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The Kinetics of the Hydrolysis of Some 2-Imidazolines

Bobby G. Harnsberger

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2-IMIDAZOLINES

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THE KINETICS OF THE HYDROLYSIS OF
SOME 2-IMIDAZOLINES

By
Bobby G. Harnsberger

A Dissertation
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy in Chemistry

The University of New Mexico
1962

This dissertation, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

W. J. Parish

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DOCTOR OF PHILOSOPHY

DATE

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To Loretta, for whom it cost so much, this work is dedicated.

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Reprints of this paper have been furnished to the following persons:

Dr. G. H. Davis, Jr., Illinois State University, Urbana, Illinois

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PART I

INTRODUCTION

In recent years, 2-imidazolines have become important industrially. Possible applications include uses as drugs, fungicides, emulsifying agents, demulsifying agents, corrosion inhibitors, fuel oil additives and gasoline additives.

Unfortunately, it was found that some of these useful imidazolines decomposed upon storage or under conditions of application and became useless for their intended purpose. It seemed probable that decomposition was a result of hydrolysis and ring opening, and such information as was available in the literature supported this hypothesis. Hydrolysis was known to occur readily with certain types of imidazolines and some information on the conditions and products of hydrolysis was found. However, no kinetic data were available and minimum conditions for hydrolysis were not known. It was, therefore, important to learn more about the conditions, rates, and products of hydrolysis and if possible to ascertain how it could be prevented. In addition, the mechanism of the reaction itself poses an interesting and fundamental chemical problem.

The 2-imidazoline ring is now numbered as follows:

In some of the older literature either nitrogen was used as the starting point for numbering. These compounds were often referred to as 4,5-dihydroimidazoles or dihydroglyoxalines.

I. PHYSICAL PROPERTIES OF 2-IMIDAZOLINES

2-Imidazolines unsubstituted at the nitrogen in the 1-position show a greater solubility in polar solvents than the 1-alkyl or 1-aryl substituted derivatives. Solubility in polar solvents decreases with increasing length of the 2-substituted alkyl group. 2-Imidazolines that are unsubstituted in the 1-position are generally solids or viscous oils. Compounds substituted in this position are generally liquids. The 2-imidazolines are oils when the 1-substituent is hydroxyethyl and the 2-substituent is a straight chain alkyl group of between two and ten carbon atoms in length. The compounds with shorter or longer chains are low melting solids.

It seems that most imidazolines are hygroscopic. Most of the compounds considered in this study would slowly absorb enough water for decomposition to occur even when they were stored in a desiccator. 1-Hydroxyethyl-2-imidazoline and

In some of the cases, the results are as follows:

The electrical conductivity of the solution is measured.

Other factors, such as the concentration of the solution, are also considered.

The results are compared with those obtained from other experiments.

The following table shows the results of the experiments.

Table 1. Results of the experiments.

The results are as follows:

The electrical conductivity of the solution is measured.

Other factors, such as the concentration of the solution, are also considered.

The results are compared with those obtained from other experiments.

The following table shows the results of the experiments.

Table 2. Results of the experiments.

The results are as follows:

The electrical conductivity of the solution is measured.

Other factors, such as the concentration of the solution, are also considered.

The results are compared with those obtained from other experiments.

The following table shows the results of the experiments.

Table 3. Results of the experiments.

The results are as follows:

The electrical conductivity of the solution is measured.

Other factors, such as the concentration of the solution, are also considered.

The results are compared with those obtained from other experiments.

The following table shows the results of the experiments.

Table 4. Results of the experiments.

1-hydroxyethyl-2-methyl-2-imidazoline were deliquescent, and considerable difficulty was experienced in handling these compounds.

Ultra-violet absorption spectra of 1,2-disubstituted imidazolines usually show a single absorption peak at or near 230 millimicrons. Maximum absorbance usually is found near 220 millimicrons in compounds unsubstituted in the 1-position. All of the imidazolines studied show a strong absorption peak at about 6.3 microns in the infra-red.

II. CHEMICAL PROPERTIES OF 2-IMIDAZOLINES

The 2-imidazolines titrate as monoacid bases with strong inorganic acids, and accordingly, neutral equivalents are easily determined. Many 2-imidazolines react with organic acids to form stable distillable complexes containing two moles of acid for each mole of imidazoline. The imidazoline may be liberated from such a complex by treatment with strong base. Imidazolines form quarternary salts with alkyl or aralkyl halides, but, in the case of 2-alkyl-imidazolines, alkylation may occur and be followed by quarternization (7,18).

The carbon to nitrogen double bond of the 2-imidazoline ring is very resistant to hydrogenation (15,32,33), although this bond is easily reduced in imidazolones (35).

2-Imidazolines may be dehydrogenated to imidazoles

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Ultraviolet absorption spectra of 1,2-disubstituted imidazolines usually show a single absorption peak at or near 230 millimicrons. Maximum absorbance usually is found near 230 millimicrons in compounds unsubstituted in the 1-position. All of the imidazolines studied show a strong absorption peak at about 230 millimicrons in the infrared.

II. CHEMICAL PROPERTIES OF 2-IMIDAZOLINES

The 2-imidazolines react as monosubstituted bases with strong inorganic acids, and accordingly, neutral equivalents are easily determined. Many 2-imidazolines react with organic acids to form stable distillable complexes containing two moles of acid for each mole of imidazoline. The imidazoline may be liberated from such a complex by treatment with strong base. Imidazolines form quaternary salts with alkyl or aralkyl halides, but in the case of 2-alkyl-imidazolines, alkylation may occur and be followed by quaternization (7,18).

The carbon to nitrogen double bond of the 2-imidazoline ring is very resistant to hydrogenation (15,32,33), although this bond is easily reduced in imidazolones (35). 2-Imidazolines may be dehydrogenated to imidazoles

by heating over powdered metal catalysts (15,19) or by treatment with a nickel-petroleum paste (20) or potassium amide (31).

The 2-imidazolines undergo ring opening under the influence of a number of reagents. This behaviour will be discussed in detail in the next section.

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influence of a
discussed in

PART II

LITERATURE SURVEY

The papers cited here will be confined to those reporting opening of the imidazoline, imidazole, and imidazolidine rings.

A general outline of the preparation and properties of the 2-imidazolines may be found in the review article by Ferm and Riebsomer (9).

I. OPENING OF THE IMIDAZOLINE RING

Ladenburg (21), Bauman (3), and Forsell (13), reported that the imidazoline ring opened during benzoylation, but it was not possible to determine where the opening occurred from their work.

Aspinall (1) reported that 2-methyl and 2-phenyl-2-imidazolines were opened to monoacyl ethylenediamines by boiling in water. The 2-phenyl-2-imidazoline was the more stable of the two compounds. Ring opening was reported during acylation with benzoyl chloride and upon treatment with benzenesulfonyl chloride, but in neither case was it possible to determine where the opening occurred.

King and McMillian (18) alkylated a number of imidazolines and then hydrolyzed the alkylation products

PART II

LITERATURE SURVEY

The papers cited here will be confined to those

reporting opening of the indole ring, indazole, and

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A general outline of the preparation and properties

of the 2-indazoles may be found in the review article

by Fern and Kibson (9).

1.1. OPENING OF THE INDOLIZINE RING

Ladenburg (10), Brown (11), and Forest (12)

reported that the indolizine ring opened during pyrolysis

reaction, but it was not possible to determine where the

opening occurred from their work.

Amis (13) reported that 2-methyl and 2-phenyl-

2-indazoles were opened to monomeric ethylenediamine

by boiling in water. The 2-phenyl-2-indazole was the

more stable of the two compounds. Ring opening was

reported during reaction with benzoyl chloride and upon

treatment with benzeneamine, but in neither

case was it possible to determine where the opening occurred.

King and Moffat (14) studied a number of

indazoles and then hydrolyzed the alkylation products

It is apparent from this study that ring fission occurred between positions 1 and 2. The reported ease of hydrolysis of the 1-acylated-2-imidazolines in acidic solution is unexpected because the 1-alkyl-2-imidazolines are quite resistant to such hydrolysis; however, the facile acid hydrolysis of the 1-acylated compounds has been corroborated by other workers (26).

Hawkins and Biggs (17) hydrolyzed a number of 2-imidazolines to 1,2 diamines in both acidic and basic aqueous solutions. The acid hydrolysis was carried out in a sealed tube using concentrated hydrochloric acid at 175°-180° for seven hours. The basic hydrolysis was carried out in refluxing 30% potassium hydroxide. It is noteworthy that 23% of 1,2,5-trimethyl-5-ethyl-2-imidazoline was recovered unreacted after seven hours of this treatment.

Miescher, Marxer, and Urech (26) found that the monoacetyl derivatives of several imidazolines are easily hydrolyzed by dilute acids:

It is apparent from this study that ring closure occurred between positions 1 and 2. The reported ease of hydrolysis of the 1-alkyl-2-imidazolinones in acidic solution is unexpected because the 1-alkyl-2-imidazolinones are quite resistant to such hydrolysis; however, the facile acid hydrolysis of the 1-alkylated compounds has been corroborated by other workers (12).

Baskins and Biggs (17) hydrolyzed a number of 2-imidazolinones to 1,2-diamines in both acidic and basic aqueous solutions. The acid hydrolysis was carried out in a sealed tube using concentrated hydrochloric acid at 175°-180° for seven hours. The basic hydrolysis was carried out in refluxing 30% potassium hydroxide. It is noteworthy that 2% of 1,2-bis(2-ethyl-2-imidazolinyl) was recovered unreacted after seven hours of this treatment. Miescher, Kiser, and Urech (18) found that the monomethyl derivatives of several imidazolinones are easily hydrolyzed by dilute acids.

III.

The same types of amides were also often isolated in the mother liquors from the acetylation.

When the parent imidazolines, I., were warmed with dilute acid, or the imidazoline hydrochloride salt was warmed in water, no hydrolysis occurred. When the free imidazoline was heated in water for thirty minutes, a monoacetylated ethylenediamine was formed. Heating of the free base in 90% ethanol containing 3% KOH gave no hydrolysis. Heating in 85% ethanol containing 10% KOH resulted in formation of the monoamide. These authors report that concentrated acids and high temperatures are required for hydrolysis to the acid and ethylenediamine.

It is of considerable interest that these authors postulate the formation of a 2-hydroxy substituted intermediate in some of their reactions. In the

 

diacetylation of 2-(diphenylaminomethyl)-2-imidazoline with pyridine and acetic anhydride, the following reaction scheme is given:

In the attempted monoacetylation of 2-benzyl-2-imidazoline, a similar intermediate is proposed.

II. OPENING OF THE IMIDAZOLE RING

The imidazole ring is normally difficult to open, but in several instances it has been shown to open easily after treatment with methyl-iodide or after subjection to the Schotten-Bauman reaction.

O. Fisher (10) treated N-methylbenzimidazole with

bicyclic of 2-(diethylaminoethyl)-2-methyl-1,3-dioxane
 pyridine and acetic anhydride, the following reaction scheme
 is given:

In the attempted monosuccinylation of 2-benzyl-2-indacolin,
 a similar intermediate is proposed.

III. OPENING OF THE INDACOLIN RING

The indacolin ring is normally difficult to open,
 but in several instances it has been shown to open easily
 after treatment with methyl-lithium or after subjected to
 the Robinson-Bauman reaction.
 O. Fisher (10) treated N-methylindacolin with

methyl iodide to give a compound which was formulated as:

This compound on treatment with base gave an hydroxy compound which was very easily hydrolyzed by aqueous base to 1,2-methylaminobenzene and formic acid.

This same type of intermediate was found in a study by Gerngross (14). N-benzoylbenzimidazol was treated with benzoyl chloride and water to give a product that was decomposed by heating or merely shaking with water.

1000

This compound is a bicyclic compound, possibly a decalin derivative, with a methyl group attached to one of the rings.

This compound is a bicyclic compound, possibly a decalin derivative, with a methyl group attached to one of the rings.

III. OPENING OF THE IMIDAZOLIDINE RING

The imidazolidines are apparently very resistant to alkaline hydrolysis, but are readily cleaved by dilute aqueous acid. Both Lob. (24) and Rameau (29) found that cleavage by aqueous acid resulted in the formation of a substituted ethylene diamine and an aldehyde.

III. OPENING OF THE IMIDAZOLIDINE RING

The imidazolidines are apparently very resistant to alkaline hydrolysis, but are readily cleaved by dilute aqueous acids. Both Lob (24) and Raman (25) found that cleavage by aqueous acid resulted in the formation of a substituted ethylene diamine and an aldehyde.

PART III

DISCUSSION

The brief review in Part II, as well as this study, indicate that hydrolysis is the chief reason for the lack of stability exhibited by many imidazolines.

In this study, rapid initial hydrolysis was found in experiments in which an imidazoline was dissolved in water at twenty-five degrees. Furthermore, samples of many imidazolines were found to decompose even when they were stored in a desiccator. Infra-red spectra of the decomposed materials show the characteristic amide band resulting from hydrolysis.

As further evidence for hydrolysis and the course of the hydrolytic reaction, a sample of 2-hendecyl-1-hydroxyethyl-2-imidazoline, m.p. 46-47°, was checked after being stored in a corked flask for several years. The imidazoline had changed completely into N-lauroyl-N'-hydroxyethyl-ethylenediamine, m.p. 97-98°.

In another experiment, a sample of 1-hydroxyethyl-2-pentyl-2-imidazoline, a liquid, was dissolved in water and allowed to stand for several months. The imidazoline ring opened to form N-pentanoyl-N'-hydroxyethyl-ethylenediamine

The first series of experiments was conducted with a view to determining the effect of the concentration of the solution on the rate of reaction. It was found that the rate of reaction increased with the concentration of the solution, and that the order of reaction was one with respect to the concentration of the solution.

The second series of experiments was conducted with a view to determining the effect of the temperature on the rate of reaction. It was found that the rate of reaction increased with the temperature, and that the order of reaction was one with respect to the temperature.

The third series of experiments was conducted with a view to determining the effect of the catalyst on the rate of reaction. It was found that the rate of reaction increased with the concentration of the catalyst, and that the order of reaction was one with respect to the concentration of the catalyst.

The fourth series of experiments was conducted with a view to determining the effect of the solvent on the rate of reaction. It was found that the rate of reaction increased with the concentration of the solvent, and that the order of reaction was one with respect to the concentration of the solvent.

The fifth series of experiments was conducted with a view to determining the effect of the pressure on the rate of reaction. It was found that the rate of reaction increased with the pressure, and that the order of reaction was one with respect to the pressure.

The sixth series of experiments was conducted with a view to determining the effect of the time on the rate of reaction. It was found that the rate of reaction decreased with the time, and that the order of reaction was one with respect to the time.

The seventh series of experiments was conducted with a view to determining the effect of the concentration of the reactants on the rate of reaction. It was found that the rate of reaction increased with the concentration of the reactants, and that the order of reaction was one with respect to the concentration of the reactants.

The eighth series of experiments was conducted with a view to determining the effect of the concentration of the products on the rate of reaction. It was found that the rate of reaction decreased with the concentration of the products, and that the order of reaction was one with respect to the concentration of the products.

The ninth series of experiments was conducted with a view to determining the effect of the concentration of the catalyst on the rate of reaction. It was found that the rate of reaction increased with the concentration of the catalyst, and that the order of reaction was one with respect to the concentration of the catalyst.

The tenth series of experiments was conducted with a view to determining the effect of the concentration of the solvent on the rate of reaction. It was found that the rate of reaction increased with the concentration of the solvent, and that the order of reaction was one with respect to the concentration of the solvent.

m.p. 71-72°. The structures of both the amides listed below were determined by nitrogen and Van Slyke amino nitrogen analysis.

An amide of the same type was also recovered in the hydrolysis of 2-heptadecyl-1-hydroxyethyl-2-imidazoline in either aqueous or ethanolic sodium hydroxide solution.

In comparing the products of hydrolysis listed above with those given in the literature, one must conclude that the hydrolytic fission of the imidazoline ring generally occurs between the singly bonded carbon and nitrogen in the 1- and 2-positions.

The hydrolysis of amides is known to be both acid and base catalyzed, so that under the proper conditions, the reaction given above may go to a free acid and diamine.

All of the above reaction products have been isolated and identified in several cases.

A considerable amount of time was expended in hydrolyzing samples of various imidazolines and attempting

to determine the degree of hydrolysis by usual chemical techniques of separation. Extraction from acidic and basic aqueous solutions was impractical because of the formation of extremely stable emulsions, and other possible methods of separation were rejected because of the probability of hydrolysis during separation. It seems probable that failure to achieve chemical separation was due, in part, to the choice of 1-hydroxyethyl substituted imidazolines as starting materials for this work; but these failures did lead to the use of instrumental methods for following the hydrolyses.

The course of the reactions were first followed successfully by using an infra-red spectrophotometer. The imidazoline ring has a strong absorption peak at 6.3 microns, while the amide resulting from hydrolysis absorbs at 6.1 microns. The concentrations of both the imidazoline and amide were determined by measuring the heights of these peaks. It was thus possible to show fairly good pseudo first-order kinetics with this method, and the spectra given in the experimental section are actually from a kinetic study. Unfortunately, the sampling technique required was rather tedious and the infra-red spectrophotometer did not always give reproducible results. The infra-red technique was therefore abandoned in favor of the ultra-violet.

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hydrolysis. The course of the reactions were first followed successfully by using an infra-red spectrophotometer. The imidazoline ring has a strong absorption peak at 6.3 microns, while the amide resulting from hydrolysis absorbs at 6.1 microns. The concentrations of both the imidazoline and amide were determined by measuring the heights of these peaks. It was thus possible to show fairly good pseudo first-order kinetics with this method, and the spectra given in the experimental section are actually from a kinetic study. Unfortunately, the sampling technique required was rather tedious and the infra-red spectrophotometer did not always give reproducible results. The infra-red technique was therefore abandoned in favor of the

ultra-violet.

The use of the ultra-violet spectrophotometer in following these reactions is described in the experimental part of this paper. This procedure seems to be applicable to any imidazoline not substituted with a group that absorbs near 230 millimicrons. The hydrolysis of 2-phenyl substituted-2-imidazolines was followed by observing the disappearance of a sideband at about 265 millimicrons, but results are subject to some doubt as to accuracy because of probable interference by the absorption of the benzene ring.

I. THE EFFECT OF SUBSTITUENTS ON THE RATE OF HYDROLYSIS OF 2-IMIDAZOLINES

Two series of hydrolytic reactions were run in order to determine the effect of various substituents in the 1- and 2-positions of imidazolines. In one series, the group in the 1-position was held constant while the substituent in the 2-position was varied. In the second series, this situation was reversed. All of these reactions were run in 95% ethanol that was 3.75×10^{-2} molar in sodium hydroxide. Pseudo first-order kinetics were observed and all half-lives were obtained graphically. Tables I and II summarize the experimental results obtained with the various compounds.

The use of the ultra-violet spectrophotometer in following these reactions is described in the experimental part of this paper. This procedure seems to be applicable to any indazole derivative. The hydrolysis of 2-substituted-2-indazoles was followed by observing the disappearance of a band at about 255 mμ, but results are subject to some doubt as to accuracy because of possible interference by the absorption of the indazole ring.

5. THE EFFECT OF SUBSTITUENTS ON THE RATE OF HYDROLYTIC REACTIONS OF 2-INDAZOLES

The series of hydrolytic reactions were run in order to determine the effect of various substituents in the 1- and 3-positions of indazole. In the first series, the group in the 1-position was held constant while the substituent in the 3-position was varied. In the second series, this situation was reversed. All of these reactions were run in 95% ethanol that was 0.2N in sodium hydroxide. Pseudo first-order kinetics were observed and all half-lives were obtained graphically. Tables I and II summarize the experimental results obtained with the various compounds.

TABLE I

THE EFFECT OF 2-SUBSTITUENTS ON HALF-LIVES AND
ACTIVATION ENERGIES OF 1-HYDROXY-
ETHYL-2-IMIDAZOLINES

R	T _{1/2} at 70.48° C Minutes	T _{1/2} at 58.26° C Minutes	T _{1/2} at 48.90° C Minutes	E activation cal./g.mole
H-	3.0 2.7	6.5 6.2	14.6 14.25	16960 ± 2780
CH ₃ -	28.5 28.5	70.5 69	153 148	16990 ± 1770
C ₂ H ₅ -	17.5 18	40.2 38	81 80	15770 ± 2190
CH(CH ₃) ₂ -	46 44	96 92	194 180	14560 ± 2660
C(CH ₃) ₃ -	95 97	264 258	612 612	18980 ± 1580
C ₅ H ₁₁ -	25 25	57.5 55	119 117	15880 ± 2670
C ₁₇ H ₃₅ -	24 24	56 52	115 114	15360 ± 3060
(C ₆ H ₅) ₂ CH-*	260			
C ₆ H ₅ -*	600			

*These are qualitative values. See Appendix.

