The Kinetics and Mechanism of the Acid-catalysed Hydrolysis of *N*-Vinylpyrrolidin-2-one

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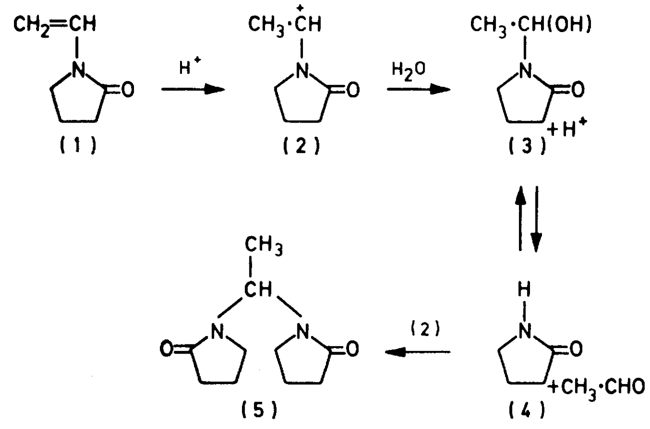
The kinetics and mechanism of the acid-catalysed hydrolysis of *N*-vinylpyrrolidin-2-one (1) has been studied using n.m.r. spectroscopy and spectrophotometry. At temperatures near 0 °C *N*-(1-hydroxyethyl)pyrrolidin-2-one (3) is the main product. At higher temperatures this decomposes into acetaldehyde and pyrrolidin-2-one (4) and the latter reacts with an excess of *N*-vinylpyrrolidin-2-one to give 1,1-bis-(*N*-2-oxopyrrolidinyl)ethane (5). The rate-determining step of the hydrolysis reaction has been established as proton transfer to *N*-vinylpyrroldin-2-one and the reaction conforms to a general acid catalysis mechanism. A Brønsted exponent value of 0.68 ± 0.03 was obtained with a series of carboxylic acids.

THE instability of *N*-vinylpyrrolidin-2-one (1) in the presence of acid has been reported by Breitenbach *et al.*[1] These workers isolated 1,1-bis-(*N*-2-oxopyrrolidinyl)-ethane (5) from aqueous solutions of (1) and hydrochloric acid and postulated the reaction sequence in the Scheme.



SCHEME

In the early stages of a project concerned with the polymerisation of (1) in aqueous solution, potassium persulphate was investigated as a radical source. Reaction readily occurred at 50° and initial rates were determined. However reaction mixtures taken to high conversion were less viscous than anticipated and on dialysis only a small amount of poly(vinylpyrrolidinone) was recovered. Further studies [2] confirmed (5) as a major reaction product, arising because of the mildly acidic conditions (pH *ca.* 3.5) of the persulphate solution. This prompted a detailed investigation of the hydrolysis reaction involving n.m.r. and kinetic measurements. The results confirm the Breitenbach reaction scheme and show that the hydrolysis of (1) is subject to general acid catalysis with initial slow proton transfer. This mechanism is identical to that established for vinyl ether hydrolysis [3,4] and that recently shown to apply to the acid-catalysed hydrolysis of *N*-vinylacetamides.[5]

EXPERIMENTAL

Materials.—(a) *N*-Vinylpyrrolidin-2-one (Haven Chemical Co.) was fractionally distilled using a spinning band column. A middle fraction, b.p. 74° at 2.5 mmHg, was collected.

(b) 1,1-Bis-(*N*-2-oxopyrrolidinyl)ethane was prepared by mixing pyrrolidin-2-one (4) and (1) in equimolar proportions and bubbling hydrogen chloride through the mixture. The resulting solid was recrystallised from acetone–ether. The structure of the product was confirmed by ^1H n.m.r. and mass spectroscopy.

(c) Analytical reagent grade carboxylic acids were used without further purification. The pH of buffer solutions, adjusted to constant ionic strength by the addition of potassium chloride, were independent of buffer concentration over the range used in kinetic experiments.

