Salt Effect.—The influence of salts on the hydrochloric acid catalyzed depolymerization of trioxane at 40° was studied for six different salts. For each kinetic run the acid concentration was 4 *M* and the salt concentration 1 *M*. The ratios k_s/k are given in Table III, where k_s and k are the rate constants for the salt mixture and the salt free mixture, respectively. The corresponding ratios for the hydrochloric acid catalyzed hydrolysis of sucrose[3a] and of methylal[3c] at 25° are included for comparison. In each case the rate is increased by addition of salt, the salts with the smaller cations being the most effective. It is also interesting to note that the magnitude of the salt effect decreases with increasing size of the molecule undergoing decomposition; *i.e.*, sucrose < trioxane < methylal.

Table III

Salt Effects on the Rates of Some Hydrochloric Acid Catalyzed Reactions

Salt (concn. = 1 *M*)	k_S/k Trioxane depolymeriz. at 40° (HCl) = 4 *M*	Sucrose[a] hydrolysis at 25° (HCl) = 1 *M*	Methylal hydrolysis at 25° (HCl) = 0.371 *M*
LiCl	2.12	1.44	2.6
NaCl	1.87	1.39	2.3
KCl	1.50	1.33	2.1
NH_4Cl	1.50	..	..
$N(CH_3)_4Cl$	1.23	..	..
C_6H_5NHCl	1.47	..	..

[a] Salt concentrations are 1 molal.

According to the Brönsted equation for medium effects on the first order rate constant (equation 1), changes in k due to the presence of salts in the reaction mixture depend upon the influence of the salt upon the ratio $a_{H^+}f_{F_t}/f_{M^+}$. In the case of the hydrolysis of methylal,[3c] Long and McIntyre showed that salt effects on the activity coefficient of methylal (corresponding to f_{F_t} in the present study) do not parallel the changes produced on the rate constant; hence for this reaction the ratio a_{H^+}/f_{M^+} must also vary with salt concentration.

The salt effect of lithium chloride was studied over a wide range of acid and salt concentrations. The rate constants for the various reaction mixtures are given in Table IV. It was found that the logarithm of the rate constant varies linearly with the salt concentration, the slope being independent of the acid concentration. Thus

$$\log k = -1.16H_0 + 0.320c_s - 6.318 \qquad (3)$$

where c_s is the molar concentration of the salt and H_0 is the acidity function for the salt free acid solution.

Table IV

Rate Constants for the Depolymerization of Trioxane in Aqueous HCl–LiCl Mixtures at 40°

HCl, *M*	LiCl, *M*	$k \times 10^6$ (sec.$^{-1}$) (exptl.)	(calcd., eq. 3)
2	5	125	120
3	0	7.68	8.0
3	1	14.8	16.6
3	4	135	151
4	0	20.0	20.0
4	1	44.5	41.7
4	2	93.3	87.0
4	3	197	182
4	4	467	380
5	0	52.3	52.5
5	1	108	110
5	2	247	229
6	0	136	138
6	1	278	288

[Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois]

Rate Processes and N.m.r. Spectra. III. Proton Exchange and Hydrolysis of Amides[1]

By A. Saika[2]

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The chemical exchange of the NH protons in pure liquid N-methylformamide (NMF) and N-methylacetamide (NMA) and the hydrolysis of the compounds in acid solution have been studied by high resolution proton magnetic resonance methods. The activation energy required for exchange among the NH protons is found to be 14 ± 2 kcal. mole^{-1} for both NMF and NMA. The rate constants of the acid hydrolysis were determined at three different temperatures, giving activation energies of 13 ± 3 and 15 ± 3 kcal. mole^{-1} for the hydrolysis of NMF and NMA, respectively. The relationship between the proton exchange and the acid hydrolysis is discussed, and it is proposed that the N-protonated form of the amides is that which undergoes the acid hydrolysis.