TABLE II
THE EFFECT OF VARIOUS SUBSTITUENTS ON HALF-LIVES
AND ACTIVATION ENERGIES OF
2-PENTYL-2-IMIDAZOLINES

R	R'	T _{1/2} at 70.48° C Minutes	T _{1/2} at 58.26° C Minutes	T _{1/2} at 48.90° C Minutes	E activation cal./g/mole
H	H	287 288	738 732	1692 1698	18160 ± 1860
CH ₃	H	32 32	66.5 66	131 132	14460 ± 1980
C ₂ H ₅	H	59 58	121.5 120	236 236	14270 ± 1960
C ₂ H ₄ OH	H	25 25	57.5 55	119 117	15880 ± 2667
C ₂ H ₄ OC ₂ H ₅	H	65 62.7	137 137	267 270	14700 ± 1800
CH(CH ₃) ₂	H	450 453	1020 1044	1878 1884	14650 ± 2050
CH(CH ₃) ₂	CH ₃	65 days approximately			

II. EFFECT OF THE CONCENTRATION OF BASE ON THE RATE OF HYDROLYSIS OF 2-IMIDAZOLINES IN WATER

The method of obtaining these data is given in the experimental part. For the purpose of the present discussion, it is summarized in Table III and a graph of the logarithm of the observed first-order rate constant against pH is given in Figure I. The logarithmic plot is given because of the wide variation of the rate constant and concentration of the hydroxyl ion.

II. EFFECT OF THE CONCENTRATION OF BASE ON THE RATE OF HYDROLYSIS OF 2-INDANOLONES IN WATER

The method of obtaining these data is given in the experimental part. For the purpose of the present discussion, it is summarized in Table II and a graph of the logarithm of the observed first-order rate constant against pH is given in Figure 1. The logarithmic plot is given because of the wide variation of the rate constant and concentration of the hydroxyl ion.

TABLE III

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 ³ /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 1. Semi-logarithmic plot of rate constants against pH for the hydrolysis of 2-methyl-2-butanol at 25.0°C.

III. MISCELLANEOUS FACTORS INFLUENCING THE RATE OF HYDROLYSIS OF 2-IMIDAZOLINES

The hydrolysis of 2-imidazolines in weakly acidic solutions is very slow or non-existent. An experiment wherein 2-heptadecyl-1-hydroxyethyl-2-imidazoline was hydrolyzed in acidic 95% ethanol gave a half-life of 13680 minutes at 70°. A series of experiments in buffered aqueous solutions below pH 7 showed no hydrolysis of 1-hydroxyethyl-2-pentyl-2-imidazoline after 6780 minutes at 25°. In view of this information, and the concurring findings of Marxer (25), it seems safe to conclude that the 2-imidazoline salts are very resistant to hydrolysis.

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 in 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 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.

IV. A PROPOSED MECHANISM FOR THE BASE CATALYZED HYDROLYSIS OF 2-IMIDAZOLINES

A mechanism for the hydrolysis of the 2-imidazolines should be compatible with the preceding data and general knowledge about the behaviour of organic compounds.

The imidazolines are weak monoacid bases. It is reasonable to assume that in aqueous solution they are normally hydrogen bonded to water molecules and that an equilibrium exists between the ionized and unionized forms.

In view of the resistance to acid hydrolysis, it seems that the ionized form of the imidazoline does not take part in hydrolysis.

The structure of the amides resulting from hydrolysis, and the fact that hydrolysis is catalyzed by hydroxide ion,

hydrolysis also varies with pH. In a buffer solution of pH 12.45, the experimental activation energy was 20500 cal/mole. In buffer solutions of pH 11.12, the activation energy was 20500 cal/mole.

IV. A PROPOSED MECHANISM FOR THE BASE CATALYZED

HYDROLYSIS OF 1-INDANOL
A mechanism for the hydrolysis of 1-indanol should be compatible with the preceding data and general knowledge about the behavior of organic compounds. The indanols are weak monobasic bases. It is reasonable to assume that an equilibrium exists between normally hydrogen bonded water molecules and water molecules which are hydrogen bonded to the indanol. An equilibrium exists between the indanol and water molecules.

In view of the resistance to acid hydrolysis, it seems that the ionized form of the indanols does not take part in hydrolysis.

The structure of the anion resulting from hydrolysis and the fact that hydrolysis is catalyzed by hydroxide ion

suggest that there is an initial attack by hydroxide on the number two carbon of the ring.

The number two carbon in the imidazoline ring should be slightly positive. Any substituent that reduces this positive charge should also reduce the probability of attack by hydroxide ion; and this should lead to a slower reaction. This effect should be observed regardless of the position of the substituent.

The electron donating ability of alkyl groups is in the order $-\text{C}(\text{CH}_3)_3 > -\text{CH}(\text{CH}_3)_2 > -\text{C}_5\text{H}_{11} > -\text{C}_2\text{H}_5 > -\text{CH}_3 > -\text{H} > -\text{C}_6\text{H}_5$; and it would be expected that the half-lives for the hydrolysis of compounds with these substituents would be in the same order. Comparison of this postulate with Tables I and II shows that the expected order was found in most cases. It is unfortunate that steric hindrance should affect the rate of reaction in the same way as would inductive effects, but at least there is no evidence for the two effects being opposed.

The compounds that do not fall in their expected

suggest that there is an initial attack by hydroxide on the number two carbon of the ring.

The number two carbon is the tertiary carbon and should be slightly positive. Any substituent that reduces this positive charge should also reduce the probability of attack by hydroxide ion, and this should lead to a slower reaction. This effect should be observed regardless of the position of the substituent.

The electron donating ability of alkyl groups is in the order $\text{CH}_3 > \text{CH}_2\text{CH}_3 > \text{CH}_2\text{CH}_2\text{CH}_3 > \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and it would be expected that CH_3 would be the most effective for the hydrolysis of compounds with these substituents. Comparison of this postulate with Tables I and II shows that the expected order was found in most cases. It is unfortunate that steric hindrance should affect the rate of reaction in the same way as would inductive effects, but at least there is no evidence for the two effects being opposed.

The compounds that do not fall in their expected

places are the 2-methyl and 2-phenyl substituted 1-hydroxyethyl-2-imidazolines, and 2-pentyl-2-imidazoline. At this time, there is no really satisfactory explanation for the unexpected stability of the 2-methyl substituted compound, but fairly plausible explanations are possible for the others. In the case of the 2-phenyl substituted compound, it seems likely that there is some resonance stabilization that may reduce the charge on the number two carbon.

This charge distribution would be expected to slow the reaction and compensate for the tendency of the benzene ring to withdraw electrons. The low reactivity of 2-pentyl-2-imidazoline may be explained reasonably by the fact that the number one nitrogen in this compound is essentially a secondary amine; and by analogy with normal secondary and tertiary amines it may be expected to be much more basic than the other compounds with which it is compared. This increased basicity should lead to decreased reactivity by decreasing the concentration of unionized imidazoline available for reaction.

The extreme stability of the 4,4- and 5,5- dialkyl substituted imidazoline is surprising but not inexplicable. The 4,4- disubstituted compounds should be subject to the inductive effects of a tertiary alkyl group acting through an easily polarizable double bond. The stability of the 5,5-disubstituted (16) compounds can be accounted for by increased basicity of the number one nitrogen and decreased charge on the number two carbon.

There are several other interesting facts in Table II. The half-lives of 1-ethyl and 1-ethoxyethyl-2-pentyl-2-imidazoline are almost the same. It would be expected that the inductive effects of these two substituents would be of about the same magnitude; so it seems that steric hindrance by straight chain substituents in the 1-position does not greatly affect the rate of hydrolysis.

The half-life of 1-isopropyl-2-pentyl-2-imidazoline is greater than might be expected on the grounds of inductive effects. It therefore appears that considerable steric hindrance occurs when the 1-substituent is a branched chain alkyl group.

Finally, the half-life of 1-hydroxyethyl-2-pentyl-2-imidazoline seems to indicate that the hydroxyethyl group is a less effective electron donor than a methyl group, and it is probably that this is so. Atomic models, however, show that the hydroxyl group may be in an excellent position

The extreme stability of the 4,4- and 5,5-disubstituted imidazolines is surprising but not unexpected. The 4,4-disubstituted compounds should be subject to the inductive effects of a tertiary alkyl group acting through an easily polarizable double bond. The stability of the 5,5-disubstituted (10) compounds can be accounted for by increased basicity of the nitrogen and decreased charge on the nitrogen atom.

There are several other interesting facts in Table II. The half-lives of 1-ethyl and 1-ethoxyethyl-2-pentyl-2-imidazolines are almost the same. It would be expected that the inductive effects of these two substituents would be of about the same magnitude; so it seems that steric hindrance by adjacent chain substituents in the 1-position does not greatly affect the rate of hydrolysis.

The half-life of 1-isopropyl-2-pentyl-2-imidazoline is greater than might be expected on the grounds of inductive effects. It therefore appears that considerable steric hindrance occurs when the 1-substituent is a branched chain alkyl group.

Finally, the half-life of 1-hydroxyethyl-2-pentyl-2-imidazoline seems to indicate that the hydroxyethyl group is a less effective electron donor than a methyl group, and it is probable that this is so. Atomic models, however, show that the hydroxyl group may be in an excellent position

to attack the number two carbon of the ring, and there is evidence for this type of attack in other compounds (5).

The variation of the rate of hydrolysis with the concentration of hydroxide ion is very unusual. Figure I 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 more qualitative than that given in Table III, but the maximum does apparently exist. The data on hydrolysis in ethanol are given in the Appendix.

Maximum rates have been reported in acid catalyzed reactions (8), and are common in enzyme catalyzed systems. Maximum rates have also been reported in catalysis by imidazole (6), and in oxidation by persulfate ion (23,25); but the attainment of a maximum rate in a base catalyzed reaction has not been previously reported.

According to Laidler (22), the observation of a maximum rate is evidence for specific basic catalysis, and there should 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:

to attach the number two carbon of the ring, and there is evidence for this type of attack in other compounds. The variation of the rate of hydrolysis with the concentration of hydroxide ion is very unusual. Figure 2 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 imidazoles in 95% ethanol. The data for this are more suggestive than that given in Table I, for the reaction does apparently exist. The data on hydrolysis in ethanol are given in the Appendix. Maximum rates have been reported in acid solutions for reactions (3), and are common in bases catalyzed systems. Maximum rates have also been reported in hydrolysis of imidazole (5), and in oxidation of benzimidazole (2, 3), but the attainment of a maximum rate in a base catalyzed reaction has not been previously reported. According to Bell (22), the observation of a maximum rate is evidence for specific basic catalysis and there should be an equilibrium between the imidazole 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. With the above reaction sequence and the previously mentioned ionization of an imidazoline, it is possible to formulate a theoretical rate equation that fits the observed variation of rate with base concentration.

Let I be an imidazoline and:

I H⁺ the imidazoline salt;

I OH⁻ the imidazoline complex with hydroxide ion;

A the amide resulting from hydrolysis;

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:

$$\text{I. } K \text{ ionization} = K_1 = \frac{C_{\text{IH}^+} C_{\text{OH}^-}}{C_{\text{I}}} \frac{f_{\text{IH}^+} f_{\text{OH}^-}}{f_{\text{I}}}$$

 

$$\text{II. } K \text{ equilibrium} = K_{\text{eq}} = \frac{C_{\text{IOH}^-}}{C_{\text{I}} C_{\text{OH}^-}} \times \frac{f_{\text{IOH}^-}}{f_{\text{I}} f_{\text{OH}^-}}$$

The reaction was followed by measuring the absorbance of portions of the reaction mixture at known time intervals. The measured absorbance was a function of the total concentration of all species of unreacted imidazoline. If we define C_{I_t} as this concentration of unreacted imidazoline, then:

$$\text{III. } C_{\text{I}_t} = C_{\text{IH}^+} + C_{\text{I}} + C_{\text{IOH}^-}$$

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

$$\text{IV. rate} = K_2 C_{\text{IOH}^-} C_{\text{H}_2\text{O}}$$

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

$$\text{V. } C_{\text{I}_t} = C_{\text{I}} + \frac{K_1 C_{\text{I}}}{C_{\text{OH}^-}} + K_{\text{eq}} C_{\text{I}} C_{\text{OH}^-}$$

$$\text{VI. } C_{\text{I}} = \frac{C_{\text{I}_t} C_{\text{OH}^-}}{C_{\text{OH}^-} + K_{\text{eq}} (C_{\text{OH}^-})^2 + K_1}$$

Substituting equation VI into equation II and rearranging gives:

$$K_{eq} = \frac{C_{OH^-} C_{I^-}}{C_{OH^-} C_{I^-}} \times \frac{C_{OH^-} C_{I^-}}{C_{OH^-} C_{I^-}}$$

The reaction was followed by measuring the absorbance of portions of the reaction mixture at known time intervals. The measured absorbance was a function of the total concentration of all species of unreacted indole. If we define C_t as this concentration of unreacted indole,

$$C_t = C_{I^-} + C_{OH^-} + C_{I^-} + C_{OH^-}$$

It is assumed that the reaction of the complex, $I^- + OH^-$, which occurs at rate controlling, then:

$$IV. \text{ rate} = k_2 C_{OH^-} C_{I^-}$$

Omitting the activity coefficient from equations I

and VI, and substituting the measured reaction I and equation II into III gives:

$$V. C_{I^-} = C_t + \frac{k_2 C_{OH^-} C_{I^-}}{k_1 C_{OH^-} + k_2 C_{I^-}}$$

$$VI. C_{I^-} = \frac{C_t (k_1 C_{OH^-} + k_2 C_{I^-})}{k_1 C_{OH^-} + k_2 C_{I^-} + k_2 C_{OH^-}}$$

Substituting equation VI into equation II and

rearranging gives:

$$\text{VII. } C_{\text{IOH}^-} = \frac{K_{\text{eq}} C_{\text{I}_t} (C_{\text{OH}^-})^2}{C_{\text{OH}^-} + K_{\text{eq}} (C_{\text{OH}^-})^2 + K_1}$$

Finally, substituting equation VII into equation IV gives:

$$\text{VIII. rate} = \frac{K_2 K_{\text{eq}} C_{\text{I}_t} (C_{\text{OH}^-})^2 C_{\text{H}_2\text{O}}}{C_{\text{OH}^-} + K_{\text{eq}} (C_{\text{OH}^-})^2 + K_1}$$

Since C_{OH^-} and $C_{\text{H}_2\text{O}}$ were constant, the observed rate is pseudo first-order and:

$$\text{IX. rate} = K_{\text{observed}} C_{\text{I}_t}$$

$$\text{X. } K_{\text{observed}} = \frac{K_2 K_{\text{eq}} (C_{\text{OH}^-})^2}{K_1 + C_{\text{OH}^-} (K_{\text{eq}} C_{\text{OH}^-} + 1)}$$

The value of K_1 was experimentally found to be approximately 6×10^{-4} . A value of $K_{\text{eq}} = 164$ 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_1 , and K_{eq} into equation X. Figure II 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

VII. $k_{obs} = k_1 + k_2$
 Finally, substituting equation VII into equation IV
 gives:

VIII. $\text{rate} = \frac{k_1 k_2 [C] [O_2]}{k_1 + k_2 [O_2]}$
 Since C_{O_2} and C_{H_2O} were constant, the observed rate
 is pseudo first-order and:

IX. $\text{rate} = k_{obs} [C]$
 X. $k_{obs} = \frac{k_1 k_2 [O_2]}{k_1 + k_2 [O_2]}$

The value of k_1 was experimentally found to be
 approximately 5×10^{-4} . A value of k_2 was found by
 determining the concentration of hydrogen ion when the
 observed rate was at a maximum and at one-half maximum.
 The value of k_2 was then found to be 0.015 minutes⁻¹.
 Substituting values of k_1 and k_2 into equation
 X, Figure 11 shows the relation between the observed rate
 constant and the calculated rate constant. The results
 logarithmic plot is used because of the wide variation in
 the rate constant and the concentration of hydrogen ion.
 It is apparent that equation X does give a good approximation
 of the observed rate constant over most of the pH range.

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

Figure 2. Rate constants from equation 4 compared to the experimental rate versus pH curve for the hydrolysis of 1-hydroxyethyl-2-pyridyl-2-imidazole.

considered.

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

$$\text{XI. } K \text{ observed} = \frac{K_2 K_{eq} (C_{OH^-})^2}{\frac{K_1 f_I}{f_{OH^-} f_{IH^+}} + C_{OH^-} (K_{eq} C_{OH^-} + 1)}$$

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 $K_1 f_I / f_{OH^-} f_{IH^+}$. 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_1 , 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_1 with temperature. At high pH, the activation energy

would depend predominantly 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 in equation II is not certain. If it is assumed that the hydroxide ion bonds to the number two carbon, then the intermediate is possibly:

This may decompose by combining with a water molecule in either of two ways:

or:

would depend predominantly on changes in the temperature
Graphs of log A against 1/T are given in Fig. 1 and 2
lines at a given point, but separated by the activation energies
so obtained need be considered as correct only under the given
experimental conditions.

The nature of the negatively charged intermediates
that was assumed in equation (1) is not certain. It is
assumed that the hydroxyls are bonded to the oxygen atom.

Then the intermediate is represented by the following structure:

This may be represented by a water molecule in
either of the ways:

or

or

or

A mechanism such as depicted in XII would seem most likely to lean to an amide of the proper structure, but it is difficult to understand why the reaction with water would be slow. The amine nitrogen should be hydrogen bonded to a water molecule and the second step in the reaction should be fast.

Mechanism XIII has two attractive features. The hydroxyimidazolidine structure shown here is similar to compounds that were mentioned in the literature survey. By analogy with these compounds, this imidazolidine would be expected to be very unstable. It would also be expected that the 3-position nitrogen would be much slower to react with water than the nitrogen in the 1-position. The nitrogen in position three has little or no basic character and would not be hydrogen bonded to water. The reaction rate should, therefore, be controlled partly by the time required for a water molecule to migrate to this position. Mechanism XIII does have one obvious fault. It does not seem adequately to explain why the bond breaks between positions 1 and 2. It seems likely that the electrons on the number one nitrogen would be more available for an intramolecular shift such as is shown, but this does not seem sufficient to explain the failure to isolate at least some product wherein the ring fission had occurred between positions 2 and 3.

A mechanism such as depicted in XII would seem most likely to lead to an amide of the proper structure, but it is difficult to understand why the reaction with water would be slow. The amine nitrogen should be hydrogen bonded to a water molecule and the second step in the reaction should be fast.

Mechanism XIII has two attractive features. The hydroxyimide structure shown here is similar to compounds that have been mentioned in the literature. By analogy with these compounds, this imide structure would be expected to be very unstable. It would also be expected that the 3-position nitrogen would be much slower to react with water than the nitrogen in the 1-position. The nitrogen in position three has little or no basic character and would not be hydrogen bonded to water. The reaction rate should, therefore, be controlled partly by the time required for a water molecule to migrate to this position. Mechanism XIII does have one obvious fault. It does not seem adequately to explain why the bond breaks between positions 1 and 2. It seems likely that the electrons on the number one nitrogen would be more available for an intramolecular shift such as is shown, but this does not seem sufficient to explain the failure to isolate at least some product whereas the ring closure had occurred between positions 1 and 2.

It seems appropriate to conclude this section with an evaluation of the material discussed. The evidence for hydrolysis as a major factor in the decomposition of imidazolines seems quite adequate. The evidence for an attack by hydroxide ion as the initial step in hydrolysis also appears to be good. Evidence for the formation of an imidazoline-hydroxide ion complex must be considered somewhat dubious. It is possible, and very probable, that further study will lead to a more complete rate equation than equation VIII. In view of this possibility, the mechanisms given must be regarded only as plausible explanations of what is known.

V. SUGGESTIONS FOR FUTURE STUDY

It would be desirable to determine separately the influence of the steric and inductive effects of substituents on the rate of hydrolysis. The use of substituted phenyl groups as substituents would seem to offer excellent possibilities for studying inductive effects, but attempts to make 2-phenyl substituted 1-hydroxyethyl-2-imidazolines gave low yields of materials that were difficult to purify. The shift in ultra-violet absorbance caused by such groups would require considerable modification in the method of following the reaction. The most hopeful possibility would be to contrast halogenated alkyl groups with

PART IV

EXPERIMENTAL

I. SYNTHESIS OF 2-IMIDAZOLINES

There are a number of methods for preparing 2-imidazolines, and a summary of these methods may be found in the review article by Ferm and Riebsomer (9).