^1H *N.m.r. Spectroscopy*.—Spectra of reaction mixtures of (1) (10—90% by volume) and acidified deuterium oxide ($[D_3O^+] = 10^{-4}$—10^{-1} mol dm^{-3}) were measured *in situ* at constant temperature (0—50°) after various time intervals, using a JEOL Minimar 100 spectrophotometer. Except with the higher acid concentrations and temperatures the reaction rate was sufficiently slow for the reaction sequence to be conveniently studied.

Kinetics.—These measurements were made using a Zeiss PMQ spectrophotometer. Acid solutions were introduced directly into two matched 1 cm silica cells thermostatted (±0.01°) within the spectrophotometer. When thermal equilibrium was established μl quantities of an aqueous solution of (1) were introduced into the sample cell and the contents immediately mixed. After allowing time for the re-establishment of temperature equilibrium, absorbance measurements were recorded on a chart recorder. Reactions catalysed by inorganic acids and cyanoacetic acid were sufficiently fast at 25° for them to be followed over at least two half-lives. With the other organic acids used initial reaction rates only were measured at 25°, although the reactions could be conveniently followed to high conversion at elevated temperatures. Reactions catalysed by hydrochloric acid, sulphuric acid, and perchloric acid were studied at 233 nm where (1) has a maximum molar absorption coefficient. Runs with nitric acid and the various organic acid buffer solutions were done at 245—260 nm because of significant light absorption at lower wavelengths.

RESULTS AND DISCUSSION

Figure 1 shows the ^1H n.m.r. spectrum of a typical reaction mixture. The peaks at τ 6.2—6.8 and at 7.4—8.2 are due to pyrrolidinone ring protons and cannot be used to distinguish the various products. Similarly, the peaks at τ 8.4—8.9 can be assigned to the deuteriated methyl group in *N*-(1-hydroxymethyl)pyrrolidin-2-one (3), (5), and the hydrated form of acetaldehyde. The peaks in the range τ 4—5 are distinctive however, and can be attributed to the C–H in (5) (triplet at τ 4.2), in (3) (triplet at τ 4.4), and in hydrated acetaldehyde[6,7] (broad absorption at τ 4.7). This enabled these products to be monitored, at least qualitatively, throughout the reaction. Unchanged *N*-vinylpyrrolidin-2-one was detected by its characteristic absorption at τ 2.6—3.0. Peak assignments were supported by spectra obtained with essentially pure compounds. The presence of pyrrolidin-2-one in reaction mixtures could not be demonstrated because of its exchangeable proton.

Spectra obtained showed several features. The most interesting result was that at low temperatures (*ca.* 0°) and acid concentrations (pH >2.5), (1) completely reacted to give (3) over a time interval where the latter showed no evidence of any further reaction. Thus under these conditions (3) is essentially the only reaction product. At higher temperatures (30°), (5) and acetaldehyde were detected in the presence of (3) and unchanged (1). This indicates that the overall activation energy of the reactions producing (3) is less than that of its subsequent decomposition reaction.