Introduction

A high resolution nuclear magnetic resonance (n.m.r.) spectrum exhibits fine structure as a result of chemical shifts and the electron coupling of nuclear spins.[3] These components are usually narrow because the random molecular tumbling in the liquid or gaseous state averages out the direct magnetic interaction between the nuclear spins.[4] However, the high resolution fine structure may in turn be broadened or averaged out by rate processes, in particular by the exchange of nuclei between chemically non-equivalent sites or among the sites in which nuclei experience the indirect spin-spin coupling. The possibility of evaluating the rate constants and activation energies for such processes was pointed out in the first paper of this series.[5]

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(1) This work was supported in part by the Office of Naval Research and by Grants-in-Aid from the E. I. du Pont de Nemours and Co. and from the Upjohn Co.

(2) On leave of absence from Himeji Technical College, Himeji, Japan. Reprints of this article may be obtained from H. S. Gutowsky.

(3) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(4) N. Bloembergen, E. M. Purcell and P. V. Pound, *Phys. Rev.*, **71**, 466 (1947).

(5) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953). Hereafter called Paper J.

In the second paper,[6] the principles were developed in more detail and applied to the study of the hindered rotation about the carbon–nitrogen bond in N-dimethyl formamide (DMF) and N-dimethylacetamide (DMA). In these compounds at room temperature, the N-dimethyl proton resonance is a doublet, the splitting being a chemical shift caused by the planar structure and resulting nonequivalence of the two N-methyl groups. The rate constants and activation energies for the hindered rotations were evaluated by observing the coalescence of the doublets at higher temperatures.

In the present paper, the coalescence of proton doublets is also used to determine rate constants. However, in this case the doublets are produced by the electron coupling of nuclear spins rather than by a chemical shift, and the rate process is not an internal rotation but a chemical exchange of protons. The compounds studied are N-methylformamide (NMF) and N-methylacetamide (NMA). As reported in brief before,[6] the proton resonance of the N-methyl group in these compounds is split into a doublet by the indirect spin–spin coupling of the N-methyl protons with the NH proton. Since doublets of this nature would appear independent of the occurrence or absence of internal rotation about the C–N bond of the molecule, we cannot investigate the internal rotation of NMF and NMA as was done with DMF and DMA.[6] Incidentally, a broadened weak resonance due to the NH proton, which had not been observed before,[6] was found in NMA at $\delta = +0.29$, δ being defined as $10^5(H_r - H_c)/H_r$ with H_2O the reference compound.

The doublets of NMF and NMA were observed to coalesce at higher temperatures. Moreover, they can be made to coalesce even at room temperature by the addition of H_3O^+ or OH^- ions. The dynamic process responsible for the coalescence thus appears to be intermolecular chemical exchange among the NH protons, which is acid and base catalyzed. This conclusion is consistent with evidence furnished by Brodskii,[7] who found that acetamide exchanges with D_2O the two hydrogen atoms bound to nitrogen. Recently, the kinetics and mechanism of this protolysis in aqueous solutions of NMA were studied by Berger, *et al.*,[8] who determined the exchange rates by observing the broadening of the n.m.r. absorption of the N-methyl doublet and of the water. Our studies of the temperature dependence of the protolysis of NMF and NMA provide activation energies for the reaction. A second set of experiments was concerned with the hydrolysis in aqueous acidic solution of NMF and NMA which occurs in addition to the proton exchange. The hydrolysis is also acid and base catalyzed,[9] but it proceeds at a much slower rate than the proton exchange. However, the hydrolysis reaction removes H^+ from the acid solutions in question, thereby decreasing the rate of the proton exchange. In turn, the change in exchange rate affects the coalescence of the N-methyl proton doublet, which is the parameter we observed and used to determine the hydrolysis rate.

Experimental

The high resolution n.m.r. spectrometer and experimental techniques used in these experiments are the same as described in Paper II, except for minor changes in the sample spinning device. The samples of NMF and NMA were Eastman Kodak Co. white label grade chemicals and were sealed in Pyrex tubes with an outside diameter of 4 mm. The acid and the alkali used were dilute hydrochloric acid and aqueous sodium hydroxide, respectively.