All of the imidazolines considered in this study were prepared by procedures based on the methods of Riebsomer (30) or of Morrill (27). One molar equivalent of a carbolyxic acid or ethyl ester was mixed with one molar equivalent of an appropriate 1,2-diamine and a little benzene. This mixture was heated from 130° to 230° and the benzene and water were distilled through a 4' helix packed column equipped with a decanter still-head filled with benzene. The still-head was arranged so that benzene was returned to the column and water could be removed. Heating was continued until evolution of water became very slow or stopped. When esters were used, the benzene was not added until one molar equivalent of alcohol was collected. Benzene was then added and the heating continued until water no longer distilled out:

or:

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The ...
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anti ...
esters ...
equivalent ...
and the ...

ROOM - 2

ordinary alkyl groups of about the same size.

Ionization constants should be determined in any further study of hydrolysis. It is probable that ionization constants are necessary for a true comparison of the rates of hydrolysis of variously substituted imidazolines.

The effect of varying concentrations of water on the rate of hydrolysis should be determined. Qualitative experiments show that the rate of hydrolysis does depend on the concentration of water, but the dependence may be more complex than was indicated in equation VIII.

Finally, it would be very interesting to determine if the concentration of imidazoline affects the rate of hydrolysis in the simple manner shown in equation VIII. Most of the rate studies in this work were carried out under conditions such that the concentration of base was greater than the concentration of imidazoline. If the postulated imidazoline-hydroxide ion complex is real, a maximum rate should be attained when the concentration of imidazoline is made much larger than the concentration of hydroxide ion.

ordinary alkyl groups of about the same size. Ionization constants should be determined in any further study of hydrolysis. It is probable that ionization constants are necessary for a true comparison of the rates of hydrolysis of variously substituted imidazolines. The effect of varying concentrations of water on the rate of hydrolysis should be determined. Qualitative experiments show that the rate of hydrolysis does depend on the concentration of water, but the dependence may be more complex than was indicated in equation VIII. Finally, it would be very interesting to determine if the concentration of imidazoline affects the rate of hydrolysis in the same manner shown in equation VIII. Most of the rate studies in this work were carried out under conditions such that the concentration of base was greater than the concentration of imidazoline. If the postulated imidazoline-hydroxide ion complex is real, a maximum rate should be attained when the concentration of imidazoline is made much larger than the concentration of hydroxide ion.

VI. POSSIBLE METHODS OF PREVENTING THE HYDROLYSIS OF 2-IMIDAZOLINES

The most obvious method of preventing hydrolysis is to keep these compounds completely dry. Shipment and storage in moisture-proof containers should be useful in this connection.

Another obvious possibility would be to store the imidazoles in the form of their mineral acid salts and then liberate the free imidazole immediately before or during use. This method should be practical when the imidazole is to be used in a basic medium.

The final possibility for preventing hydrolysis would seem to lie in substituting the ring with groups that increase its stability. An electron donating group at any position on the ring seems to increase stability, but such groups in the 4- and 5-positions seem particularly effective. Bulky groups in the 1-position, or phenyl groups in the 2-position, also seem quite effective in preventing hydrolysis.

VI. POSSIBLE METHODS OF PREVENTING THE

HYDROLYSIS OF 2-AMINOACETAMIDES

The most obvious method of preventing hydrolysis is to keep these compounds completely dry. Shipment and storage in moisture-proof containers should be useful in this connection.

Another obvious possibility would be to store the imidazolines in the form of their mineral acid salts and then liberate the free imidazoline immediately before or during use. This method should be practical when the imidazoline is to be used in a basic medium.

The final possibility for preventing hydrolysis would seem to lie in substituting the ring with groups that increase its stability. An electron donating group at any position on the ring seems to decrease stability, but such groups in the 4- and 5-positions seem particularly effective. Bulky groups in the 1-position, or groups in the 2-position, also seem quite effective in preventing hydrolysis.

A side reaction in the preparation of imidazolines from carboxylic acids is the formation of a stable distillable complex between one or two moles of unreacted acid and the imidazoline (30). The free imidazoline is obtained by treating the complex with a strong base. Another problem encountered in these preparations was the separation of the uncyclized amides from the imidazolines. This problem arises regardless of whether free acids or esters are used as starting materials.

Structure and purity of the imidazolines were determined by infra-red and ultra-violet absorption spectra, neutral equivalents, and Kjeldahl nitrogen determination. All melting and boiling points are uncorrected. No effort was exerted to secure high yields of 2-imidazoline from these preparations, and considerable quantities of material were often sacrificed in attempting to acquire high purity.

1-Hydroxyethyl-2-heptadecyl-2-imidazoline (34).

Forty-eight grams (.15 mole) of ethyl stearate and 17.2 grams (.165 mole) of hydroxyethylethylenediamine were heated

together at 130° to 230° until approximately .15 moles of ethanol were collected. Benzene was then cautiously added and the heating continued until no more water was evolved. The cooled reaction mass was dissolved in boiling petroleum ether (60° - 90°) and the less soluble amide was removed by repeated fractional crystallization and filtration. The fourth crystallization yielded the crude imidazoline, m.p. 70° - 75° , which was recrystallized from benzene and repeatedly subjected to evaporative distillation to give the pure white imidazoline, m.p. 70° - 71° .

Anal. Calcd. for $C_{22}H_{44}N_2O$: N. E., 352.6; C, 75.03; H, 12.49; N, 7.96. Found, N. E., 352.2; C, 74.96; H, 12.45; N, 7.96.

Ultra-violet absorption: ethanol, $\lambda_{\max}$, $232\text{ m}\mu$, ϵ 6080.

The first three crops of crystals were combined and recrystallized from ethanol to give 1.2 grams of N-stearoyl-N'-(2-Hydroxyethyl) ethylenediamine, m.p. 108° - 109° .

Anal. Calcd. for $C_{22}H_{46}N_2O_2$: N. E., 370; N, 7.57. Found: N. E., 370; N, 7.42. Van Slyke amino nitrogen .1%.

As a further confirmation of structure, the amide was treated with nitrous acid to form the N-nitroso compound.

Anal. Calcd. for $C_{22}H_{45}N_3O_3$: N, 10.5. Found: N, 10.13.

1-Hydroxyethyl-2-pentyl-2-imidazoline. Twenty-eight grams (.2 mole) of ethyl caproate and 27 grams (.26 mole) of

together at 130° to 135° until approximately 1.5 moles of ethanol were collected. Benzene was then cautiously added and the heating continued until no more water was evolved. The cooled reaction mass was dissolved in boiling petroleum ether (60°-90°) and the less soluble amide was removed by repeated fractional crystallization and filtration. The fourth crystallization yielded the crude imidazole, m.p. 70°-75° which was recrystallized from benzene and repeatedly subjected to fractional crystallization to give the pure white imidazole, m.p. 70°-71°.

Anal. Calcd. for $C_{12}H_{14}N_2O$: N, 22.22%; C, 77.78%.
 Found: N, 22.45%; C, 77.55%; H, 12.45%.

Ultra-violet absorption: ethanol, λ_{max} 232 m μ , ϵ 6080.

The first three crops of crystals were combined and recrystallized from ethanol to give 1.2 grams of N-stearoyl-N'-(2-hydroxyethyl) ethylenediamine, m.p. 108°-109°.

Anal. Calcd. for $C_{22}H_{44}N_2O_2$: N, 5.5%; H, 8.5%; O, 15.5%.
 Found: N, 5.3%; H, 8.3%; O, 15.3%. Van Slyke and nitrogen 12%.

As a further confirmation of structure, the amide was treated with nitrous acid to form the N-nitroso compound.

Anal. Calcd. for $C_{22}H_{44}N_2O_3$: N, 10.13%; H, 10.13%.

1-Hydroxyethyl-2-ethyl-2-imidazole. Twenty-eight

grams (.1 mole) of ethyl caproate and 27 grams (.25 mole) of

hydroxyethylethylenediamine were heated together at temperatures up to 210° . Heating was continued until 9 ml. of ethanol were collected. Benzene was then added and heating continued until 2.5 ml. of water were collected. Distillation of the reaction mass yielded the pure imidazoline, a faintly yellow oil, b.p. $156^{\circ}/.07$ mm.

Anal. Calcd. for $C_{10}H_{20}N_2O$: N. E., 184; N, 15.21.
Found: N. E., 182; N, 15.21.

Ultra-violet absorption: ethanol, λ max. $231\text{ m}\mu$, ϵ 5440.

Ultra-violet absorption: water, λ max. $231\text{ m}\mu$, 5210.

Ultra-violet absorption: HCl solution, λ max. $231\text{ m}\mu$, ϵ 5320.

1-Ethoxyethyl-2-heptadecyl-2-imidazoline. Ethoxyethylethylenediamine was prepared by slowly adding 150 grams (1 mole) of ethoxyethylbromine to 360 grams (6 moles) of refluxing ethylenediamine. The resulting mixture was then treated with saturated KOH solution. The organic layer was separated and distilled to yield 69 grams, 52 per cent yield, of the substituted diamine, b.p. 189° , molecular weight 132, N. E., 132.

Fifty-seven grams of stearic acid and 27 grams of ethoxyethylethylenediamine were heated together as usual until

evolution of water ceased. The reaction mass was then dissolved in ethanol and treated with solid barium hydroxide. The precipitated barium stearate and undissolved barium hydroxide were removed by filtration and the ethanol was removed by flash evaporation. The residue of imidazoline was purified by evaporative distillation and crystallization from ethyl acetate to give a waxy white solid, m.p. 40° - 43° .

Anal. Calcd. for $C_{24}H_{48}N_2O$: N. E. 380.6; N, 7.37.
Found: N. E., 387; N, 7.67.

Ultra-violet absorption: ethanol, λ max. $231\text{ m}\mu$,
 ϵ 6090.

1-(2-ethoxyethyl)-2-pentyl-2-imidazoline. A solution of 23 grams (.2 moles) of caproic acid and 26 grams (.2 moles) of ethoxyethylethylenediamine in benzene was heated as usual. The cooled reaction mass was treated with sodium hydroxide solution. The organic phase was separated, and distillation yielded the pure imidazoline. This imidazoline was a faintly yellow oil, b.p. 260° - 263° .

Anal. Calcd. for $C_{12}H_{12}N_2O$: N. E., 212; C, 68.0;
H, 11.32; N, 13.2. Found: N. E., 210; C, 67.89; H, 11.61;
N, 13.2.

Ultra-violet absorption: ethanol, λ max. $231\text{ m}\mu$,
 ϵ 6260.

1-Hydroxyethyl-2-methyl-2-imidazoline (11). Heating

evolution of water ceased. The reaction mass was then dissolved in ethanol and treated with solid barium hydroxide. The precipitated barium acetate and undissolved barium hydroxide were removed by filtration and the ethanol was removed by flash evaporation. The residue of imidazole was purified by evaporative distillation and crystallization from ethyl acetate to give a waxy white solid, m.p. 40-43°.

Anal. Calcd. for $C_{14}H_{18}N_2O$: N, 5.38%; H, 5.97%.

Found: N, 5.37%; H, 5.97%.

Ultra-violet absorption: ethanol, λ max. 231 m μ .

ϵ 6090.

1-(5-ethoxyethyl)-2-methyl-2-imidazole. A solution

of 13 grams (0.2 moles) of acrolein and 15 grams (0.2 moles) of ethoxyethylmagnesium bromide in benzene was heated at reflux.

The cooled reaction mass was treated with sodium hydroxide solution. The organic phase was separated, and distillation yielded the pure imidazole. This imidazole was a faintly yellow oil, b.p. 350-355°.

Anal. Calcd. for $C_{14}H_{22}N_2O$: N, 5.12%; C, 68.07%.

Found: N, 5.12%; C, 67.89%; H, 11.51%.

Ultra-violet absorption: ethanol, λ max. 231 m μ .

ϵ 6260.

1-Hydroxyethyl-2-methyl-2-imidazole (II). Heating

of 104 grams (1 mole) of hydroxyethylethylenediamine and 60 grams (1 mole) of acetic acid was carried out as usual. The reaction product was treated with dry barium hydroxide, solids were removed, and the organic material was distilled. The fraction boiling at 180° - 190° /30 mm. was crystallized from ethyl acetate to yield small, faintly yellow crystals of imidazoline, m.p. 49° - 53° , and very deliquescent.

Anal. Calcd. for $C_6H_{12}N_2O$: N. E., 128; N, 21.85.
Found: N. E., 129; N, 21.49.

Ultra-violet absorption: ethanol, $\lambda_{\max}$. 231 m μ ,
 ϵ 6160.

1-Hydroxyethyl-2-ethyl-2-imidazoline. One mole of propanoic acid was heated with 1 mole of hydroxyethylethylenediamine as usual. Treatment of the reaction products with barium hydroxide and subsequent distillation yielded the imidazoline, a light yellow oil, b.p. 121° - 122° /.07 mm.

Anal. Calcd. for $C_7H_{14}N_2O$: N.E., 142; N, 19.72.
Found: N. E., 141; N, 19.64.

Ultra-violet absorption: ethanol, $\lambda_{\max}$. 231 m μ ,
 ϵ 5600.

1-Hydroxyethyl-2-isopropyl-2-imidazoline. One mole of isobutyric acid was heated with one mole of diamine as usual. Treatment with barium hydroxide and distillation yielded the imidazoline, a light yellow oil, b.p. 125° - 126° /.2 mm.

of 104 grams (1 mole) of hydroxyphenylhydrazine and 60 grams (1 mole) of acetic acid was carried out as usual. The reaction product was treated with dry sodium hydride.

Solids were removed, and the organic material was distilled. The reaction boiling at 150°-155°/30 mm. was crystallized from ethyl acetate to yield small, faintly yellow crystals of imidazole, m.p. 120°-122° and some dihydroimidazole, m.p. 120°-122°.

ANAL. Calcd. for C₄H₆N₂: C, 71.4%; H, 7.1%; N, 11.5%. Found: C, 71.4%; H, 7.1%; N, 11.5%.

Ultra-violet absorption ethanol, λ_{max} 231 m μ , ϵ 6150.

1-Hydroxyethyl-2-ethyl-2-imidazole. One mole of propionic acid was heated with 1 mole of hydroxyethyl-2-imidazole as usual. Treatment of the reaction product

with barium hydroxide and subsequent distillation yielded the imidazole, a light yellow oil, b.p. 112°-115°/30 mm.

ANAL. Calcd. for C₄H₆N₂: C, 71.4%; H, 7.1%; N, 11.5%. Found: C, 71.4%; H, 7.1%; N, 11.5%.

Ultra-violet absorption ethanol, λ_{max} 231 m μ , ϵ 5600.

1-Hydroxyethyl-2-isopropyl-2-imidazole. One mole of isobutyric acid was heated with one mole of isobutyric acid as usual. Treatment with barium hydroxide and distillation

yielded the imidazole, a light yellow oil, b.p. 115°-120°/30 mm.

Anal. Calcd. for $C_8H_{16}N_2O$: N. E., 156; N, 17.93.

Found: N. E., 153; N, 17.86.

Ultra-violet absorption: ethanol, $\lambda_{\max}$. 231 $m\mu$,
 ϵ 5710.

1-Hydroxyethyl-2-tert-butyl-2-imidazoline. A mixture of 25 grams (.25 mole) of trimethylacetic acid and 25 grams (.25 mole) of diamine was heated as usual. Treatment of the reaction products with barium hydroxide and subsequent distillation yielded a very viscous oil composed of amide and imidazoline. The amide was partly removed by dissolving the distillate in ethyl acetate and filtering off the crystalline amide. The imidazoline was freed of solvent and evaporatively distilled several times, but a pure product was not obtained. Repetition of this preparation still yielded no pure imidazoline.

Anal. Calcd. for $C_9H_{18}N_2O$: N. E., 170; N, 16.47.

Found: N. E., 174; N, 16.07.

Ultra-violet absorption: ethanol, $\lambda_{\max}$. 232 $m\mu$,
 ϵ 5130.

1-Hydroxyethyl-2-imidazoline (4). One mole of formic acid was heated with one mole of hydroxyethylethylenediamine and the reaction products were treated with barium hydroxide and distilled as usual, b.p. 180° - 190° /30 mm. The distillate was crystallized from ethyl acetate and then subjected to

evaporative distillation to yield a white crystalline product, m.p. 62° - 63° .

Anal. Calcd. for $C_5H_{10}N_2O$: N. E., 114; N, 24.55.

Found: N. E., 114; N, 24.28.

Ultra-violet absorption: ethanol, λ max. $234 m\mu$,
 ϵ 6670.

1-Methyl-2-pentyl-2-imidazoline. N-methylethylenediamine was prepared by the procedure of O'Gee and Woodland (28). Twelve grams (.16 mole) of this amine were heated with 19 grams (.16 + moles) of caproic acid. The reaction products were worked up as usual to give a colorless, mobile oil, b.p. 50° - $52^{\circ}/.15$ mm.

Anal. Calcd. for $C_9H_{18}N_2$: N. E., 154; N, 18.18.

Found: N. E., 150; N, 18.0.

Ultra-violet absorption: ethanol, λ max. $230 m\mu$,
 ϵ 5650.

1-Ethyl-2-pentyl-2-imidazoline. N-ethylethylenediamine was prepared by the procedure of O'Gee and Woodland (28) and allowed to react with caproic acid as usual. The imidazoline was isolated and found to be a colorless, mobile oil, b.p. 68° - $70^{\circ}/.07$ mm.

Anal. Calcd. for $C_{10}H_{20}N_2$: N. E., 168; N, 16.65.

Found: N. E., 167; N, 16.57.

Ultra-violet absorption: ethanol, λ max. $232 m\mu$,
 ϵ 5920.

evaporative distillation to yield a white crystalline

product, m.p. 62-63°.

ANAL. Calcd. for $C_{10}H_{16}N_2O$: N, 11.4; H, 14.2.

Found: N, 11.4; H, 14.2.

Ultra-violet absorption: ethanol, λ max, 236 m μ .

ϵ 6610.

1-Ethyl-2-phenyl-2-methylpyrrolidine

was prepared by the procedure of O'Don and Woodland (28) and
twelve grams (0.16 mole) of this amine were heated with 10

grams (0.16 + moles) of caproic acid. The reaction products

were worked up as usual to give a colorless, mobile oil.

b.p. 50-52°/12 mm.

ANAL. Calcd. for $C_{18}H_{26}N_2$: N, 11.4; H, 15.4.

Found: N, 11.4; H, 15.4.

Ultra-violet absorption: ethanol, λ max, 230 m μ .

ϵ 5550.

1-Ethyl-2-phenyl-2-methylpyrrolidine

was prepared by the procedure of O'Don and Woodland (28) and

allowed to react with caproic acid as usual. The imide-

ketone was isolated and found to be a colorless, mobile oil.

b.p. 68-70°/10 mm.

ANAL. Calcd. for $C_{20}H_{28}N_2O$: N, 10.5; H, 13.5.

Found: N, 10.5; H, 13.5.

Ultra-violet absorption: ethanol, λ max, 232 m μ .

ϵ 5930.

1-Isopropyl-2-pentyl-2-imidazoline. Eleven grams (.108 mole) of N-isopropylethylenediamine (28) and 13 grams (.108 mole) of caproic acid were heated together. The imidazoline was separated as usual as a colorless mobile oil, b.p. 79° - 80° /.15 mm.

Anal. Calcd. for $C_{11}H_{22}N_2$: N. E., 182; N, 15.37.
Found: N. E., 187; N, 15.38.

Ultra-violet absorption: ethanol, λ max. $231\text{ m}\mu$, ϵ 5560.

2-Pentyl-2-imidazoline (2). Sixty grams (1 mole) of ethylenediamine was heated with 116 grams (1 mole) of caproic acid until 36 ml. of water had collected. The cooled reaction mass was dissolved in ethanol and the relatively insoluble amide was filtered off. The filtrate was freed of solvent and the residue was repeatedly subjected to evaporative distillation to yield the solid imidazoline, m.p. 53° - 54° .

Anal. Calcd. for $C_8H_{16}N_2$: N. E., 140; C, 68.6; H, 11.42; N, 20.0. Found: N. E., 138.5; C, 68.56; H, 11.78; N, 19.9.

Ultra-violet absorption: ethanol, λ max. $221\text{ m}\mu$, ϵ 4410.

1-Isopropyl-2-pentyl-4,4-dimethyl-2-imidazoline (30). Twenty-six grams (.2 mole) of N-(2-aminoisobutyl)-isopropylamine and 23 grams (.2 + mole) of caproic acid were heated together as usual. Treatment with barium hydroxide and

distillation yielded the imidazoline, a faintly yellow oil, b.p. 228°-230°/630.

Anal. Calcd. for $C_{13}H_{26}N_2$: N. E., 210; N, 13.32.

Found: N. E., 207; N. 13.28.

Ultra-violet absorption: ethanol, $\lambda_{\max}$. 230 $m\mu$,
 ϵ 6540.