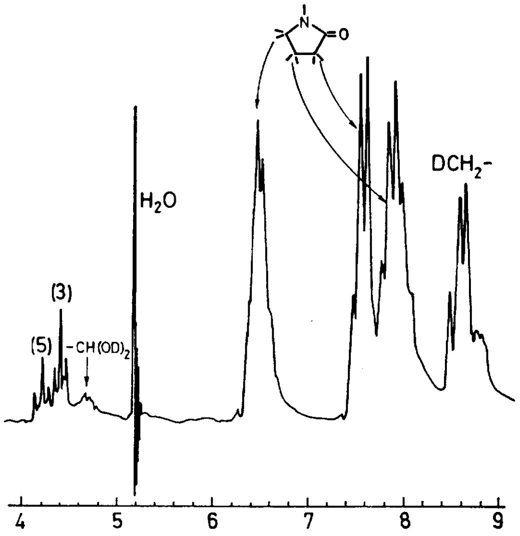


FIGURE 1 ^{1}H N.m.r. spectrum of *N*-vinylpyrrolidin-2-one in acidified D$_2$O

The reversibility of the decomposition reaction of *N*-(1-hydroxyethyl)pyrrolidin-2-one to acetaldehyde and pyrrolidin-2-one was confirmed by mixing these compounds in deuterium oxide in the presence of acid at 31°. Observation of the n.m.r. spectrum showed the relatively rapid protection of (3), followed by the slower formation of (5). In the presence of excess of acetaldehyde (5) was not observed. An acidified solution of (5) in D$_2$O reacted slowly, the n.m.r. spectrum showing the production of acetaldehyde and (3). This indicates that the acid-catalysed reaction between pyrrolidin-2-one and *N*-vinylpyrrolidin-2-one is also reversible, although the equilibrium at normal temperature is well in favour of the addition compound.

A detailed kinetic study of the hydrolysis reaction was carried out by monitoring the consumption of (1) spectrophotometrically in the presence of strong acids and various carboxylic acid buffer solutions. The results confirmed a first-order dependence on *N*-vinylpyrrolidin-2-one concentration in all cases. Pseudo-first-order rate constants (k') calculated at different inorganic acid concentrations, together with the corresponding second-order rate constants, are shown in the Table. Values of k increase slightly with acid concentration. This was shown to be the effect of increasing ionic strength, since

Rate constant data obtained with different concentrations of various strong acids at 24.7 °C

Acid	10^2[Acid]/mol dm^{-3}	10^4k^1/s^{-1}	10^2k/ dm^3 mol^{-1} s^{-1}
HCl	0.585 ± 0.015	1.52	2.60 ± 0.07
	0.878 ± 0.015	2.32	2.62 ± 0.05
	1.17 ± 0.02	3.04	2.59 ± 0.05
	1.76 ± 0.03	4.61	2.62 ± 0.04
	2.34 ± 0.04	6.12	2.61 ± 0.05
	4.83 ± 0.11	13.0	2.69 ± 0.06
	9.76 ± 0.10	27.0	2.77 ± 0.03
HNO$_3$	0.1 ± 0.01	0.256	2.59 ± 0.25
	1.49 ± 0.03	3.97	2.66 ± 0.06
	3.38 ± 0.05	9.14	2.70 ± 0.04
	5.88 ± 0.12	16.4	2.79 ± 0.06
	7.48 ± 0.12	20.9	2.80 ± 0.05
	9.96 ± 0.10	28.5	2.86 ± 0.03
HClO$_4$	0.450 ± 0.015	1.20	2.67 ± 0.09
	2.36 ± 0.04	6.38	2.70 ± 0.05
	3.26 ± 0.05	9.02	2.77 ± 0.05
	5.06 ± 0.12	14.1	2.79 ± 0.07
	7.64 ± 0.12	21.5	2.82 ± 0.05
	11.2 ± 0.10	32.2	2.87 ± 0.03
H$_2$SO$_4$	0.248 ± 0.01	1.33	5.38 ± 0.22
	0.497 ± 0.015	2.42	4.88 ± 0.15
	2.48 ± 0.04	12.8	5.16 ± 0.08
	4.97 ± 0.11	25.6	5.16 ± 0.12

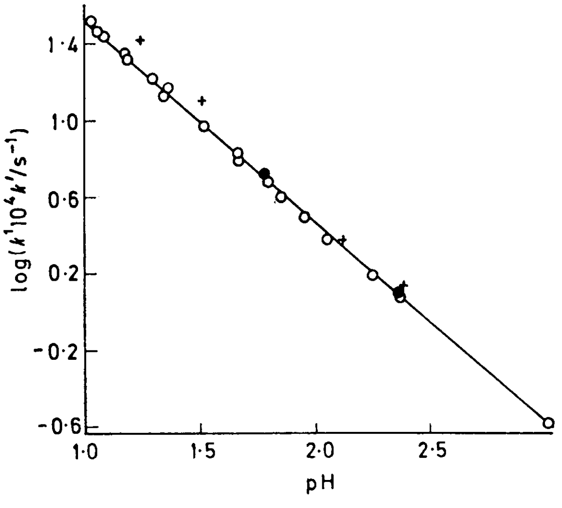


FIGURE 2 Plot of logarithm of pseudo-first-order rate constant against measured pH for reactions conducted in (○) HCl, HClO$_4$ and HNO$_3$; (+) H$_2$SO$_4$; and (●) HCO$_2$H. Temperature 24.7°