Results

Before discussing the experimental results, it should be noted that the coalescence of the doublets discussed in the present paper corresponds physically to that described in the first treatment of the general question,[3] rather than that given in papers I and II, since the doublets of NMF and NMA are caused by indirect spin–spin coupling rather than by chemical shifts as mentioned above. However, the mathematical features for both of the particular cases are the same as shown in Paper I and, therefore, the method developed in Paper II is used in analyzing the present data. This simple treatment is applicable, first of all, because the dynamic process is a chemical exchange which disrupts the spin–spin coupling and, secondly, because the difference in resonance frequency between the NH and $N-CH_3$ protons is large enough compared to the coupling constant that the components of the doublet have virtually the same intensity.[3]

The spin–spin doublet splitting is affected by the mean lifetime τ_N of the NH proton in a given spin state. In the present case this is essentially the mean chemical lifetime of the NH proton in the molecule and corresponds to 2τ used throughout Paper II. Spin-lattice relaxation also affects the doublet splitting.[3] This contribution and its dependence upon experimental conditions are relatively small; the latter is neglected by absorbing the effect in the correction applied to the splitting to allow for broadening of the components by field inhomogeneities.[6] With this in mind, we can apply equation 7 of Paper II intact in analyzing the following data.

TABLE I

TEMPERATURE DEPENDENCE OF $1/\tau\delta\omega$

N-methylformamide			N-methylacetamide		
T, °K.	$\delta\omega_e$, radian/sec.	$1/\tau\delta\omega$, radian^{-1}	T, °K.	$\delta\omega_e$, radian/sec.	$1/\tau\delta\omega$, radian^{-1}
301.5	30.0	0.00	302	29.5	0.00
368	28.1	.13	410	28.5	.09
373	28.3	.11	413	28.2	.11
379	27.1	.17	418	28.3	.10
383	25.7	.21	422	27.6	.15
386	24.6	.26	426	27.4	.15
390	23.6	.27	431	26.7	.19
393	21.0	.34	435	26.0	.22
395	19.2	.37	441	25.4	.24
395.5	18.7	.38	445	24.1	.28
			449	20.5	.37
			449.5	20.2	.37
			451.5	17.0	.43

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(6) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956). Hereafter called Paper II.

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(8) A. Berger, A. Loewenstein and S. Meiboom, THIS JOURNAL, **81**, 62 (1959).

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TABLE II

SUMMARY OF RESULTS FOR THE NH PROTON EXCHANGE IN N-METHYLFORMAMIDE AND N-METHYLACETAMIDE

	T_2,[a] sec.	$\delta\omega_\infty$, radian/sec.	$\delta\omega$, radian/sec.	T_c,[b] °K.	E_a, kcal./mole	ν_0, sec.$^{-1}$
NMF	0.13 ± 0.01	30.0 ± 0.2	30.2 ± 0.2	404 ± 1	14 ± 2	10^7 to 10^{10}
NMA	0.16 ± 0.01	29.5 ± 0.2	29.6 ± 0.2	461 ± 1	14 ± 2	10^6 to 10^8

[a] T_2 is defined as $2/\Delta\omega_{1/2}$, where $\Delta\omega_{1/2}$ is the width of each component of the doublet at half-maximum. [b] T_c is the temperature at which the doublet coalesces to a single line.

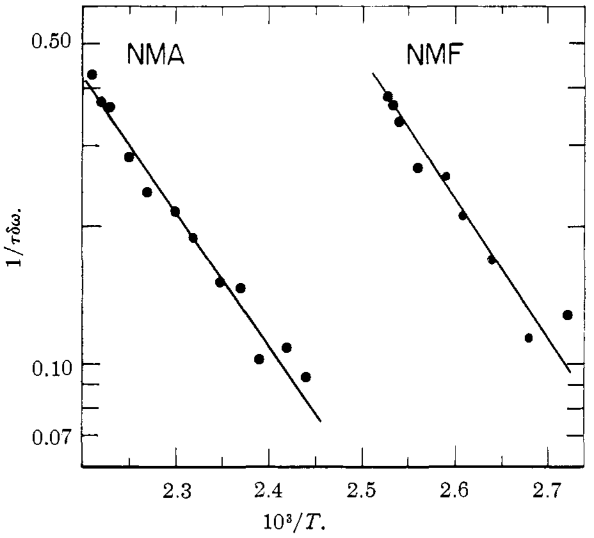

Fig. 1.—Temperature dependence of the NH proton exchange rate in pure liquid N-methylformamide (NMF) and N-methylacetamide (NMA). The exchange rate is proportional to $1/\tau\delta\omega$, the log of which is plotted *versus* the reciprocal temperature, $10^3/T$. The least squares straight lines give activation energies for the exchange of 14 ± 2 kcal. mole^{-1} for both NMF and NMA.