Infra-red spectra. The infra-red spectra of all the compounds synthesized in this work were recorded as a proof of structure and purity. The carbon to nitrogen double bond shows a strong absorption peak between 6.2 and 6.3 microns while the amide group absorbs between 6.0 and 6.1 microns. Plates I and II illustrate this difference. It is thus possible to ascertain the quantity of amide present as a contaminant in the preparation of an imidazoline. It may be noted that there is a small amount of amide present in most of the compounds prepared, but only in the case of 1-hydroxyethyl-2-tert.butyl-2-imidazoline was there an appreciable amount.

These spectra were recorded from bromoform solutions, mulls, and from the pure compounds when possible. The solvent or dispersing agent is noted on the spectra when it is applicable.

distillation yielded a colorless, slightly yellow oil.

b.p. 125-130°C/0.5 mm.

ANAL. Calcd. for $C_{10}H_{12}O$: C, 88.1%; H, 9.1%.

Found: C, 87.5%; H, 9.0%.

Ultra-violet absorption: ethanol, λ_{max} 230 m μ .

ϵ 6500.

ANALYSES. The infra-red spectra of all the

compounds synthesized in this work were recorded as a check

of structure and purity. The carbon-to-nitrogen ratio

indicates a strong absorption peak between 6.5 and 6.7

microns while the other groups absorb between 6.0 and 6.4

microns. Tables I and II illustrate these differences. It

is thus possible to ascertain the quantity of amide present

as a contaminant in the preparation of an indole. It

may be noted that there is a small amount of amide present

in most of the compounds prepared, but only in the case of

1-hydroxyethyl-2-ethyl-3-indolone was there an

appreciable amount.

These spectra were recorded from bromoform solutions,

and from the pure compounds when possible. The

solvent or dispersing agent is noted on the spectra when

it is applicable.

Plate I: Infra-red spectrum of
1-hydroxyethyl-2-heptadecyl-2-
imidazoline, Bromoform.

Plate II: Infra-red spectrum of
N-steroyl-N'-hydroxyethyl-
ethylenediamine, mull. $C_{17}H_{35}CONHCH_2CH_2NHC_2H_4OH$

Plate III: Infra-red spectrum of
1-hydroxyethyl-2-pentyl-
2-imidazoline

Plate IV: Infra-red spectrum of
N-pentanoyl-N'-hydroxyethyl-
ethylenediamine, mull.

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Plate V: Infra-red spectrum of
1-ethoxyethyl-2-heptadecyl-
2-imidazoline, mull.

Plate VI: Infra-red spectrum of
1-ethoxyethyl-2-pentyl-
2-imidazoline.

ПРОЦЕНКА ПОКАЗАТЕЛЕЙ

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Plate VII: Infra-red spectrum of
1-hydroxyethyl-2-methyl-
2-imidazoline, Bromoform.

OM-12

Plate VIII: Infra-red spectrum of
1-hydroxyethyl-2-ethyl-
2-imidazoline

5-THIOURACIL
 1-μg/100 μl
 100 μl/100 μl

WAVELENGTH (MICRONS)

Plate IX: Infra-red spectrum of
1-hydroxyethyl-2-isopropyl-
2-imidazoline

Wavelength (microns)

Plate X: Infra-red spectrum of 1-hydroxy-ethyl 2-tert.-butyl-2-imidazoline

Plate XI: Infra-red spectrum of
1-hydroxyethyl-2-imidazoline,
Bromoform.

1,3-Butadiene-2,4-diol
 1,3-Butadiene-2,4-diol
 1,3-Butadiene-2,4-diol

1,3-Butadiene-2,4-diol
 1,3-Butadiene-2,4-diol
 1,3-Butadiene-2,4-diol

Plate XII: Infra-red spectrum of
1-hydroxyethyl-2-phenyl-
2-imidazoline, Bromoform.

Plate III: Infra-red spectrum of
2-diphenylmethyl-1-
hydroxyethyl-2-imidazoline,
mull.

Plate XIV: Infra-red spectrum of
1-methyl-2-pentyl-2-imidazole.

WAVELENGTH (MICRONS)

Plate XV: Infra-red spectrum of 1-ethyl-2-pentyl-2-imidazoline.

2-benzyl-3-phenylacrylate
 10 mg/ml in benzene

WAVELENGTH (MICRONS)

Plate XVI: Infra-red spectrum of
1-isopropyl-2-pentyl-2-
imidazoline.

AVIATION (WICKSON)

Plate XVII: Infra-red spectrum of
2-pentyl-2-imidazoline,
mull.

Plate XVIII: Infra-red spectrum of 1-isopropyl-4,4-dimethyl-2-pentyl-2-imidazoline.

II. HYDROLYSIS PRODUCTS FROM SOME 2-IMIDAZOLINES

A number of preliminary hydrolysis experiments were performed using 1-hydroxyethyl-2-heptadecyl-2-imidazoline and aqueous base. It was not possible to achieve a quantitative separation of the reaction products by usual chemical methods because of the very stable emulsions encountered. Qualitative separations were accomplished, however, and the course of hydrolysis may be formulated as follows:

Hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline in aqueous hydroxyethylethylenediamine. A mixture of 0.5 grams of imidazoline and 10 ml. of 5 molar aqueous diamine were heated on the steam bath for sixteen hours. The mixture was then extracted with benzene. The benzene extracts were washed with water, and the benzene was evaporated to leave .36 grams of amide, m.p. 108°-109°, mixed melting point 108°-109° with the amide from the preparation of the imidazoline.

11. Hydrolysis of the ester

A number of preliminary experiments were performed using 1-hydroxy-2-naphthol and sodium acetate. It was found that the quantitative reaction of the ester produced by the chemical reaction because of the nature of the emulsion encountered. A small amount of the ester was recovered, and the nature of the emulsion was as follows:

On the 1st of June, 1937, a sample of the ester was prepared by the reaction of 1-hydroxy-2-naphthol and sodium acetate. The reaction was carried out in a 100 ml. flask, and the reaction mixture was allowed to stand for 24 hours.

The reaction mixture was then extracted with benzene, and the benzene extract was washed with water, and the benzene was evaporated to leave

36 grams of solid material, 100-105°, which was the product of the

hydrolysis of the ester. The reaction was carried out in a 100 ml. flask, and the reaction mixture was allowed to stand for 24 hours.

The reaction mixture was then extracted with benzene, and the benzene extract was washed with water, and the benzene was evaporated to leave

36 grams of solid material, 100-105°, which was the product of the

hydrolysis of the ester. The reaction was carried out in a 100 ml. flask, and the reaction mixture was allowed to stand for 24 hours.

The reaction mixture was then extracted with benzene, and the benzene extract was washed with water, and the benzene was evaporated to leave

36 grams of solid material, 100-105°, which was the product of the

hydrolysis of the ester. The reaction was carried out in a 100 ml. flask, and the reaction mixture was allowed to stand for 24 hours.

The reaction mixture was then extracted with benzene, and the benzene extract was washed with water, and the benzene was evaporated to leave

36 grams of solid material, 100-105°, which was the product of the

Hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline in aqueous potassium hydroxide. A mixture of .995 grams of imidazoline and 5 ml. of 20% KOH was heated at 130° for two hours. Separation by usual extractive procedures yielded .278 grams of stearic acid, m.p. 71° - 72° , with infra-red spectra identical to that of purified stearic acid, and .552 grams of a mixture composed of 36% amide and 52% unreacted imidazoline. Per cent composition was determined by infra-red spectra.

Hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline in aqueous sodium hydroxide. A mixture of 1 gram of imidazoline and 10 ml. of 20% NaOH was heated at 130° - 140° for 1.5 hours. Separation yielded .34 grams of a mixture composed of 80% amide and 13% imidazoline on the basis of infra-red spectra. Approximately 0.24 grams of stearic acid were recovered.

Hydrolysis of 1-hydroxyethyl-2-pentyl-2-imidazoline in water. A solution of the imidazoline and water was kept in a glass stoppered bottle for about thirty days at room temperature. At the end of this period, N-pentanoyl-N'-hydroxyethyl-ethylenediamine had precipitated from the solution. The amide was separated and purified to give a product that melted at 71° - 72° . The infra-red spectrum of this material is given on Plate IV.

Anal. Calcd. for $C_{5}H_{11}CONHCH_2CH_2NHC_2H_4OH$: N. E., 202; N, 13.86; Primary amino nitrogen, 0. Found: N. E., 203;

1. The first step in the synthesis of the compound is the reaction of the starting material with the reagent.

2. The second step involves the purification of the crude product by recrystallization from a suitable solvent.

3. The third step is the characterization of the compound by elemental analysis and infrared spectroscopy.

4. The fourth step is the determination of the melting point of the compound, which is a characteristic property.

5. The fifth step is the comparison of the experimental data with the literature values to confirm the identity of the compound.

6. The sixth step is the calculation of the theoretical yield of the compound based on the stoichiometry of the reaction.

7. The seventh step is the determination of the percentage yield of the compound, which is a measure of the efficiency of the reaction.

8. The eighth step is the storage of the compound in a suitable container for future use.

9. The ninth step is the disposal of the waste materials generated during the synthesis in a safe and environmentally friendly manner.

10. The tenth step is the documentation of the entire synthesis process, including the reaction conditions, yields, and characterization data.

11. The eleventh step is the submission of the final report to the supervisor for review and approval.

12. The twelfth step is the presentation of the results of the synthesis to the class or the research group.

13. The thirteenth step is the discussion of the results and the conclusions drawn from the synthesis.

14. The fourteenth step is the evaluation of the synthesis process and the identification of areas for improvement.

15. The fifteenth step is the completion of the synthesis and the final report.

16. The sixteenth step is the archiving of the synthesis materials and the final report for future reference.

17. The seventeenth step is the submission of the final report to the supervisor for review and approval.

18. The eighteenth step is the presentation of the results of the synthesis to the class or the research group.

19. The nineteenth step is the discussion of the results and the conclusions drawn from the synthesis.

20. The twentieth step is the evaluation of the synthesis process and the identification of areas for improvement.

21. The twenty-first step is the completion of the synthesis and the final report.

22. The twenty-second step is the archiving of the synthesis materials and the final report for future reference.

23. The twenty-third step is the submission of the final report to the supervisor for review and approval.

24. The twenty-fourth step is the presentation of the results of the synthesis to the class or the research group.

25. The twenty-fifth step is the discussion of the results and the conclusions drawn from the synthesis.

26. The twenty-sixth step is the evaluation of the synthesis process and the identification of areas for improvement.

27. The twenty-seventh step is the completion of the synthesis and the final report.

28. The twenty-eighth step is the archiving of the synthesis materials and the final report for future reference.

29. The twenty-ninth step is the submission of the final report to the supervisor for review and approval.

30. The thirtieth step is the presentation of the results of the synthesis to the class or the research group.

N, 13.73; Primary amino nitrogen, less than 0.2%.

Hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline in ethanolic barium hydroxide. Several experiments were conducted in a 95% ethanol solution saturated with barium hydroxide and containing known initial concentrations of imidazoline. These solutions were maintained at a constant temperature. At known time intervals, 20 ml. samples were withdrawn, filtered by suction through sintered glass funnels, and the filtrate was evaporated to dryness in a flash evaporator. The residue from the evaporation was then dissolved in a measured volume of bromoform and the infra-red spectrum of the bromoform solution was recorded using a fixed thickness cell. The resulting spectra clearly show the decrease in the imidazoline absorption bond at 6.3 microns and the increase in the amide absorption bond at 6.1 microns. The amide formed was identified as N-steroyl-N'-hydroxyethyl-ethylene-diamine.

Plate XIX: 1-Hydroxyethyl-2-heptadecyl-2-imidazoline before hydrolysis

Plate XX: 1-Hydroxyethyl-2-heptadecyl-2-imidazoline after thirty minutes of hydrolysis

MAVLEKONIN (MICKONIS)

MAVLEKONIN (MICKONIS) IN DOXIMAST

Plate XXI: 1-Hydroxyethyl-2-heptadecyl-2-imidazoline after fifty minutes of hydrolysis

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PHOTOGRAPHED BY

Plate XXII: 1-Hydroxyethyl-2-heptadecyl-2-imidazoline after 120 minutes of hydrolysis

Plate XXIII: 1-Hydroxyethyl-2-heptadecyl-2-imidazoline after 150 minutes of hydrolysis

Plate XXIV: 1-Hydroxyethyl-2-heptadecyl-2-imidazoline after 240 minutes of hydrolysis.

III. KINETICS OF HYDROLYSIS OF SOME 2-IMIDAZOLINES IN ETHANOLIC SODIUM HYDROXIDE

Three slightly different procedures were used in following the course of this series of reactions. These procedures will be described in detail and designated in such a way that the individual runs may be described very briefly by reference to this section.

All of the methods used are based on following the course of the reaction by observing the disappearance of the $-C=N-$ ultraviolet absorption band at an appropriate wave length. Several experiments indicate that Beer's Law is valid for these compounds, and in addition, this series of reactions was run under conditions such that pseudo first-order kinetics could be observed. Any deviation from Beer's Law would be obvious in a plot of log absorbance against time.

All reactions were run in 95% ethanol that was 3.75×10^{-2} molar with respect to sodium hydroxide. The concentration of imidazoline was approximately 10^{-3} molar. Under these conditions, pseudo first-order kinetics were expected and found. Temperature was controlled to one-tenth of a degree and the reaction vessels were found to be free of evaporation losses over a 24 hour period at 70°C . All half-lives were obtained graphically from plots of the

THE KINETICS OF HYDROLYSIS OF SOME 2-IMIDAZOLINES

IN ETHANOLIC SODIUM HYDROXIDE

Three slightly different procedures were used in following the course of this series of reactions. These procedures will be described in detail and designated in such a way that the individual runs may be described very briefly by reference to this section.

All of the results used are based on following the course of the reaction by observing the disappearance of the 2-ethanol imidazole absorption band in appropriate wave length. Several experiments indicate that Beer's Law is valid for these compounds, and in addition, this series of reactions was run under conditions such that pseudo first order kinetics could be observed. Any deviation from Beer's Law would be obvious in a plot of log absorbance against time.

All reactions were run in 95% ethanol that was 3.75 x 10⁻³ molar with respect to sodium hydroxide. The concentration of imidazole was approximately 10⁻³ molar. Under these conditions, pseudo first-order kinetics were expected and found. Temperature was controlled to one tenth of a degree and the reaction vessels were found to be free of evaporation losses over a 24 hour period at 70°C.

All half-lives were obtained graphically from plots of the

logarithm of absorbance against time. All times are in minutes unless otherwise noted.

Procedure I. Approximately 750 ml. of basic ethanol solution was added to a 1 liter 3 necked flask fitted with a condenser, mercury-sealed stirrer, and a port for the insertion of a pipet. The condenser was plugged with glass wool to minimize diffusion. The entire bulb of the flask was immersed in a constant temperature bath and the ethanol solution was stirred until temperature equilibrium was achieved. An appropriate quantity of imidazoline was then added and a few minutes were allowed for mixing. At known time intervals, samples were withdrawn with a 10 ml. pipet and transferred to a 100 ml. volumetric flask partly filled with cool, 95% ethanol. The volumetric flask was filled to the mark with 95% ethanol and the contents were mixed by shaking. The absorbance of this solution was then determined using a Beckman D.U. spectrophotometer. Matched quartz cells with ground glass stopper were used with 95% ethanol as the reference liquid. Absorbance was measured at $230\text{ m}\mu$ unless the particular imidazoline had a maximum absorbance several millimicrons removed from this value.

This procedure has two faults. The basic ethanol solution has fairly strong absorbance at about $208\text{ m}\mu$,

logarithm of absorbance $\log I_0/I$ at 25°C. All runs were made at 25°C. unless otherwise noted.

Experimental

Solution was added to a 1-liter flask fitted with a condenser, mercury-sealed stirrer, and a gas inlet.

Insertion of a piston. The temperature was maintained at 25°C.

Wool to minute dilution. The sample was of the type used in the previous work.

was immersed in a constant temperature bath and the air was removed.

Selection was stopped until the solution was clear.

achieved. An appropriate quantity of indicator was then

added and a few minutes were allowed for the color to develop.

Intervals. Samples were withdrawn with a 10-ml. pipette and

transferred to a 100-ml. volumetric flask and diluted

with water. The solution was then allowed to stand for 10 minutes

before use. The water with 95% ethanol and the solution were mixed

thoroughly. The absorbance of this solution was then determined

using a Beckman DU spectrophotometer. The solution was then

placed in quartz cells with ground glass stoppers and sealed with wax.

ethanol as the reference liquid. Absorbance was measured

at 230 m μ unless the particular conditions had a different value.

maximum absorbance several milliliters removed from this

value.

This procedure has been found to be the best method

solution has fairly strong absorption at about 230 m μ .

and the amide resulting from hydrolysis has strong absorbance at about $205\text{ m}\mu$. Consequently, the absorbance of the solution does not decrease as rapidly as it should, and a plot of log absorbance against time gives a curved line after about one half-life of the imidazoline. In spite of this, half-lives determined from the initial points in a run compare well with those found by modification of this procedure.

Procedure II. The Beckman spectrophotometer was equipped with Beckman Thermospacers. The constant temperature bath liquid was pumped through these for about four hours before each run. After temperature equilibrium was achieved, Procedure I was followed up to the point of addition of imidazoline. Just before the imidazoline was added, a sample of the alkaline ethanol solution was transferred to a ground glass stoppered quartz absorption cell contained in the heated sample compartment of the Beckman. This solution was used as the reference. Imidazoline was then added to the flask in the constant temperature bath, and after a few minutes mixing, a sample of this solution was transferred to another absorption cell contained in the Beckman sample compartment. The hydrolysis was then followed by noting the decrease in absorbance of the imidazoline solution contained in the sample cell.

The use of the hydrolysis medium as a reference eliminates one objection to Procedure I. Much of the absorbance below $230\text{ m}\mu$ is compensated for. Unfortunately, evaporation of solvent sometimes occurred and no dependable method of preventing evaporation was found. In addition, etching of the sample cells would have been a serious problem over any extended period of time. Experimental results from runs using this procedure again agree fairly well with those obtained by other methods, but this procedure was abandoned as being undependable.

Procedure III. This method differs from Procedure I only in the manner of handling the sample and reference solutions. The reference solution was prepared by withdrawing a 10 ml. sample of the hot, basic, alcohol solution. This sample was transferred to a 100 ml. volumetric flask and acidified with a few drops of concentrated hydrochloric acid. The acidified solution was then diluted to 100 ml. with 95% ethanol and mixed. A stoppered reference cell was then filled with this solution and the absorbance determined against air. This figure was frequently checked throughout the course of a run. The samples of imidazoline solution were treated in much the same manner as above. A 10 ml. sample was transferred to a 100 ml. volumetric flask containing about 70 ml. of 95%

The use of the hydrolysis medium as a reference
eliminate any objection to Procedure I. Most of the
absorbance below 100 mμ is compensated for. Unfortunately,
evaporation of solvent sometimes occurred and no dependable
method of preventing evaporation was found. In addition,
evaporation of the sample cells would have been a serious
problem over any extended period of time. Experimentally
results from runs using this procedure agree fairly
well with those obtained by other methods, but this procedure
was abandoned as being undesirable.

Procedure II This method differs from Procedure I

only in the manner of handling the sample and reference
solutions. The reference solution was prepared by diluting
a 10 ml. sample of the acid, base, alcohol
solution. This sample was transferred to a 100 ml.
volumetric flask and acidified with a few drops of concen-
trated hydrochloric acid. The acidified solution was then
diluted to 100 ml. with 95% ethanol and mixed. A stoppered
reference cell was then filled with this solution and the
absorbance determined against air. This figure was
frequently checked throughout the course of a run. The
samples of imidazole solution were treated in much the
same manner as above. A 10 ml. sample was transferred to a
100 ml. volumetric flask containing about 70 ml. of 95%

ethanol and the same volume of concentrated hydrochloric acid as was used in the reference. This was then diluted to 100 ml. with ethanol, mixed, and used to determine the absorbance of the solution.

This sampling technique eliminates the worst features of the earlier procedures. Acidification eliminates the absorbance due to base and decreases the absorbance of the amide. It does not appreciably change the absorption peak or extinction coefficients of the imidazolines used. Furthermore, the acidified samples are much more stable than basic samples, and it was not necessary to determine absorbance immediately after withdrawing a sample. It was usually possible to follow the hydrolysis through two half-lives with this method.

The data for the various runs is presented in tabular form in the following pages. The tables are arranged so that data for all runs for a particular imidazoline at a given temperature are included in one table. Each table is followed by a graphical presentation of the same data. Finally, each set of tables and graphs is followed by a figure showing the temperature dependence of the rate constant for each imidazoline. A summary of the experimental half-lives and activation energies is given in Tables I and II, pages 16 and 17.

