{IH}$. The values of f_{OH^-} and f_{IH} are decreased by an increase in the ionic strength of the solution but the value of f_I is only slightly affected by ionic strength. The result of these changes in activity coefficients should be a decrease in the observed rate constant with increasing ionic strength of the solution. At high pH, the $C_{OH^-} (K_{eq} C_{OH^-} + 1)$ term is large compared to the term in K_i , and the value of K_{eq} should not be affected by the ionic strength of the solution. The observed rate constant should therefore be independent of ionic strength.

The same factors probably explain the variation in the observed activation energies at high and low pH. At low pH, the activation energy is partly dependent on changes in K_i with temperature. At high pH, the activation energy would depend predominately on changes in K_{eq} with temperature. Graphs of $\log K$ against $1/T$ do give fairly good straight lines at a given pH, but apparently the activation energies so obtained must be considered accurate only under the given experimental conditions.

The nature of the negatively charged intermediate that was assumed above is uncertain. If it is assumed that the hydroxide ion bonds to the number two carbon the extinction coefficient for the $-C=N-$ absorption should be less in basic solution than it is in an acidic solution. Acidification does give a larger extinction coefficient; however the difference is small and this does not seem compatible with the large equilibrium constant obtained for the formation of the intermediate. It is possible that the hydroxide ion is simply attracted to the imidazoline molecule by strong electrostatic forces, and that reaction occurs when this species is approached by a water molecule, *i.e.*:



The above sequence seems plausible, however, further study is needed to confirm this mechanism.

EXPERIMENTAL

Synthetic.

1-Hydroxyethyl-2-pentyl-2-imidazoline.

Twenty-eight g. (0.2 mole) of ethyl caproate and 27 g. (0.26 mole) of hydroxyethylethylenediamine were heated together at temperatures up to 210°. Heating was continued until 9 ml. of ethanol was collected. Benzene was then added and heating continued until 2.5 ml. of water was collected. Distillation of the reaction mass yielded the pure imidazoline, a faintly yellow oil, b.p. 156°/0.7 mm.

Anal. Calcd. for C₁₀H₂₀N₂O: N.E., 184; N, 15.21. Found: N.E., 182; N, 15.21.

U.V. λ max (ethanol) 231 mμ, ε, 5,440. U.V. λ max (water) 231 mμ, ε, 5,210. U.V. λ max (HCl solution) 231 mμ, ε, 5,320.

Kinetic Studies.

The method for following these reactions is the same as was reported earlier (2). Imidazoline concentration was about 1 x 10⁻³ molar and temperature was maintained at 29.6°. All pH measurements were made with a Beckman model G pH meter using a blue glass electrode.

Acknowledgment.

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- (1) This paper was abstracted from a dissertation presented by Dr. B. G. Harnsberger to the faculty of the Graduate School of the University of New Mexico. Dr. Harnsberger's present address is: Texaco, Inc. P. O. Box 425, Bellaire, Texas.
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