repetition of the experiments with hydrochloric acid at a constant ionic strength of 9.75×10^{-2} mol dm^{-3} (adjusted by the addition of potassium chloride) gave a constant value for k $2.75 \pm 0.04 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} Arrhenius plots for the reaction catalysed by hydrochloric and nitric acid yielded activation parameters of E 83 ± 5 kJ mol^{-1} and ΔS^* 22 ± 17 J mol^{-1} K^{-1} for the second-order rate constant. The value obtained for ΔS^* is reasonable for an ion–neutral molecule rate-determining reaction where electrostatic effects are expected to be small.[8] Comparison of the data in the Table for the monobasic acids suggests slight specific effects on the reaction rate attributable to the anion, in the order perchlorate $\geqslant$ nitrate $>$ chloride ion. Similar observations have been made in the acid-catalysed hydration of 2-methylpropene [9] and 2-methylbut-2-ene.[10] The Table also shows that the second-order rate constant is greater, by a factor of *ca.* 2, when the reaction is catalysed by sulphuric acid. In Figure 2 the effect is further displayed in a plot of log k' against the measured pH of the solution. This rate enhancement can be attributed to a relatively pronounced salt effect of the hydrogensulphate ion. However, it more likely arises through a mechanism of general acid catalysis involving slow proton transfer to *N*-vinylpyrrolidin-2-one from the hydrogensulphate ion. There is slight evidence from Figure 2 that undissociated formic acid molecules may also function as a general acid.

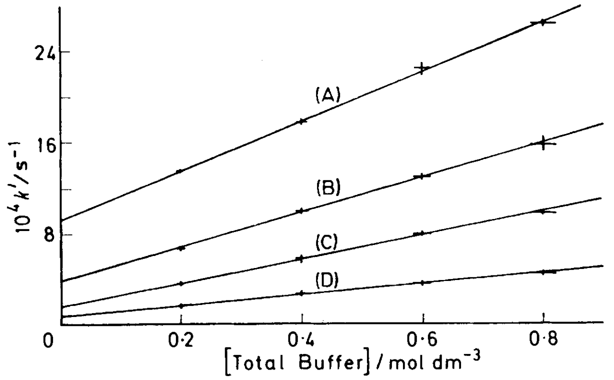


FIGURE 3 Plot of pseudo-first-order rate constant against total buffer concentration for hydrolysis of (1) with solutions of $[HCO_2H]/[HCO_2Na]$ = 4.0 (A), = 1.5 (5), = 0.67 (C), = 0.25 (D). Ionic strength (adjusted by the addition of KCl) = 1 mol dm^{-3}. Temperature = 53.9°. Uncertainties shown represent 90% confidence limits

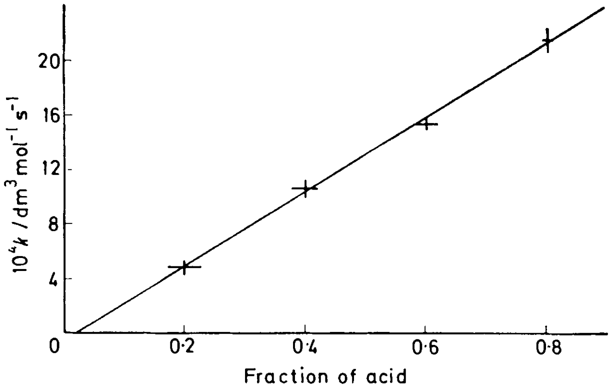


FIGURE 4 Plot of second-order velocity constant calculated from the slopes of straight line plots of Figure 3 against fraction of formic acid in buffer solution. Uncertainties shown represent 90% confidence limits