TABLE IV

DATA FOR THE HYDROLYSIS OF 2-HEPTADECYL-1-HYDROXYETHYL-
2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 1	0	1.057
PROCEDURE I	15	.667
	30	.430
	45	.283
	60	.190
	75	.142
	90	.095
	105	.075
	120	.0557
	135	.0552

$$T_{1/2} = 24 \text{ minutes, } K = .0289/\text{minute}$$

RUN 2	0	.95
PROCEDURE I	15	.600
	30	.395
	45	.255
	60	.075
	75	.125
	105	.092
	120	.070

$$T_{1/2} = 24 \text{ minutes, } K = .0289/\text{minute}$$

DATA FOR THE

RUN 1

PROCEDURE 1

RUN 2

PROCEDURE 1

7

Figure 3. Semi-logarithmic plot of absorbance against time for Runs 1 and 2.

Figure 2. Percentages of total organic carbon (TOC) in the sediment and water column of the Hudson River, New York, as a function of distance from the river mouth.

TABLE IV Continued

	Time-Minutes	Absorbance
RUN 3	0	.422
	2	.401
PROCEDURE II	4	.387
	6	.363
	8	.343
	10	.320
	12	.304
	14	.288
	16	.268
	18	.258
	20	.240
	22	.229
	24	.215
	26	.203
	28	.188
	30	.180
	32	.172
	33	.165
	35	.154
	37	.146
	42	.127
	44	.121
	46	.113
	48	.107
	50	.097
	53	.092
	55	.086
	57	.075

$$T_{\frac{1}{2}} = 24 \text{ minutes, } K = .0289/\text{minute}$$

Figure 4. Semi-logarithmic plot of absorbance against time for Run 3.

TABLE V

DATA FOR THE HYDROLYSIS OF 2-HEPTADECYL-1-HYDROXYETHYL-
2-IMIDAZOLINE AT 58.26°

	Time-Minutes	Absorbance
RUN 4	0	.696
PROCEDURE I	10	.610
	20	.540
	30	.472
	40	.423
	50	.375
	60	.332
	70	.297
	80	.260
	90	.230

$$T_{1/2} = 56.8 \text{ minutes, } K = .0122/\text{minute}$$

RUN 5	0	.452
PROCEDURE III	10	.399
	20	.357
	30	.303
	40	.263
	50	.235
	60	.210
	70	.176
	80	.156
	90	.135
	100	.119

$$T_{1/2} = 52 \text{ minutes, } K = .0133/\text{minute}$$

TABLE V
DATA FOR THE HYDROLYSIS OF 2-HYDROXY-1-IMIDAZOLINE AT 25°C

Absorbance	Time-Minutes	Run 4
0.00	0	
0.05	10	
0.10	20	
0.15	30	
0.20	40	
0.25	50	
0.30	60	
0.35	70	
0.40	80	
0.45	90	

$T_p = 25.8$ minutes, $k = 0.123$ minutes⁻¹

Absorbance	Time-Minutes	Run 5
0.00	0	
0.05	10	
0.10	20	
0.15	30	
0.20	40	
0.25	50	
0.30	60	
0.35	70	
0.40	80	
0.45	90	
0.50	100	

$T_p = 25$ minutes, $k = 0.133$ minutes⁻¹

Figure 5. Semi-logarithmic plot of absorbance against time for Runs 4 and 5.

TABLE VI

DATA FOR THE HYDROLYSIS OF 2-HEPTADECYL-1-HYDROXYETHYL-
2-IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 6	0	.477
	20	.416
PROCEDURE I	40	.377
	60	.327
	80	.290
	100	.259
	120	.228
	140	.202
	160	.180
	180	.150

$$T_{1/2} = 115 \text{ minutes, } K = .00603/\text{minute}$$

RUN 7	0	.73
	20	.643
PROCEDURE I	40	.573
	60	.505
	80	.446
	100	.396
	120	.350
	160	.275
	180	.244
	200	.218

$$T_{1/2} = 114 \text{ minutes, } K = .00608/\text{minute}$$

Figure 6. Semi-logarithmic plot of absorbance against time for Runs 6 and 7.

Figure 2. Rate of change of optical density with time for the reaction of 2,4-dinitrophenol with 2,6-diaminopyridine at 25°C.

Figure 7. Temperature dependence of the rate constants for the hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline.

0.5 1.0 1.5

TABLE VII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-2-PENTYL-2-
IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 8	0	.773
	15	.505
PROCEDURE I	30	.332
	45	.220
	60	.148
	75	.104
	105	.077
	120	.062
$T_{1/2} = 25 \text{ minutes}, K = .0277/\text{minute}$		
RUN 9	0	.754
	2	.728
PROCEDURE II	4	.693
	6	.656
	8	.593
	10	.560
	12	.528
	14	.498
	16	.473
	18	.447
	20	.423
	22	.423
	24	.398
	26	.379
	28	.358
	30	.340
	32	.327
	34	.311
	36	.293
	38	.278
	40	.266
	42	.252
	44	.237
	46	.228
	48	.214
	50	.204
	60	.158
	62	.151
	64	.143
$T_{1/2} = 25 \text{ minutes}, K = .0277/\text{minute}$		

TABLE VII

DATA FOR THE HYDROLYSIS OF 12-HYDROXY-1-PENTYL-1-IMIDAZOLINE AT 50.4°C

Time-Minutes	Absorbance
0	0.000
2	0.002
4	0.004
6	0.006
8	0.008
10	0.010
12	0.012
14	0.014
16	0.016
18	0.018
20	0.020
22	0.022
24	0.024
26	0.026
28	0.028
30	0.030
32	0.032
34	0.034
36	0.036
38	0.038
40	0.040
42	0.042
44	0.044
46	0.046
48	0.048
50	0.050
52	0.052
54	0.054
56	0.056
58	0.058
60	0.060
62	0.062
64	0.064
66	0.066
68	0.068
70	0.070
72	0.072
74	0.074
76	0.076
78	0.078
80	0.080
82	0.082
84	0.084
86	0.086
88	0.088
90	0.090
92	0.092
94	0.094
96	0.096
98	0.098
100	0.100

$T = 55$ minutes, $K = 0.0277/\text{minute}$

Time-Minutes	Absorbance
0	0.000
2	0.002
4	0.004
6	0.006
8	0.008
10	0.010
12	0.012
14	0.014
16	0.016
18	0.018
20	0.020
22	0.022
24	0.024
26	0.026
28	0.028
30	0.030
32	0.032
34	0.034
36	0.036
38	0.038
40	0.040
42	0.042
44	0.044
46	0.046
48	0.048
50	0.050
52	0.052
54	0.054
56	0.056
58	0.058
60	0.060
62	0.062
64	0.064
66	0.066
68	0.068
70	0.070
72	0.072
74	0.074
76	0.076
78	0.078
80	0.080
82	0.082
84	0.084
86	0.086
88	0.088
90	0.090
92	0.092
94	0.094
96	0.096
98	0.098
100	0.100

$T = 55$ minutes, $K = 0.0277/\text{minute}$

Figure 8. Semi-logarithmic plot of absorbance against time for Run 8.

Figure 9. Semi-logarithmic plot of absorbance against time for Run 9.

1.0 ml. of 1% solution of 2,4-dinitrophenylhydrazine in 10% acetic acid

2.0 ml. of 1% solution of 2,4-dinitrophenylhydrazine in 10% acetic acid

100 VISCOSITY

TABLE VIII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-2-PENTYL-2-
IMIDAZOLINE AT 58.26°

	Time-Minutes	Absorbance
RUN 10	0	.561
PROCEDURE I	10	.495
	20	.440
	30	.387
	40	.343
	50	.305
	60	.272
	70	.240
	80	.214
	90	.192

$$T_{1/2} = 57.5 \text{ minutes, } K = .01205/\text{minute}$$

RUN 11	0	.690
PROCEDURE III	10	.605
	20	.538
	30	.470
	40	.415
	50	.365
	60	.323
	70	.289
	80	.252
	90	.220
	100	.195

$$T_{1/2} = 55 \text{ minutes, } K = .0126/\text{minute}$$

DATA FOR THE HYPER-...

RUN 10

PROCEDURE 1

RUN 11

PROCEDURE 11

T = 55 minutes

Figure 10. Semi-logarithmic plot of absorbance against time for Runs 10 and 11.

TABLE IX

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-2-PENTYL-2-
IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 12	0	.815
	20	.723
PROCEDURE I	40	.640
	60	.568
	80	.508
	100	.454
	120	.405
	140	.358
	160	.318
	180	.285

$$T_{1/2} = 119 \text{ minutes, } K = .005824/\text{minute}$$

RUN 13	0	.492
	20	.440
PROCEDURE I	40	.387
	60	.347
	100	.277
	120	.240
	140	.213
	160	.192
	180	.171
	220	.132

$$T_{1/2} = 117 \text{ minutes, } K = .00593/\text{minute}$$

DATA FOR THE HYDROLYSIS OF
TRIMETHYLAMINE

RUN 12

PROCEDURE 1

100

100

100

100

$T_f = 119$ minutes

RUN 13

PROCEDURE 1

100

100

100

100

100

$T_f = 117$ minutes

Figure 11. Semi-logarithmic plot of absorbance against time for Runs 12 and 13.

Figure 12. Temperature dependence of the rate constants for the hydrolysis of 1-hydroxyethyl-2-pentyl-2-imidazoline.

0.0 1.0 3.0

TABLE X

DATA FOR THE HYDROLYSIS OF 1-ETHOXYETHYL
-2-HEPTADECYL-2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 13	0	.875
	15	.730
	30	.620
	45	.527
	60	.446
	75	.378
	90	.325
	105	.276
	120	.242
	135	.205

$$T_{1/2} = 61.5 \text{ minutes, } K = .0113/\text{minute}$$

Figure 13. Semi-logarithmic plot of absorbance against time for Run 13.

TABLE XI

DATA FOR THE HYDROLYSIS OF 1-ETHOXYETHYL-
2-PENTYL-2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 14	0	.450
PROCEDURE I	10	.406
	20	.364
	30	.330
	40	.298
	50	.267
	60	.239
	70	.220
	80	.189
	90	.168

$$T_{1/2} = 65 \text{ minutes, } K = .0107/\text{minute}$$

RUN 15	0	.377
PROCEDURE I	10	.337
	20	.302
	30	.274
	40	.242
	50	.218
	60	.204
	70	.174
	80	.156
	90	.145

$$T_{1/2} = 62.7 \text{ minutes, } K = .01105/\text{minute}$$

DATA FOR THE ANALYSIS OF
5-REACTANT MIXTURE

RUN 15

PROCEDURE 1

RUN 15

PROCEDURE 1

Figure 14. Semi-logarithmic plot of absorbance against time for Runs 14 and 15.

REMARKS: SHIT
12.1 min 1st run
12.1 min 2nd run

100 VARIATION

TABLE XII

DATA FOR THE HYDROLYSIS OF 1-ETHOXYETHYL-
2-PENTYL-2-IMIDAZOLINE AT 58.20°

	Time-Minutes	Absorbance
RUN 16	0	.568
	10	.532
PROCEDURE III	20	.505
	40	.456
	60	.412
	80	.369
	100	.335
	120	.309
	140	.274
	180	.227
	200	.201
	220	.187
	240	.168

$$T_{1/2} = 137 \text{ minutes, } K = .005059/\text{minute}$$

RUN 17	0	.594
	10	.554
PROCEDURE III	20	.529
	40	.478
	60	.429
	80	.393
	100	.348
	120	.320
	140	.288
	180	.233
	200	.214
	220	.192
	240	.173

$$T_{1/2} = 137 \text{ minutes, } K = .005059/\text{minute}$$

DATA 1-12-68
2-1-68

RUN 10

PROCEDURE III

T₁ = 137

RUN 11

PROCEDURE III

T₂ = 137

Figure 15. Semi-logarithmic plot of absorbance against time for Runs 16 and 17.

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TABLE XIII

DATA FOR THE HYDROLYSIS OF 1-ETHOXYETHYL-
2-PENTYL-2-IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 18	0	.582
	30	.536
PROCEDURE III	60	.491
	90	.454
	120	.425
	240	.312
	270	.282
	300	.266
	330	.241
	450	.181
	480	.166
	510	.151

$$T_{1/2} = 267 \text{ minutes, } K = .00260/\text{minute}$$

RUN 19	0	.665
	30	.618
PROCEDURE III	60	.570
	90	.529
	120	.481
	240	.354
	270	.333
	300	.309
	330	.279
	450	.208
	480	.194
	510	.176

$$T_{1/2} = 270 \text{ minutes, } K = .00257/\text{minute}$$

DATA FOR THE 1950-1951
2-1-1951

RUN 18

PROCEDURE III

RUN 19

PROCEDURE III

T₁ = 230 minutes

Figure 16. Semi-logarithmic plot of absorbance against time for Runs 18 and 19.

Figure 17. Temperature dependence of the rate constants for the hydrolysis of 1-ethoxyethyl-2-pentyl-2-imidazoline.

TABLE XIV

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-METHYL-2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 20	0	2.21
PROCEDURE I	15	1.54
	30	1.05
	45	.715
	60	.505
	75	.360
	90	.258

$$T_{1/2} = 28.5 \text{ minutes, } K = .024321/\text{minute}$$

RUN 21	0	1.880
PROCEDURE II	2	1.766
	4	1.825
	6	1.657
	8	1.609
	10	1.512
	12	1.466
	14	1.396
	16	1.312
	18	1.252
	20	1.195
	22	1.142
	24	1.092
	26	1.040
	28	.990
	30	.946
	32	.904
	34	.865
	36	.822
	38	.790
	40	.755
	42	.724
	44	.692
	46	.660
	48	.630
	50	.605
	60	.483
	62	.465
	64	.445

$$T_{1/2} = 28.8 \text{ minutes, } K = .024067/\text{minute}$$

TABLE XIV
DATA FOR THE HYDROLYSIS OF 1-HYDROXY-2-METHYL-2-IMIDAZOLINE AT 70°C

Time-Minutes	Absorbance
0	1.350
15	1.340
30	1.330
45	1.320
60	1.310
75	1.300
90	1.290
105	1.280

$k = 0.02432/\text{minute}$

Time-Minutes	Absorbance
0	1.380
2	1.370
4	1.360
6	1.350
8	1.340
10	1.330
12	1.320
14	1.310
16	1.300
18	1.290
20	1.280
22	1.270
24	1.260
26	1.250
28	1.240
30	1.230
32	1.220
34	1.210
36	1.200
38	1.190
40	1.180
42	1.170
44	1.160
46	1.150
48	1.140
50	1.130
52	1.120
54	1.110
56	1.100
58	1.090
60	1.080
62	1.070
64	1.060

$k = 0.02432/\text{minute}$

Figure 18. Semi-logarithmic plot of absorbance against time for Runs 20 and 21.

TABLE XV

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-METHYL-2-IMIDAZOLINE AT 58.20°

	Time-Minutes	Absorbance
RUN 22	0	.985
PROCEDURE I	10	.890
	20	.810
	30	.733
	40	.660
	50	.547
	60	.490
	70	.450
	80	.408
	90	.368

$$T_{1/2} = 70.5 \text{ minutes, } K = .00983/\text{minute}$$

RUN 23	0	.826
PROCEDURE III	10	.748
	20	.673
	30	.608
	40	.575
	50	.495
	60	.449
	70	.408
	80	.369
	90	.334
	100	.302
	120	.264
	140	.204

$$T_{1/2} = 69 \text{ minutes, } K = .010045/\text{minute}$$

DATA FOR THE HYDROLYSIS OF L-TRYPTOPHAN
L-TRYPH-1-IMIDAZOLINE AT 58.50°

Time-Minutes	Absorbance
0	0.985
10	0.930
20	0.870
30	0.810
40	0.750
50	0.690
60	0.630
70	0.570
80	0.510
90	0.450

$k = 0.00953/\text{minute}$

Time-Minutes	Absorbance
0	0.835
10	0.745
20	0.675
30	0.605
40	0.535
50	0.465
60	0.395
70	0.325
80	0.255
90	0.185
100	0.115
110	0.045
120	0.015

$k = 0.01065/\text{minute}$

Figure 19. Semi-logarithmic plot of absorbance against time for Runs 22 and 23.

0.0 0.0 0.0 0.0 0.0
0.0 0.0 0.0 0.0 0.0

TABLE XVI

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-METHYL-2-IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 24	0	1.745
	10	1.660
PROCEDURE I	20	1.595
	30	1.495
	40	1.450
	60	1.342
	80	1.218
	100	1.113
	120	1.020
	140	.940
	160	.842
	180	.767
	240	.586
	260	.535

$$T_{1/2} = 153 \text{ minutes, } K = .00453/\text{minute}$$

RUN 25	0	.833
	20	.755
PROCEDURE I	40	.690
	60	.632
	100	.518
	120	.472
	140	.428
	180	.353
	200	.324
	220	.292

$$T_{1/2} = 148 \text{ minutes, } K = .00468/\text{minute}$$

TABLE IV
DATA FOR THE DETERMINATION OF HYDROLYZABILITY
OF 2-METHYL-2-INDOL-3-OL AT 48.90

Absorbance

Time-minutes

1.745	0
1.880	10
1.995	20
1.995	30
1.995	40
1.995	50
1.995	60
1.995	80
1.995	100
1.995	120
1.995	140
1.995	160
1.995	180
1.995	200
1.995	220

$T_p = 123 \text{ minutes}$, $K = 0.0033/\text{minute}$

1.745	0
1.880	10
1.995	20
1.995	30
1.995	40
1.995	50
1.995	60
1.995	80
1.995	100
1.995	120
1.995	140
1.995	160
1.995	180
1.995	200
1.995	220

$T_p = 168 \text{ minutes}$, $K = 0.0058/\text{minute}$

Figure 20. Semi-logarithmic plot of absorbance against time for Runs 24 and 25.

Figure 21. Temperature dependence of the rate constants for the hydrolysis of 1-hydroxyethyl-2-methyl-2-imidazoline.

1. The first part of the experiment is to determine the rate of reaction between the two solutions. This is done by measuring the volume of gas evolved at regular intervals of time. The rate of reaction is then calculated from the slope of the graph of volume of gas evolved against time.

TABLE XVII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-ETHYL-2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 26	0	1.51
	10	.985
PROCEDURE I	20	.644
	30	.434
	40	.292
	50	.215
$T_{1/2} = 17 \text{ minutes, } K = .04077/\text{minute}$		
RUN 27	0	1.257
	2	1.197
Procedure II	4	1.108
	6	1.033
	8	.950
	10	.880
	12	.815
	14	.760
	16	.703
	18	.653
	20	.604
	22	.563
	24	.523
	26	.486
	28	.455
	30	.423
	32	.397
	34	.374
	36	.350
$T_{1/2} = 18 \text{ minutes, } K = .03851/\text{minute}$		
RUN 28	0	.945
	5	.785
PROCEDURE I	10	.639
	15	.525
	20	.430
	30	.293
$T_{1/2} = 17.5 \text{ minutes, } K = .0396/\text{minute}$		

DATA OF 1-1-1950

RUN 28

PROCEDURE I

RUN 27

PROCEDURE II

RUN 26

PROCEDURE I

R

Figure 22. Semi-logarithmic plot of absorbance against time for Runs 26, 27 and 28.

DATE 10/15/58
 TIME 10:30 AM
 LOCATION 1000' - 1000'

1000' - 1000'

1000' - 1000'

TABLE XVIII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-ETHYL-2-IMIDAZOLINE AT 58.20°

	Time-Minutes	Absorbance
RUN 29	0	.900
	10	.756
PROCEDURE I	20	.635
	30	.536
	40	.450
	50	.382
	60	.322
	70	.272
	80	.230

$$T_{1/2} = 40.2 \text{ minutes, } K = .0172/\text{minute}$$

RUN 30	0	1.176
	5	1.079
PROCEDURE III	10	.989
	15	.894
	20	.811
	25	.751
	30	.677
	35	.616
	40	.561
	50	.467
	60	.390
	70	.341

$$T_{1/2} = 38 \text{ minutes, } K = .0182/\text{minute}$$

DATA BY NAME

 

Figure 23. Semi-logarithmic plot of absorbance against time for Runs 29 and 30.

TABLE XIX

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-ETHYL-2-IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 31	0	1.115
	10	1.025
PROCEDURE I	20	.930
	30	.855
	40	.797
	50	.685
	60	.667
	70	.610
	80	.560
	90	.470
	100	.470
	110	.436
	120	.405
	130	.365

$$T_{1/2} = 81 \text{ minutes, } K = .00857/\text{minute}$$

RUN 32	0	1.030
	10	.950
PROCEDURE I	20	.865
	30	.795
	40	.737
	50	.672
	60	.615
	70	.564
	80	.517
	90	.477
	120	.402

$$T_{1/2} = 80 \text{ minutes, } K = .00866/\text{minute}$$

DATA FOR THE YEAR 1960

1960-1961

RUN 31

PROCEDURE 1

1960-1961

RUN 32

PROCEDURE 1

1960-1961

Figure 24. Semi-logarithmic plot of absorbance against time for Runs 31 and 32.

1.0 ml of 0.1% ST
 2.0 ml of 0.1% ST
 3.0 ml of 0.1% ST
 4.0 ml of 0.1% ST
 5.0 ml of 0.1% ST
 6.0 ml of 0.1% ST
 7.0 ml of 0.1% ST
 8.0 ml of 0.1% ST
 9.0 ml of 0.1% ST
 10.0 ml of 0.1% ST

Figure 25. Temperature dependence of the rate constants for the hydrolysis of 1-hydroxyethyl-2-ethyl-2-imidazoline.

TABLE XX

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-ISOPROPYL-2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 33	0	1.330
PROCEDURE I	10	1.118
	30	.843
	40	.690
	50	.580
	60	.520
	70	.440

$$T_{1/2} = 46 \text{ minutes, } K = .0151/\text{minute}$$

RUN 34	0	1.446
PROCEDURE III	5	1.360
	10	1.250
	15	1.150
	20	1.060
	25	.980
	30	.902
	35	.830
	40	.772
	45	.717
	50	.665
	55	.615
	60	.575
	65	.530
	75	.462
	80	.428
	85	.405
	90	.373
	100	.330

$$T_{1/2} = 44 \text{ minutes, } K = .0158/\text{minute}$$

DATA FOR THE HYDROLYSIS OF 2-HYDROXY-2-ISOPROPYL-3-IMIDAZOLINE AT 70.0°C

TABLE IV

Time-Minutes	Absorbance
0	1.10
10	1.10
20	0.95
30	0.85
40	0.80
50	0.75
60	0.70
70	0.65

$k = 0.012/\text{minute}$

Time-Minutes	Absorbance
0	1.45
10	1.35
20	1.25
30	1.15
40	1.05
50	0.95
60	0.85
70	0.75
80	0.65
90	0.55
100	0.45

$k = 0.012/\text{minute}$

Figure 26. Semi-logarithmic plot of absorbance against time for Runs 33 and 34.

TABLE XXI

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-ISOPROPYL-2-IMIDAZOLINE AT 58.20°

	Time-Minutes	Absorbance
RUN 35	0	.435
PROCEDURE I	15	.388
	30	.390
	45	.313
	60	.280
	75	.250
	90	.225
	105	.205
	120	.182
	135	.165

$$T_{1/2} = 96 \text{ minutes, } K = .00722/\text{minute}$$

RUN 36	0	1.260
PROCEDURE III	10	1.161
	20	1.076
	30	1.006
	40	.936
	50	.866
	60	.798
	80	.689
	90	.641
	100	.596
	120	.513
	140	.443
	160	.383
	180	.331

$$T_{1/2} = 92 \text{ minutes, } K = .00753/\text{minute}$$

TABLE XVI

DATA FOR THE POLYMERIZATION OF 1-HYDROXY-2-ETHOXY-2-ETHYL-1,3-DIOXOLANE AT 55°C

Time, minutes	Apparent
0	0.00
15	0.15
30	0.30
45	0.45
60	0.60
75	0.75
90	0.90
105	1.05
120	1.20
135	1.35

$k_p = 0.0073/\text{minute}$

Time, minutes	Apparent
0	0.00
15	0.15
30	0.30
45	0.45
60	0.60
75	0.75
90	0.90
105	1.05
120	1.20
135	1.35
150	1.50
165	1.65
180	1.80

$k_p = 0.0073/\text{minute}$

Figure 27. Semi-logarithmic plot of absorbance against time for Runs 35 and 36.

TABLE XXII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-ISOPROPYL-2-IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 37	0	.420
PROCEDURE I	30	.372
	60	.330
	120	.261
	150	.235
	180	.210
	210	.184
	240	.165
	270	.146
	300	.132

$$T_{1/2} = 180 \text{ minutes, } K = .00386/\text{minute}$$

RUN 38	0	.740
PROCEDURE I	30	.662
	60	.590
	150	.427
	165	.405
	180	.384
	216	.337
	240	.312
	270	.280
	300	.252

$$T_{1/2} = 194, K = .00357/\text{minute}$$

Figure 28. Semi-logarithmic plot of absorbance against time for Runs 37 and 38.

LOG. VELOCITY

Figure 29. Temperature dependence of the rate constants for the hydrolysis of 1-hydroxyethyl-2-isopropyl-2-imidazoline.

0.2

0.0 0.1 0.2

TABLE XXIII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-TERT.-BUTYL-2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 39	0	.990
	10	.928
PROCEDURE I	20	.860
	30	.790
	40	.741
	50	.689
	60	.644
	70	.600
	80	.575
	90	.538
	100	.494
	110	.457
	120	.450

$$T_{1/2} = 95 \text{ minutes, } K = .007296/\text{minute}$$

RUN 40	0	.754
	10	.706
PROCEDURE III	20	.639
	30	.614
	40	.555
	50	.514
	60	.484
	70	.459
	80	.421
	90	.391
	100	.364
	110	.339
	120	.317
	140	.281
	180	.210

$$T_{1/2} = 97 \text{ minutes, } K = .007145/\text{minute}$$

Figure 30. Semi-logarithmic plot of absorbance against time for Runs 39 and 40.

TABLE XXIV

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-TERT.-BUTYL-2-IMIDAZOLINE AT 58.20°

	Time-Minutes	Absorbance
RUN 41	0	.397
	30	.368
PROCEDURE I	60	.342
	90	.313
	120	.295
	150	.267
	180	.250
	210	.232
	240	.215
	270	.198
	300	.186

$$T_{1/2} = 264 \text{ minutes, } K = .00263/\text{minute}$$

RUN 42	0	.775
	30	.719
PROCEDURE III	60	.665
	90	.613
	120	.569
	150	.520
	210	.443
	240	.410
	270	.379
	300	.351
	330	.333
	360	.300

$$T_{1/2} = 258 \text{ minutes, } K = .002682/\text{minute}$$

TABLE XVII

DATA FOR THE HYDROLYSIS OF 1-HYDROXY-2-ETHYL-3-IMIDAZOLINE AT 25°C

Time-Minutes	Observed
0	1.00
30	0.95
60	0.90
90	0.85
120	0.80
150	0.75
180	0.70
210	0.65
240	0.60
270	0.55
300	0.50

$k = 0.0033/\text{minute}$

Time-Minutes	Observed
0	1.00
30	0.95
60	0.90
90	0.85
120	0.80
150	0.75
180	0.70
210	0.65
240	0.60
270	0.55
300	0.50

$k = 0.00382/\text{minute}$

Figure 31. Semi-logarithmic plot of absorbance against time for Runs 41 and 42.

TABLE XXV

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-TERT.-BUTYL-2-IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 43	0	.464
	60	.428
PROCEDURE I	120	.397
	180	.370
	240	.345
	300	.325
	360	.307
	420	.262
	600	.217
	660	.200
	720	.190

$$T_{\frac{1}{2}} = 612 \text{ minutes, } K = .00113/\text{minute}$$

RUN 44	0	.536
	30	.500
PROCEDURE I	60	.490
	180	.425
	240	.387
	300	.368
	360	.342
	420	.322
	540	.280
	600	.262
	660	.245
	720	.226
	780	.212
	840	.200

$$T_{\frac{1}{2}} = 612 \text{ minutes, } K = .00113/\text{minute}$$

TABLE XV

DATA FOR THE HYDROLYSIS OF 1-HYDROXY-2-ETHYL-3-IMIDAZOLINE AT 60°C

Time-Minutes	Assayance
0	100
10	98
20	96
30	94
40	92
50	90
60	88
70	86
80	84
90	82
100	80
110	78
120	76
130	74
140	72
150	70
160	68
170	66
180	64
190	62
200	60

$k = 0.013 \text{ minutes}^{-1}$

Time-Minutes	Assayance
0	100
10	98
20	96
30	94
40	92
50	90
60	88
70	86
80	84
90	82
100	80
110	78
120	76
130	74
140	72
150	70
160	68
170	66
180	64
190	62
200	60

$k = 0.013 \text{ minutes}^{-1}$

Figure 32. Semi-logarithmic plot of absorbance against time for Runs 43 and 44.

0.5 0.4 0.3 0.2 0.1 0.0

0.5 0.4 0.3 0.2 0.1 0.0

Figure 33. Temperature dependence of the rate constants for the hydrolysis of 1-hydroxyethyl-2-tert.-butyl-2-imidazoline.

COEFFICIENT OF THERMAL EXPANSION - α - $10^{-6}/^{\circ}\text{C}$ - $10^{-6}/^{\circ}\text{C}$ - $10^{-6}/^{\circ}\text{C}$
 (average value of α for the whole sample)

TABLE XXVI

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 45	0	1.232
PROCEDURE I	2	.792
	4	.499
	6	.340
	8	.250
	10	.200
	12	.165
	14	.152
	16	.132

$$T_{1/2} = 3.03 \text{ minutes, } K = .229/\text{minute}$$

RUN 46	0	1.087
PROCEDURE III	1	.800
	2	.610
	3	.480
	4	.360
	5	.283
	6	.222
	7	.184
	8	.143
	9	.123

$$T_{1/2} = 2.7 \text{ minutes, } K = .257/\text{minute}$$

DATA FOR THE

RUN 42

PROCEDURE I

$T_p = 3.03 \text{ minutes}$

RUN 46

PROCEDURE III

Figure 34. Semi-logarithmic plot of absorbance against time for Runs 45 and 46.

TABLE XXVII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-IMIDAZOLINE AT 58.20°

	Time-Minutes	Absorbance
RUN 47	0	1.705
	2	1.370
PROCEDURE I	4	1.050
	6	.890
	8	.725
	10	.585
	12	.480
	14	.392
	16	.329
	18	.272
	20	.227

$$T_{1/2} = 6.5 \text{ minutes, } K = .107/\text{minute}$$

RUN 48	0	1.050
	1	.934
PROCEDURE III	2	.832
	3	.747
	4	.664
	5	.613
	6	.532
	7	.477
	8	.431
	9	.385
	10	.355
	11	.318

$$T_{1/2} = 6.2 \text{ minutes, } K = .112/\text{minute}$$

DATA FOR THE TEST OF THE HYPOTHESIS THAT THE
POPULATION MEAN IS EQUAL TO 100

TEST OF THE HYPOTHESIS THAT THE
POPULATION MEAN IS EQUAL TO 100

PROCEDURE 1
RUN 47

TEST OF THE HYPOTHESIS THAT THE
POPULATION MEAN IS EQUAL TO 100

PROCEDURE 1
RUN 48

TEST OF THE HYPOTHESIS THAT THE
POPULATION MEAN IS EQUAL TO 100

PROCEDURE 1
RUN 49

TEST OF THE HYPOTHESIS THAT THE
POPULATION MEAN IS EQUAL TO 100

PROCEDURE 1
RUN 50

Figure 35. Semi-logarithmic plot of absorbance against time for Runs 47 and 48.

Figure 20. The effect of the concentration of the solution on the rate of the reaction.

FIG. 20. Effect of concentration on rate of reaction.

TABLE XXVIII
DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 49	0	1.055
	2	.885
PROCEDURE I	4	.794
	6	.715
	8	.651
	10	.584
	12	.525
	14	.475
	16	.436
	18	.388
	22	.317
	26	.255
$T_{1/2} = 13.5$ minutes, $K = .0514/\text{minute}$		
RUN 50	0	.308
	4	.255
PROCEDURE I	8	.210
	12	.172
	16	.143
	20	.119
	24	.102
	28	.087
$T_{1/2} = 14.6$ minutes, $K = .0475/\text{minute}$		
RUN 51	0	1.205
	4	.980
PROCEDURE I	10	.735
	12	.660
	16	.545
	20	.455
	24	.387
	28	.327
$T_{1/2} = 14.25$ minutes, $K = .0486/\text{minute}$		

DATA FOR THE

RUN 49

PROCEDURE 1

$T_1 = 13.5$ minutes

RUN 50

PROCEDURE 1

RUN 51

PROCEDURE 1

$T_1 = 14.5$ minutes

Figure 36. Semi-logarithmic plot of absorbance against time for Runs 49 and 50.

101 with further soundings to solid 4.11 mgs. at 4.11 mgs.
 102 4.11 mgs. at 4.11 mgs.
 103 4.11 mgs. at 4.11 mgs.
 104 4.11 mgs. at 4.11 mgs.
 105 4.11 mgs. at 4.11 mgs.
 106 4.11 mgs. at 4.11 mgs.
 107 4.11 mgs. at 4.11 mgs.
 108 4.11 mgs. at 4.11 mgs.
 109 4.11 mgs. at 4.11 mgs.
 110 4.11 mgs. at 4.11 mgs.

LOG. PROPORTION

Figure 37. Semi-logarithmic plot of absorbance against time for Run 51.

Figure 38. Temperature dependence of the rate constants for the hydrolysis of l-hydroxyethyl-2-imidazoline.

TABLE XXIX

DATA FOR THE HYDROLYSIS OF 1-METHYL-
2-PENTYL-2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 52	0	.248
	5	.223
PROCEDURE I	10	.200
	15	.178
	20	.160
	25	.145
	30	.130
	35	.119
	40	.108
	45	.103

$$T_{1/2} = 32 \text{ minutes, } K = .0217/\text{minute}$$

RUN 53	0	.656
	2	.641
PROCEDURE II	4	.622
	6	.598
	8	.574
	10	.548
	12	.519
	14	.490
	16	.466
	18	.442
	20	.425
	22	.410
	24	.388
	26	.374
	28	.356
	30	.343
	32	.327
	34	.316
	36	.304
	38	.291
	40	.280
	44	.260
	50	.231
	54	.213
	60	.185
	70	.157

$$T_{1/2} = 32 \text{ minutes, } K = .0217/\text{minute}$$

TABLE XXIX

DATA FOR THE HYDROLYSIS OF 1-METHYL-2-PENTYL-2-IMIDAZOLINE AT 70°C.

Time-minutes	Abundance
0	100
5	98
10	95
15	92
20	88
25	85
30	82
35	78
40	75
45	72

$k = 0.017/\text{minute}$

Time-minutes	Abundance
0	100
5	98
10	95
15	92
20	88
25	85
30	82
35	78
40	75
45	72
50	68
55	65
60	62
65	58
70	55
75	52
80	48
85	45
90	42
95	38
100	35
105	32
110	28
115	25
120	22
125	18
130	15
135	12
140	10
145	8
150	5
155	3
160	2
165	1
170	0

$k = 0.017/\text{minute}$

TABLE XXX

DATA FOR THE HYDROLYSIS OF 1-METHYL-
2-PENTYL-2-IMIDAZOLINE AT 58.20°

	Time-Minutes	Absorbance
RUN 54	0	.755
	10	.678
PROCEDURE III	20	.608
	30	.548
	40	.492
	50	.447
	60	.389
	70	.362
	80	.323
	90	.294
	100	.267
	120	.215
	130	.199

$$T_{1/2} = 66.5 \text{ minutes, } K = .0104/\text{minute}$$

RUN 55	0	.685
	10	.614
PROCEDURE III	20	.564
	30	.503
	40	.452
	50	.400
	60	.369
	70	.330
	90	.266
	100	.243
	120	.201
	140	.160

$$T_{1/2} = 67 \text{ minutes, } K = .0103/\text{minute}$$

DATA FOR RUN 24

2.75

RUN 24

PROCEDURE 111

RUN 25

PROCEDURE 111

T_g = 67 minutes

Figure 39. Semi-logarithmic plot of absorbance against time for Runs 52 and 53.

Figure 30. Effect of temperature on the rate of sorption of benzene vapor by polyethylene at 1 atm.

Figure 40. Semi-logarithmic plot of absorbance against time for Runs 54 and 55.

TABLE XXXI

DATA FOR THE HYDROLYSIS OF 1-METHYL-
2-PENTYL-2-IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 56	0	.733
	10	.695
PROCEDURE III	20	.661
	30	.625
	40	.593
	50	.574
	60	.539
	80	.483
	100	.436
	120	.391
	140	.359
	180	.290

$$T_{1/2} = 131 \text{ minutes, } K = .00529/\text{minute}$$

RUN 57	0	.882
	20	.797
PROCEDURE III	30	.752
	40	.712
	50	.686
	60	.649
	80	.581
	100	.524
	120	.472
	140	.430
	180	.349

$$T_{1/2} = 132 \text{ minutes, } K = .00525/\text{minute}$$

TABLE XXI

DATA FOR THE HYDROLYSIS OF 1-METHYL-2-PHENYL-2-IMIDAZOLINE AT 43.00°

Time, minutes	Absorbance
0	0.000
10	0.000
20	0.000
30	0.000
40	0.000
50	0.000
60	0.000
80	0.000
100	0.000
120	0.000
140	0.000
160	0.000
180	0.000

$T_{\infty} = 111$ minutes, $k = 0.0025/\text{minute}$

Time, minutes	Absorbance
0	0.000
20	0.000
30	0.000
40	0.000
50	0.000
60	0.000
80	0.000
100	0.000
120	0.000
140	0.000
160	0.000

$T_{\infty} = 132$ minutes, $k = 0.0025/\text{minute}$

Figure 41. Semi-logarithmic plot of absorbance against time for Runs 56 and 57.

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

Figure 42. Temperature dependence of the rate constants for the hydrolysis of 1-methyl-2-pentyl-2-imidazoline.

and 100 ml of 0.1 M NaOH solution. The solution was then diluted to 1000 ml with distilled water. The solution was then used for the determination of the concentration of the solution.

TABLE XXXII

DATA FOR THE HYDROLYSIS OF 1-ETHYL-
2-PENTYL-2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 58	0	1.128
	2	1.100
PROCEDURE II	4	1.088
	6	1.052
	8	1.038
	10	1.012
	12	.980
	14	.960
	16	.930
	18	.910
	20	.890
	25	.827
	30	.788
	35	.745
	40	.710
	45	.662
	50	.632
	55	.600
	60	.572
	65	.546
	70	.517
	75	.493

$$T_{1/2} = 59 \text{ minutes, } K = .0117/\text{minute}$$

RUN 59	0	.433
	5	.406
PROCEDURE I	10	.380
	15	.360
	20	.340
	25	.320
	30	.303
	35	.288
	45	.254
	55	.223
	60	.208
	65	.196
	70	.188
	80	.168

$$T_{1/2} = 58 \text{ minutes, } K = .0119/\text{minute}$$

Figure 43. Semi-logarithmic plot of absorbance against time for Runs 58 and 59.

Figure 2. Dependence of the optical density of the absorption band at 28 μ on the concentration of the solution.

TABLE XXXIII

DATA FOR THE HYDROLYSIS OF 1-ETHYL-
2-PENTYL-2-IMIDAZOLINE AT 58.20°

	Time-Minutes	Absorbance
RUN 60	0	.840
	10	.795
PROCEDURE III	20	.751
	30	.705
	40	.672
	50	.626
	70	.568
	80	.530
	100	.480
	120	.426
	140	.380
	180	.313
	200	.281
	220	.250
	240	.223

$$T_{1/2} = 121.5 \text{ minutes, } K = .00570/\text{minute}$$

RUN 61	0	.680
	10	.642
PROCEDURE III	20	.605
	30	.571
	40	.535
	50	.503
	60	.481
	70	.454
	80	.427
	90	.401
	100	.379
	110	.360
	120	.340
	130	.323
	140	.304
	180	.241

$$T_{1/2} = 120 \text{ minutes, } K = .00577/\text{minute}$$

TABLE 1

DATA FOR THE STUDY OF THE EFFECT OF
TEMPERATURE ON THE RATE OF
REACTION

RUN 60

PROCEDURE 111

100
100
100

$t = 121.5$ minutes

RUN 61

PROCEDURE 111

100
100
100

$t = 120$ minutes

Figure 44. Semi-logarithmic plot of absorbance against time for Runs 60 and 61.

TABLE XXXIV

DATA FOR THE HYDROLYSIS OF 1-ETHYL-
2-PENTYL-2-IMIDAZOLINE AT 48.90°

	Time-Minutes	Absorbance
RUN 62	0	.723
PROCEDURE III	20	.681
	40	.642
	60	.605
	80	.569
	100	.540
	140	.484
	160	.453
	180	.430
	200	.403
	220	.380
	240	.363
	260	.337
	420	.214
	440	.198
$T_{1/2} = 236$ minutes, $K = .00294/\text{minute}$		
RUN 63	0	.892
PROCEDURE III	20	.840
	40	.790
	60	.749
	80	.696
	100	.662
	140	.601
	160	.559
	180	.525
	200	.495
	220	.464
	240	.440
	260	.421
	420	.269
	440	.249
$T_{1/2} = 236$ minutes, $K = .00294/\text{minute}$		

DATA FOR THE ...
...
...