Conclusive evidence for a general acid catalysis mechanism was obtained by determining the pseudo-first-order rate constant with a number of formic acid–sodium formate buffer solutions. Analysis of the results (Figures 3 and 4) shows that at constant hydronium ion concentration, k' is directly dependent on the concentration of undissociated formic acid and independent of the concentration of formate ion. Similar results were obtained using acetic acid and chloroacetic acid buffers at 65.0 and 35.0°, respectively. Thus the measured pseudo-first-order rate constant is given by equation (1) where k_{HA} is the rate constant for the

$$k' = k[H_3O^+] + k_{HA}[HA] \qquad (1)$$

general acid proton transfer reaction. Studies at 25° with a series of carboxylic acid buffers enabled k_{HA} to be evaluated for these from the slope of plots similar to Figure 3. The data so determined are plotted as a Brønsted relation in Figure 5, statistical factors of $p = 1$ and $q = 2$ being assumed. The value obtained for the Brønsted exponent, α, given by the calculated line of best slope is 0.68 ± 0.03, which is similar to values determined for the carboxylic acid catalysed hydrolysis of vinyl ethers.[11] Deviations from this relationship observed with rate data for *N*-vinylpyrrolidin-2-one hydrolysis catalysed by hydrogen sulphate ion ($p = 1$, $q = 4$) and hydronium ion ($p = 3$, $q = 1$) also follow the pattern observed in vinyl ether hydrolysis. The rate accelerating effect associated with negatively charged catalysts such as the HSO_4^- ion has been attributed to an energy lowering interaction with the partially positively charged substrate centre of the transition state (6).[12] In contrast interaction in the transition state with a positively charged proton source, leads to higher free

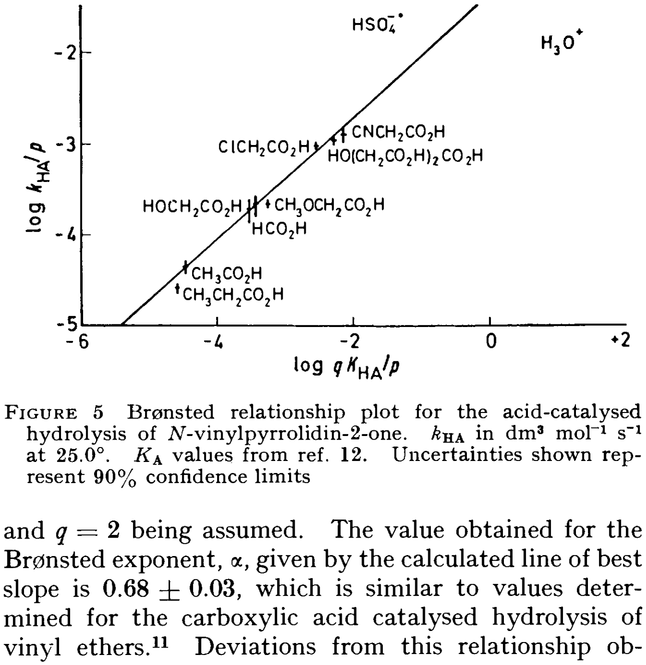
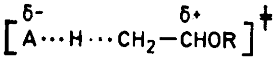


FIGURE 5 Brønsted relationship plot for the acid-catalysed hydrolysis of *N*-vinylpyrrolidin-2-one. k_{HA} in dm^3 mol^{-1} s^{-1} at 25.0°. K_A values from ref. 12. Uncertainties shown represent 90% confidence limits

energies of activation than expected with neutral carboxylic acids.

Comparison of rates for the hydrochloric acid catalysed reaction in water and deuterium oxide gave k_{H^+}/k_{D^+} 3.45 at 24.6°. This ratio can be compared with values of 2.95 at 26.7° and 3.8 at 25° measured for the acid-catalysed hydrolysis of ethyl vinyl ether [7] and *N*-vinylacetamide,[5] respectively. The observed kinetic isotope effect is that expected for a mechanism involving rate controlling proton addition to the vinyl group.



$$\left[\overset{\delta-}{A}\cdots H\cdots CH_2-\overset{\delta+}{C}HOR\right]^{\ddagger}$$

(6)

We thank Dr. G. V. Meehan for helpful discussions.

[8/969 *Received*, 23*rd May*, 1978]

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