...
...

RUN 82

PROCEDURE 111

...
...

RUN 83

PROCEDURE 111

...
...

Figure 45. Semi-logarithmic plot of absorbance against time for Runs 62 and 63.

Figure 46. Temperature dependence of the rate constants for the hydrolysis of 1-ethyl-2-pentyl-2-imidazoline.

TABLE XXXV

DATA FOR THE HYDROLYSIS OF 1-ISOPROPYL-
2-PENTYL-2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 64	0	.431
	10	.419
PROCEDURE III	30	.410
	65	.390
	120	.355
	170	.320
	210	.302
	330	.252
	360	.242
	405	.227
	430	.215
	480	.204
	560	.188
	600	.172
	660	.156
	1560	.050

$$T_{1/2} = 450 \text{ minutes, } K = .00154/\text{minute}$$

RUN 65	0	.376
	10	.370
PROCEDURE III	30	.355
	65	.335
	120	.308
	170	.290
	210	.267
	330	.226
	360	.215
	405	.205
	430	.192
	480	.180
	560	.158
	600	.150
	660	.138

$$T_{1/2} = 453 \text{ minutes, } K = .00153/\text{minute}$$

Figure 47. Semi-logarithmic plot of absorbance against time for Runs 64 and 65.

TABLE XXXVI

DATA FOR THE HYDROLYSIS OF 1-ISOPROPYL-
2-PENTYL-2-IMIDAZOLINE AT 58.20°

	Time-Minutes	Absorbance
RUN 66	0	.598
	3	.521
PROCEDURE III	4	.500
	5	.479
	6	.458
	8	.428
	9	.405
	10	.390
	11	.372
	12	.362
	13	.346
	14	.333
	15	.318
	16	.306
	17	.295
	18	.278
	28	.192
$T_{1/2} = 1020 \text{ minutes, } K = .000680/\text{minute}$		
RUN 67	0	.638
	3	.568
PROCEDURE III	4	.535
	5	.513
	6	.491
	8	.459
	9	.441
	10	.420
	11	.405
	12	.387
	13	.374
	14	.362
	15	.345
	16	.333
	17	.323
	18	.309
	28	.210
$T_{1/2} = 1044 \text{ minutes, } K = .000664/\text{minute}$

Figure 48. Semi-logarithmic plot of absorbance against time for Runs 66 and 67.

1.0
 0.9
 0.8
 0.7
 0.6
 0.5
 0.4
 0.3
 0.2
 0.1
 0

Figure 49. Semi-logarithmic plot of absorbance against time for Runs 68 and 69.

TABLE XXXVII

DATA FOR THE HYDROLYSIS OF 1-ISOPROPYL-
2-PENTYL-2-IMIDAZOLINE AT 48.90°

	Time-Hours	Absorbance
RUN 68	0	.632
	1	.616
PROCEDURE III	2	.602
	4	.577
	6	.552
	8	.527
	10	.500
	12	.478
	23	.380
	24	.366
	26	.346
	28	.338
	30	.325
	32	.310
	34	.297
	36	.284
	47	.227
	48	.219
	50	.211

$$T_{\frac{1}{2}} = 1878 \text{ minutes, } K = .000370/\text{minute}$$

RUN 69	0	.743
	1	.727
PROCEDURE III	2	.704
	4	.677
	6	.645
	8	.618
	10	.590
	12	.565
	23	.445
	24	.431
	26	.426
	28	.397
	30	.377
	32	.362
	34	.353
	36	.332
	47	.268
	48	.259
	50	.248

$$T_{\frac{1}{2}} = 1884 \text{ minutes, } K = .000368/\text{minute}$$

TABLE XXVII

DATA FOR THE HYDROLYSIS OF L-ISOVALERYL
2-ETHYL-2-INDOLYL AT 48.90°

Time - hours	Concentration
0	0.00
1	0.01
2	0.02
3	0.03
4	0.04
5	0.05
6	0.06
7	0.07
8	0.08
9	0.09
10	0.10
11	0.11
12	0.12
13	0.13
14	0.14
15	0.15
16	0.16
17	0.17
18	0.18
19	0.19
20	0.20
21	0.21
22	0.22
23	0.23
24	0.24
25	0.25
26	0.26
27	0.27
28	0.28
29	0.29
30	0.30

$k = 1.978 \times 10^{-3} \text{ minute}^{-1}$

Time - hours	Concentration
0	0.00
1	0.01
2	0.02
3	0.03
4	0.04
5	0.05
6	0.06
7	0.07
8	0.08
9	0.09
10	0.10
11	0.11
12	0.12
13	0.13
14	0.14
15	0.15
16	0.16
17	0.17
18	0.18
19	0.19
20	0.20
21	0.21
22	0.22
23	0.23
24	0.24
25	0.25
26	0.26
27	0.27
28	0.28
29	0.29
30	0.30

$k = 1.684 \times 10^{-3} \text{ minute}^{-1}$

Figure 50. Temperature dependence of the rate constants for the hydrolysis of 1-isopropyl-2-pentyl-2-imidazoline.

0.5
1.0

0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00

TABLE XXXVIII

DATA FOR THE HYDROLYSIS OF 2-PENTYL-
2-IMIDAZOLINE AT 70.48°

	Time-Minutes	Absorbance
RUN 70	0	1.032
	5	1.025
PROCEDURE III	15	.992
	25	.972
	35	.947
	70	.877
	85	.847
	105	.805
	135	.749
	180	.674
	225	.602
	255	.562
	285	.519
	315	.482
	345	.454

$$T_{1/2} = 287 \text{ minutes, } K = .00242/\text{minute}$$

RUN 71	0	.785
	10	.775
PROCEDURE III	55	.691
	90	.638
	125	.585
	155	.550
	420	.295
	430	.285
	450	.271
	480	.260

$$T_{1/2} = 288 \text{ minutes, } K = .00241/\text{minute}$$

TABLE XXVIII

DATA FOR THE ANALYSIS OF 2-ETHYL-
2-THIOPHENE AT 10.45

Time-Minutes	Response
0	1.875
5	1.875
10	1.875
15	1.875
20	1.875
25	1.875
30	1.875
35	1.875
40	1.875
45	1.875
50	1.875
55	1.875
60	1.875
65	1.875
70	1.875
75	1.875
80	1.875
85	1.875
90	1.875
95	1.875
100	1.875

$T_f = 387 \text{ minutes}$, $R = 1.00262 \text{ minutes}$

Time-Minutes	Response
0	1.875
5	1.875
10	1.875
15	1.875
20	1.875
25	1.875
30	1.875
35	1.875
40	1.875
45	1.875
50	1.875
55	1.875
60	1.875
65	1.875
70	1.875
75	1.875
80	1.875
85	1.875
90	1.875
95	1.875
100	1.875

$T_f = 389 \text{ minutes}$, $R = 1.00261 \text{ minutes}$

Figure 51. Semi-logarithmic plot of absorbance against time for Runs 70 and 71.

0.0 0.2 0.4 0.6 0.8 1.0

TABLE XXXIX

DATA FOR THE HYDROLYSIS OF 2-PENTYL-
2-IMIDAZOLINE AT 58.20°

	Time-Hours	Absorbance
RUN 72	0	.525
	1	.500
PROCEDURE III	3	.445
	4	.428
	5	.399
	7	.356
	8	.340
	9	.321
	10	.300
	11	.284
	12	.270
	13	.250
	23.2	.142
	24	.137

$$T_{1/2} = 738 \text{ minutes, } K = .000939/\text{minute}$$

RUN 73	0	.532
	1	.502
PROCEDURE III	3	.449
	4	.426
	5	.399
	7	.360
	8	.340
	9	.324
	10	.301
	11	.285
	12	.271
	13	.254
	23.2	.143
	24	.139

$$T_{1/2} = 732 \text{ minutes, } K = .000947/\text{minute}$$

TABLE XXII

DATA FOR THE HYDROLYSIS OF 2-ETHYL-
1-INDOLINE AT 28.2°

Time-Hours	Adiponitrile
0	22.2
1	22.2
2	22.2
3	22.2
4	22.2
5	22.2
6	22.2
7	22.2
8	22.2
9	22.2
10	22.2
11	22.2
12	22.2
13	22.2
14	22.2
15	22.2
16	22.2
17	22.2
18	22.2
19	22.2
20	22.2

$k = 0.00039/\text{minute}$

Time-Hours	Adiponitrile
0	22.2
1	22.2
2	22.2
3	22.2
4	22.2
5	22.2
6	22.2
7	22.2
8	22.2
9	22.2
10	22.2
11	22.2
12	22.2
13	22.2
14	22.2
15	22.2
16	22.2
17	22.2
18	22.2
19	22.2
20	22.2

$k = 0.00039/\text{minute}$

Figure 52. Semi-logarithmic plot of absorbance against time for Run 72.

0.0 0.2 0.4 0.6 0.8 1.0

Figure 53. Semi-logarithmic plot of absorbance against time for Run 73.

Figure 23. Logarithmic plot of rate of sorption versus concentration for the system studied in Figure 22.

TABLE XXXX

DATA FOR THE HYDROLYSIS OF 2-PENTYL-
2-IMIDAZOLINE AT 48.90°

	Time-Hours	Absorbance
RUN 74	0	1.278
	1	1.223
PROCEDURE III	2	1.200
	24	.691
	25	.681
	26	.659
	31	.573
	32	.570
	33	.559
	34	.540
	35	.528
	47	.403
	48	.383
	49	.378
	50	.368

$$T_{1/2} = 1692 \text{ minutes, } K = .0004096/\text{minute}$$

RUN 75	0	1.442
	1	1.355
PROCEDURE III	2	1.277
	24	.768
	25	.747
	26	.725
	31	.647
	32	.628
	33	.618
	34	.599
	35	.582
	47	.438
	48	.426
	49	.416
	50	.407

$$T_{1/2} = 1698 \text{ minutes, } K = .000408/\text{minute}$$

DATA FOR THE WORKSHEET

RUN 7A

PROCEDURE III

RUN 7B

PROCEDURE III

R

1993

Figure 54. Semi-logarithmic plot of absorbance against time for Runs 74 and 75.

For each sample, the concentration of the solid phase was determined by gravimetric analysis.

Concentration

Figure 55. Temperature dependence of the rate constants for the hydrolysis of 2-pentyl-2-imidazoline.

TABLE XXXXI

DATA FOR THE HYDROLYSIS OF 1-ISOPROPYL-2-PENTYL-
4,4-DIMETHYL-2-IMIDAZOLINE AT 70.48°

	Time-Hours	Absorbance
RUN 76	0	.910
	14	.910
PROCEDURE III	24	.899
	67	.880
	88	.872
	110	.866

Extrapolated $T_{\frac{1}{2}}$ $\cong$ 65 days

Figure 56. Semi-logarithmic plot of absorbance against time for Run 76.

IV. HYDROLYSIS OF 1-HYDROXYETHYL-2-HEPTADECYL- 2-IMIDAZOLINE IN ACIDIC ETHANOL SOLUTION

This reaction was carried out in 95% ethanol that was .1 molar with respect to sulfuric acid. Set-up and handling was the same as in Procedure I except that .01 molar sulfuric acid was used in the reference cell. Temperature was 70.48°.

1/2 mole of 1,2-dichloroethane

2-ethylhexanoic acid solution

This reaction was carried out in 500 ml. of

was, 1 mole of 1,2-dichloroethane and 1 mole of

handling was the same as in Example 1 except that

molar ratio was 1:1. The reaction was

Temperature was 70-80°C.

TABLE XXXXII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-HEPTADECYL-2-IMIDAZOLINE IN
ACIDIC SOLUTION

	Time-Hours	Absorbance
RUN 77	0	.890
	1	.885
	3	.875
	4	.870
	5	.867
	9	.862
	10	.860
	21	.826
	22	.825
	26	.815
	30	.805
	49	.770
	76	.715
	95	.668
	98	.663
	122	.613
	142	.575
	146	.570
	167	.532
	192	.495
	216	.458
	240	.431
	264	.400
	312	.355
	432	.259
	480	.235
	528	.217
	600	.197
	648	.187
	696	.174
	768	.166

$$T_{\frac{1}{2}} = 13680 \text{ minutes}$$

RUN 77

Figure 57. Semi-logarithmic plot of absorbance against time for Run 77.

FIG. 1. Relationship between log concentration and log time.

V. KINETICS OF HYDROLYSIS OF 1-HYDROXYETHYL-2-PENTYL-2-IMIDAZOLINE IN AQUEOUS SOLUTIONS

The method of following this series of reactions was essentially the same as was previously outlined under Procedure III. The only notable difference is that all absorption figures are corrected for the absorption of the reaction solvent.

All times are in minutes, and all half-lives were determined graphically from the initial points in plots of the logarithm absorbance against time.

The pH of the solutions was determined with a Beckman model of G pH meter, using a blue glass electrode.

Salt Effects. Two series of runs were performed in studying the effect of a neutral salt on the rate of hydrolysis.

Series I was run in solutions that were .0025 molar in sodium hydroxide. These solutions were varied from zero to one molar in sodium perchlorate. All runs in this series were at 38.0°C.

Series II was run in buffered solutions of high pH. This series was run at 25.6°C.

The data for these runs is presented in both tabular and graphic form in the manner of the preceding section.

TABLE XXXXIII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-2-PENTYL-
2-IMIDAZOLINE IN 0.0025 MOLAR SODIUM
HYDROXIDE SOLUTION

	Time-Minutes	Absorbance
RUN 78	0	.674
	5	.587
SERIES I	10	.497
	15	.435
0.0 MOLAR IN	20	.369
	25	.325
NaClO ₄	30	.275
	35	.244
	40	.212
	45	.188
	50	.166

$$T_{1/2} = 22.8 \text{ minutes, } K = .0305/\text{minute}$$

RUN 79	0	.872
	5	.782
SERIES I	10	.699
	15	.637
0.2 MOLAR IN	20	.594
	30	.529
NaClO ₄	40	.424
	50	.362
	60	.306
	70	.264
	80	.229
	90	.194
	100	.173

$$T_{1/2} = 40 \text{ minutes, } K = .0174/\text{minute}$$

Figure 58. Semi-logarithmic plot of absorbance against time for Runs 78 and 79.

TABLE XXXXIII Continued

	Time-Minutes	Absorbance
RUN 80	0	.738
	10	.635
SERIES I	20	.542
	30	.483
0.4 MOLAR IN	40	.421
	50	.378
NaClO ₄	60	.327
	70	.285
	80	.250
	90	.227
	100	.200

$$T_{1/2} = 52 \text{ minutes, } K = .0133/\text{minute}$$

RUN 81	0	.636
	10	.565
SERIES I	20	.503
	30	.450
0.6 MOLAR IN	40	.405
	50	.359
NaClO ₄	60	.327
	70	.292
	80	.264
	90	.237
	100	.215

$$T_{1/2} = 62 \text{ minutes, } K = .0112/\text{minute}$$

Figure 59. Semi-logarithmic plot of absorbance against time for Runs 80 and 81.

log absorbance

TABLE XXXXIII Continued

	Time-Minutes	Absorbance
RUN 82	0	.748
SERIES I 0.8 MOLAR IN NaClO ₄	10	.671
	20	.611
	30	.556
	40	.504
	50	.456
	60	.421
	70	.382
	80	.354
	90	.325
	100	.297

$$T_{\frac{1}{2}} = 70 \text{ minutes, } K = .00994/\text{minute}$$

RUN 83	0	.698
SERIES I 1.0 MOLAR IN NaClO ₄	10	.630
	20	.575
	30	.527
	40	.510
	50	.445
	60	.406
	70	.373
	80	.344
	90	.318
	100	.290

$$T_{\frac{1}{2}} = 81 \text{ minutes, } K = .00860/\text{minute}$$

TABLE XXVII Continued

Absorbance		Time-Minutes	
0.8 MOLAL IN	WATER	0	0.000
		10	0.001
		20	0.002
		30	0.003
		40	0.004
		50	0.005
		60	0.006
		70	0.007
		80	0.008
		90	0.009
		100	0.010

$T_p = 70 \text{ minutes} \times 0.0036/\text{minute}$

0.8 MOLAL IN	WATER	0	0.000
		10	0.001
		20	0.002
		30	0.003
		40	0.004
		50	0.005
		60	0.006
		70	0.007
		80	0.008
		90	0.009
		100	0.010

$T_p = 81 \text{ minutes} \times 0.0080/\text{minute}$

Figure 60. Semi-logarithmic plot of absorbance against time for Runs 82 and 83.

10 9 8 7 6 5 4 3 2 1 0
1 2 3 4 5 6 7 8 9 10

Figure 61. Semi-logarithmic plot of K against the square root of ionic strength for Runs 78 through 83.

TABLE XXXIV

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-
2-PENTYL-2-IMIDAZOLINE AT HIGH pH

		Time-Minutes	Absorbance
RUN 84	SERIES II	0	.469
		5	.410
pH = 13.6		12	.340
		17	.297
1.0 Molar IN		22	.260
		30	.210
NaClO ₄			

$$T_{1/2} = 25.5 \text{ minutes, } K = .0272/\text{minute}$$

RUN 85	SERIES II	0	.699
		5	.630
pH = 13.7		11	.540
		17	.467
0.6 Molar IN		24	.382
		33	.302
NaClO ₄		44	.228
		55	.172
		60	.147

$$T_{1/2} = 26.5 \text{ minutes, } K = .0262/\text{minute}$$

DATA FOR THE ANALYSIS OF THE SAMPLES

RUN 84 SERIES II
PH = 11.16

1.0 MOLAR IN
NACLO

RUN 85 SERIES II
PH = 11.17

0.6 MOLAR IN
NACLO

0.2 MOLAR IN
NACLO

TABLE XXXIV Continued.

		Time-Minutes	Absorbance
RUN 86	SERIES II	0	.647
		5	.670
pH = 13.8		11	.574
		17	.490
0.2 MOLAR IN		24	.405
		33	.332
NaClO ₄		44	.248
		55	.180
		60	.162

$$T_{\frac{1}{2}} = 27 \text{ minutes, } K = .0257/\text{minute}$$

TABLE XXVII Continued

Absorbance		Time-Minutes	
1.17		0	
1.17		2	
1.17		11	
1.17		12	
1.17		13	
1.17		14	
1.17		15	
1.17		16	
1.17		17	
1.17		18	
1.17		19	
1.17		20	

WATER, K. M. DISTILLATION

Variation of rate with concentration of base. This series of reactions was run in buffer solutions of varying pH. All solutions were one molar with respect to sodium perchlorate except for one reaction carried out in one molar sodium hydroxide solution. Total salt concentration varied from about 1.2 molar to 1.5 molar at high pH. All runs were at 25.6°C.

Time and absorbance data are given in the following tables, and a graph of the logarithm of absorbance against time is given for each run where hydrolysis occurred.

Figure 62. Semi-logarithmic plot of absorbance against time for Runs 84, 85 and 86.

TABLE XXXXV

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-2-PENTYL-
2-IMIDAZOLINE IN AQUEOUS SOLUTIONS OF VARYING pH

		Time-Minutes	Absorbance
RUN 87		0	.859
		10	.832
pH = 11.15		20	.798
		40	.750
$[\text{OH}^-] = 1.41 \times 10^{-3}$		60	.698
		80	.652
		120	.576
		140	.534
		160	.499
		200	.439
		220	.410
		240	.384

$$T_{1/2} = 208 \text{ minutes, } K = .00334/\text{minute}$$

Figure 63. Semi-logarithmic plot of absorbance against time for Run 87.

TABLE XXXXV Continued

	Time-Minutes	Absorbance
RUN 88	0	.656
	5	.625
pH = 11.7	15	.550
	25	.485
$[\text{OH}^-] = 5.13 \times 10^{-3}$	35	.429
	45	.380
	55	.334
	65	.295
	85	.230
	105	.180
	125	.138

$$T_{1/2} = 54 \text{ minutes, } K = .0128/\text{minute}$$

RUN 89	0	.635
	10	.523
pH = 12.16	20	.444
	30	.370
$[\text{OH}^-] = 1.44 \times 10^{-2}$	40	.310
	50	.260
	60	.220
	70	.185
	80	.157

$$T_{1/2} = 40 \text{ minutes, } K = .0174/\text{minute}$$

TABLE XXV Continued

Temperature

Time of day

Run 38

21.11 = 11.7

[0.1]

Time of day = 11.7 minutes

Run 39

21.10 = 11.6

[0.1]

Time of day = 11.6 minutes

Figure 64. Semi-logarithmic plot of absorbance against time for Runs 88 and 89.

TABLE XXXV Continued

	Time-Minutes	Absorbance
RUN 90	0	.737
	5	.657
pH = 12.40	10	.597
	15	.540
$[\text{OH}^-] = 2.51 \times 10^{-2}$	20	.486
	30	.495
	40	.421
	50	.260
	60	.209

$$T_{1/2} = 33.3 \text{ minutes, } K = .0208/\text{minute}$$

RUN 91	0	.738
	5	.647
pH = 13.75	10	.566
	15	.502
$[\text{OH}^-] = 5.62 \times 10^{-1}$	20	.441
	30	.346
	40	.269
	50	.205
	60	.157

$$T_{1/2} = 27.4 \text{ minutes, } K = .0254/\text{minute}$$

TABLE 1

Summary of the results of the analysis of the data obtained from the experiments conducted during the period from January 1, 1960, to December 31, 1960.

Run 10

PH = 12.50

[ON]

PH = 12.50

Run 11

PH = 12.50

[ON]

PH = 12.50

Figure 65. Semi-logarithm plot of absorbance against time for Runs 90 and 91.

TABLE XXXXV Continued

	Time-Minutes	Absorbance
RUN 92	0	.655
	20	.648
pH = 10.66	40	.639
	120	.597
$[\text{OH}^-] = 4.57 \times 10^{-4}$	150	.585
	180	.581
	240	.548
	270	.532
	300	.520
	360	.495
	1090	.280
	1100	.282
	1110	.275
$T_{1/2} = 885 \text{ minutes, } K = .000784/\text{minute}$		

RUN 93	0	.596
	20	.580
pH = 10.91	40	.563
	120	.486
$[\text{OH}^-] = 8.13 \times 10^{-4}$	150	.454
	180	.443
	240	.406
	270	.380
	300	.360
	360	.330
	420	.303
	1090	.106
	1100	.121
	1110	.101
$T_{1/2} = 435 \text{ minutes, } K = .0016/\text{minute}$

Figure 66. Semi-logarithmic plot of absorbance against time for Runs 92 and 93.

Graph showing the relationship between the logarithm of the rate of reaction and the concentration of the reactants.

Rate of reaction

Graph showing the relationship between the logarithm of the rate of reaction and the concentration of the reactants.

TABLE XXXXV Continued

	Time-Minutes	Absorbance
RUN 94	0	.705
	10	.705
pH = 10.30	1240	.494
	1250	.489
$[\text{OH}^-] = 1.99 \times 10^{-4}$	1260	.490
	2730	.329
	2740	.329
	2750	.325
$T_{1/2} = 2420 \text{ minutes}, K = .000287/\text{minute}$		
RUN 95	0	.914
	10	.914
pH = 9.1	1240	.894
	1250	.894
$[\text{OH}^-] = 1 \times 10^{-5}$	2730	.870
	2740	.870
$T_{1/2} \text{ extrapolated} = 38000 \text{ minutes}, K = .0000182/\text{minute}$		
RUN 96	0	.734
	1065	.735
pH = .81	6780	.734
RUN 97	0	.702
	1065	.701
pH = 2.92	6780	.703
RUN 98	0	.704
	1065	.702
pH = 4.70	6780	.707
RUN 99	0	.738
	1070	.740
pH = 6.21	6780	.742
RUN 100	0	.720
	1070	.720
pH = 6.95	6780	.721

TABLE IX (continued)

Run 94	0	10.30	$[\text{OH}^-] = 1.99 \times 10^{-4}$
	10	10.30	
	20	10.30	
	30	10.30	
	40	10.30	
	50	10.30	
	60	10.30	
	70	10.30	
	80	10.30	
	90	10.30	
Run 95	0	9.1	$[\text{OH}^-] = 1 \times 10^{-2}$
	10	9.1	
	20	9.1	
	30	9.1	
	40	9.1	
	50	9.1	
	60	9.1	
	70	9.1	
	80	9.1	
	90	9.1	
Run 96	0	10.1	
	10	10.1	
	20	10.1	
	30	10.1	
	40	10.1	
	50	10.1	
	60	10.1	
	70	10.1	
	80	10.1	
	90	10.1	
Run 97	0	10.1	
	10	10.1	
	20	10.1	
	30	10.1	
	40	10.1	
	50	10.1	
	60	10.1	
	70	10.1	
	80	10.1	
	90	10.1	
Run 98	0	4.70	
	10	4.70	
	20	4.70	
	30	4.70	
	40	4.70	
	50	4.70	
	60	4.70	
	70	4.70	
	80	4.70	
	90	4.70	
Run 99	0	6.21	
	10	6.21	
	20	6.21	
	30	6.21	
	40	6.21	
	50	6.21	
	60	6.21	
	70	6.21	
	80	6.21	
	90	6.21	
Run 100	0	6.92	
	10	6.92	
	20	6.92	
	30	6.92	
	40	6.92	
	50	6.92	
	60	6.92	
	70	6.92	
	80	6.92	
	90	6.92

Figure 67. Semi-logarithmic plot of absorbance against time for Runs 94 and 95.

LOG K VERSUS LOG C

TABLE XXXV Continued

	Time-Minutes	Absorbance
RUN 101	0	.638
	5	.570
pH = 12.67	10	.505
	15	.448
$[\text{OH}^-] = 4.68 \times 10^{-2}$	20	.394
	25	.350
	35	.274
	45	.215
	60	.154

$$T_{1/2} = 28.7 \text{ minutes, } K = .0243/\text{minute}$$

RUN 102	0	.683
	5	.600
pH = 12.99	10	.528
	15	.465
$[\text{OH}^-] = 9.77 \times 10^{-2}$	23	.372
	30	.311
	40	.240
	50	.185
	55	.164

$$T_{1/2} = 26.5 \text{ minutes, } K = .0263/\text{minute}$$

JAMES W. KELLEY

101 W. 101

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Figure 68. Semi-logarithmic plot of absorbance against time for Runs 101 and 102.

Variation of Rate with Temperature. The effect of temperature on the rate of hydrolysis was determined at pH 12.45 and 11.25. Data are presented in the manner of the preceding sections.

TABLE XXXXVI

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-2-PENTYL-2-IMIDAZOLINE AT pH 12.45

	Time-Minutes	Absorbance
RUN 103	0	.571
	5	.510
AT 25.6°	10	.450
	15	.403
	20	.398
	30	.286
	40	.223
	65	.121
	70	.111

$$T_{\frac{1}{2}} = 29.8 \text{ minutes, } K = .0233/\text{minute}$$

10
Variation of Rate with Temperature

Temperature on the rate of reaction is indicated by the following data. The rate of reaction was measured at 11.45 and 11.55. The preceding sections.

TABLE I

DATA FOR THE HYDROLYSIS OF 2-THIOBENZYL PHTHALATE

Time (min)	Concentration (M)	Rate (M/min)
0	0.005	0.000
10	0.004	0.001
20	0.003	0.002
30	0.002	0.003
40	0.001	0.004
50	0.000	0.005

Run 103
At 25.5°

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Figure 70. Semi-logarithmic plot of absorbance against time for Runs 104 and 105.

Wavelength (nm) vs. Optical Density (OD) for 100 mM and 10 mM solutions of the same substance.

Optical Density (OD)

TABLE XXXXVI Continued

	Time-Minutes	Absorbance
RUN 104	0	.428
	3	.350
AT 38.0°	6	.282
	9	.230
	12	.184
	15	.152
	18	.122
	21	.101
	24	.084

$$T_{\frac{1}{2}} = 10 \text{ minutes, } K = .0695/\text{minute}$$

RUN 105	0	.518
	2	.362
AT 48.9°	4	.255
	6	.182
	8	.126
	10	.091
	12	.062
	14	.045
	16	.033

$$T_{\frac{1}{2}} = 3.95 \text{ minutes, } K = .176/\text{minute}$$

104 RUN

AT 38.0°

105 RUN

AT 38.0°

106 RUN

AT 38.0°

Figure 69. Semi-logarithmic plot of absorbance against time for Run 103.

Figure 71. Temperature dependence of the rate constant for the hydrolysis of 1-hydroxyethyl-2-pentyl-2-imidazoline at pH 12.45.

TABLE XXXXVII

DATA FOR THE HYDROLYSIS OF 1-HYDROXYETHYL-2-PENTYL-
2-IMIDAZOLINE AT pH 11.25

	Time-Minutes	Absorbance
RUN 106	0	.698
	5	.688
AT 25.6°	15	.657
	30	.611
	50	.557
	90	.459
	155	.338
	215	.258
	259	.212

$$T_{1/2} = 151 \text{ minutes, } K = .00460/\text{minute}$$

TABLE XXXVII

DATA FOR THE KINETICS OF 1-HYDROXY-2-ETHYL-3-IMIDAZOLINE AT 25.0°C

Time, minutes	Optical density
0	0.00
5	0.05
10	0.10
15	0.15
20	0.20
25	0.25
30	0.30
35	0.35
40	0.40
45	0.45
50	0.50
55	0.55
60	0.60
65	0.65
70	0.70
75	0.75
80	0.80
85	0.85
90	0.90
95	0.95
100	1.00

$k = 1.21 \times 10^{-3} \text{ min}^{-1}$

Figure 72. Semi-logarithmic plot of absorbance against time for Run 106.

TABLE XXXXVII Continued

	Time-Minutes	Absorbance
RUN 107	0	.659
	5	.590
AT 38.0°	10	.540
	15	.490
	20	.440
	25	.399
	30	.357
	35	.330
	45	.269
	59	.205

$$T_{1/2} = 36 \text{ minutes, } K = .0193/\text{minute}$$

RUN 108	0	.638
	5	.454
AT 48.9°	9	.346
	12	.283
	14	.247
	16	.217
	19	.177
	24	.132
	29	.092
	37	.058
	42	.045

$$T_{1/2} = 10.3 \text{ minutes, } K = .0674/\text{minute}$$

TABLE XXVII Continued

Absorbance

Time-Minutes

0.639	0
0.590	5
0.540	10
0.490	15
0.440	20
0.392	25
0.357	30
0.330	35
0.303	40
0.265	45

RUN 107

AT 38.10°

$k = 0.0193/\text{minute}$

0.638	0
0.584	5
0.546	10
0.503	15
0.467	20
0.437	25
0.417	30
0.397	35
0.378	40
0.363	45

RUN 108

AT 48.7°

$k = 0.0674/\text{minute}$

Figure 73. Semi-logarithmic plot of absorbance against time for Runs 107 and 108.

Figure 74. Temperature dependence of the rate constant for the hydrolysis of 1-hydroxyethyl-2-pentyl-2-imidazoline at pH 11.25.

APPENDIX

A considerable number of experiments were performed before any understanding of the hydrolysis of imidazolines was achieved. More recent experiments and better understanding cast considerable doubt on the absolute validity of much of this earlier work, yet it is of some qualitative value.

This section will be devoted to description and discussion of some of this work.

Preparation and hydrolysis of 2-phenyl-1-hydroxy-ethyl-2-imidazoline. This compound was prepared by heating benzoic acid with hydroxyethylethylenediamine. The reaction products were purified by extraction and evaporative distillation.

Anal. Calcd. for $C_{11}H_{14}N_2O$: N. E., 190.

Found: N.E., 189.

The hydrolysis was carried out in ethanol at 70.48° , using Procedure I. Absorbance readings were recorded at $265\text{ m}\mu$ where there is a side band on the main absorption peak at $234\text{ m}\mu$. A graph of log absorbance versus time shows curvature so the recorded $T_{1/2}$ was found graphically by drawing a tangent to the initial portion of the curve. The curved line is probably caused by interference from the absorption peak at $234\text{ m}\mu$. The data for this run are presented graphically in Figure 75.

APPENDIX

A considerable number of experiments were performed before any understanding of the hydrolysis of imidazolines was achieved. Some recent experiments and better understanding each considerably doubt on the absolute validity of much of this earlier work, yet it is of some qualitative value.

This section will be devoted to description and discussion of some of this work.

Preparation and hydrolysis of 2-phenyl-1-hydroxy-

ethyl-2-imidazoline. This compound was prepared by heating benzoic acid with hydroxyethylimidamine. The reaction products were purified by extraction and evaporative distillation.

Anal. Calcd. for $C_{11}H_{14}N_2O$: N, 8.190.

Found: N, 8.190. The hydrolysis was carried out in ethanol at 70-80°C. using product I. Absorbance readings were recorded at 252 m μ where there is a side band on the main absorption peak at 235 m μ . A graph of log absorbance versus time shows curvature so the recorded T was found graphically by drawing a tangent to the initial portion of the curve. The curved line is probably caused by interference from the absorption peak at 235 m μ . The data for this run are presented graphically in Figure 1.

Figure 75. Semi-logarithmic plot of absorbance against time for the hydrolysis of 1-hydroxyethyl-2-phenyl-2-imidazoline.

Preparation and hydrolysis of 2-diphenylmethyl-1-hydroxyethyl-2-imidazoline. The imidazoline was prepared by heating 0.1 mole of ethyl diphenyl acetate with .1 mole of diamine. Usual purification procedures gave a low yield of product, m.p. 132-135.

Anal. Calcd. for $C_{18}H_{20}N_2O$: N. E., 280; N. 10.0.
Found: N.E., 283; N. 9.82.

Considerable quantities of diphenyl methane were isolated in this and subsequent preparations.

The hydrolysis of this compound was carried out in the same manner as with the preceding compound. Absorbance was measured at 235 $m\mu$ in this case. The spectrum of this compound shows strong absorption from 200 to 225 $m\mu$ and again the disappearance of a side band was used to follow the reaction. Figure 76 gives the data for this run.

Hydrolysis of 2-heptadecyl-1-hydroxyethyl-2-imidazoline in ethanol. Several experiments were performed in attempting to determine the rate of hydrolysis of this compound in 95% ethanol. Graphs of logarithm absorbance versus time gave curved lines with every indication that the reaction was approaching an equilibrium; but later experiments indicated that the effect was due to interference from the amide peak at 205 $m\mu$. The data given in Figure 77 are from a run at 70.48°.

Hydrolysis of 2-pentyl-1-hydroxyethyl-2-imidazoline in water. This reaction was run in aqueous one molar sodium

Hydrolysis of 2-ethoxy-1-phenylethanol

The hydrolysis of 2-ethoxy-1-phenylethanol was carried out by heating 2.1 mole of ethyl diphenyl acetate with 1.0 mole of diamine. Usual purification procedures gave a low yield of product, e.g., 55-65%.

Anal. Calcd. for $C_{18}H_{21}NO$: C, 82.0%; H, 8.0%; N, 10.0%.

Found: C, 82.3%; H, 8.3%; N, 9.8%.

Considerable quantities of diphenyl acetate were

isolated in this and subsequent preparations. The hydrolysis of this compound was carried out in

the same manner as with the preceding compound. Absorption

was measured at 255 m μ . In this case, the spectrum of

this compound shows strong absorption from 200 to 255 m μ .

and again the disappearance of a side band was noted.

Following the reaction, Figure 5 gives the data for this run.

Hydrolysis of 2-ethoxy-1-phenylethanol in ethanol

Several experiments were performed in attempting

to determine the rate of hydrolysis of this compound in 95%

ethanol. Graphs of logarithmic absorbance versus time gave

curved lines with every indication that the reaction was

approaching an equilibrium; but later experiments indicated

that the effect was due to interference from the amine

peak at 205 m μ . The data given in Figure 5 are from a

run at 50.48°.

Hydrolysis of 2-ethoxy-1-phenylethanol in water

This reaction was run in aqueous and other solvents.

Figure 76. Semi-logarithmic plot of absorbance against time for the hydrolysis of 2-diphenylmethyl-1-l-hydroxyethyl-2-imidazoline.

Fig. 1

Figure 77. Semi-logarithmic plot of absorbance against time for the hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline in 95% ethanol.

Figure 11. Plot of $\log_{10} \frac{1}{1 - \alpha}$ versus $\log_{10} \frac{1}{1 - \alpha}$ for the reaction of $\text{C}_2\text{H}_5\text{MgBr}$ with $\text{C}_2\text{H}_5\text{MgI}$ in benzene at -78°C . The data were obtained from the titration curves shown in Figure 10.

perchlorate at 38° . The data are of value only in that they show the initial rapidity of hydrolysis in water. The dashed line in Figure 78 indicates a half-life of about 240 minutes at the initial rate of reaction.

Influence of water on the rate of hydrolysis of 2-heptadecyl-1-hydroxyethyl-2-imidazoline in ethanol. Several early experiments indicate that the rate of hydrolysis in basic ethanol solution is strongly affected by the amount of water present.

In one pair of experiments, a half-life of approximately 180 minutes was found in 95% ethanol, but there was no detectable hydrolysis after six hours in ethanol that was .0028 molar in imidazoline and .01 molar in water.

In a set of comparable experiments at higher temperature, a half-life of about 40 minutes was found in 95% ethanol. When dry ethanol containing equal molar quantities of imidazoline and water was used as a solvent, the concentration of imidazoline decreased by only 14% in 180 minutes.

Influence of base concentration on the rate of hydrolysis of 2-heptadecyl-1-hydroxyethyl-2-imidazoline in ethanol. These experiments were set up as described on pages 74 and 75 of the experimental section. Weighed quantities of base were added to a known volume of solution of imidazoline in ethanol and the disappearance

[illegible]

Figure 78. Semi-logarithmic plot of absorbance against time for the hydrolysis of 1-hydroxyethyl-2-pentyl-2-imidazoline in water.

of imidazoline was followed by Procedure I, page 75, for a certain length of time. Another weighed quantity of base was then added and the reaction followed as before. Half-lives were obtained by extrapolation.

The results obtained here must be considered purely qualitative because of the uncertainty of extrapolation and the possible interference by amide in the latter stages of the reaction. It is also doubtful that the concentration of base added is representative of the amount of hydroxide ion present since ionization may be incomplete at high base concentration.

In spite of the probable lack of accuracy of this work, it does strongly indicate that a maximum rate is reached in ethanol solution.

The first experiment of this group used barium hydroxide as a catalyst. Time and absorbance values are depicted in Figure 79.

The tendency for the rate of reaction to approach a maximum is clearly indicated by the tabulation of the extrapolated half-lives from Figure 79 and the graph of K versus $[\text{Ba}(\text{OH})_2]$ in Figure 80.

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The first experiment of
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depicted in Figure 1.
The tendency for the
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extrapolated half-lives from Figure 1
K versus $\frac{1}{[A]_0}$ in Figure 2.

Figure 79. The effect of barium hydroxide concentration on the rate of hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline.

Figure 10

The effect of pH on the rate of polymerization of styrene in the presence of various concentrations of the initiator

Figure 80. The variation of rate constants with barium hydroxide concentration in the hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline.

Figure 10. The curve of the function $y = x^2$ for $x \in [0, 1]$.

$\underline{[\text{Ba}(\text{OH})_2] \times 10^4}$	$\underline{T_{\frac{1}{2}} \text{ minutes}}$	$\underline{K \times 10^3/\text{minute}}$
2.1	550	1.26
6.0	300	2.3
14.0	192	3.6
28.0	122	5.7
80.0	115	6.0

The final two experiments used sodium hydroxide as a catalyst. Figures 81 and 82 present the significant data from these experiments.

The tabulation of extrapolated half-lives for a given concentration of base again shows a maximum rate. The final two figures also indicate that the rate is dependent on the concentration of water present in the alcohol.

$\underline{[\text{NaOH}] \times 10^4}$	$\underline{T_{\frac{1}{2}} \text{ minutes}}$	$\underline{K \times 10^3/\text{minute}}$
7.15	340	2.0
44.0	207	3.35
176.0	110	6.3
383.0	100	6.9
335.0	106	6.5
1003.0	120	5.76
982*	90	7.7
932**	50	13.8

* 92% ethanol by volume

** 84% ethanol by volume.

The above data are presented graphically in Figure 82.

[NaOH] x 10³ T, minutes k x 10³ / minute

2.1	250	0.26
2.0	200	0.3
1.8	150	0.3
1.6	125	0.7
1.5	115	0.9

The final two experiments used sodium hydroxide as a catalyst. Figures 81 and 82 present the significant data from these experiments.

The calculation of extrapolated half-lives for a given concentration of base again shows a maximum rate. The final two figures also indicate that the rate is dependent on the concentration of water present in the alcohol.

[NaOH] x 10³ T, minutes k x 10³ / minute

1.5	260	1.0
1.6	205	0.25
1.7	110	0.3
1.8	100	0.8
1.9	105	0.3
2.0	120	0.35
2.1	90	0.7
2.2	50	0.8

* 92% ethanol by volume
 ** 84% ethanol by volume

The above data are presented graphically in Figure 81.

Figure 81. The effect of sodium hydroxide concentration on the rate of hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline.

Figure 81, Continued. The effect of sodium hydroxide concentration on the rate of hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline.

Figure 82. The variation of rate constants with sodium hydroxide concentration in the hydrolysis of 1-hydroxyethyl-2-heptadecyl-2-imidazoline.

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