NH Proton Exchange in Pure N-Methylformamide and N-Methylacetamide.—These experiments were performed upon the pure liquids to which no acid or base had been added. It was found that the N-methyl proton resonance of NMF and NMA, which is a doublet at room temperature, coalesced to a single line at 404 and 461° K., respectively, and we have attributed this to chemical exchange among the NH protons. The exchange rate must be too slow at room temperature to average out the doublet splitting and the rate should increase as the temperature goes up. The experimentally observed doublet splitting, $\delta\omega_e$, at various temperatures for NMF and NMA is given in Table I together with the values of $1/\tau\delta\omega$ calculated from the observed values. We took the value of $\delta\omega_\infty$, the observed doublet splitting as $\tau \rightarrow \infty$, to be the value at room temperature, since the coalescence temperatures for NMF and NMA are well above room temperature. Table II lists the values of the inverse line width T_2 and of $\delta\omega_\infty$ employed in these calculations. The splitting, $\delta\omega$, assuming no exchange and no overlap of the resonance components, is calculated from $\delta\omega_\infty$ and T_2 using eq. 8 of II.

The temperature dependence of the exchange rate may be represented by the form

$$k_N = \nu_0 \exp(-E_a/RT) \qquad (1)$$

where k_N is the exchange rate constant of the NH proton, ν_0 the frequency factor and E_a the activation energy for the exchange. k_N and τ_N are related by $k_N = 1/\tau_N = 1/2\tau$, and eq. 1 can be rewritten as

$$\log\,(1/\tau\delta\omega) = \log(2\nu_0/\delta\omega) - E_a/(2.3\,RT) \qquad (2)$$

$\text{Log}(1/\tau\delta\omega)$ taken from the data of Table I is plotted *versus* $10^3/T$ in Fig. 1, and is fitted by eq. 2 within experimental error. The activation energies estimated from the data are 14 ± 2 kalc.mole^{-1} for both NMF and NMA and the frequency factors, ν_0, are 10^7 to 10^{10} and 10^6 to 10^8, respectively. Inasmuch as the activation energies are about the same, the higher coalescence temperature for NMA is due to its lower apparent frequency factor compared with NMF. The difference in frequency factors could result from the steric effect of the C-methyl group. However, the frequency factors for the internal rotation of DMF and DMA differ in the opposite direction. It may be significant that the frequency factors are low in all four compounds. This could be attributed at least in part to a temperature dependent term in E_a, say as a result of the temperature dependent molecular association. Relatively small terms of this sort are needed to explain the low apparent frequency factors.

Hydrolysis of the Amides.—A kinetic study of the acid and base hydrolysis of amides was first made by Reid,[9] who found that the reactions follow a second order rate law, with the rate proportional to [amide][H^+] or [amide][OH^-]. More detailed studies have since been made by several other workers.[10] In our experiments barely enough acid or base was added to NMF or NMA, at a given temperature, so that the NH proton exchange coalesced the N-methyl doublet. The proton exchange rate is also proportional to[8] [amide][H_3O^+] or [amide][OH^-] and by making [H_3O^+] or [OH^-] large enough, the doublets can be coalesced even at room temperature. However, the hydrolysis occurs in addition to the proton exchange, thereby decreasing [H_3O^+] or [OH]$^-$. Therefore, as the hydrolysis proceeds, the proton exchange rate decreases and the coalesced doublet starts to split again. The reappearance of the doublet and, in particular, the measurement of the splitting as a function of time enabled us to determine the rate of hydrolysis of NMF and NMA. From the splittings, $\delta\omega_e$, the values of $1/\tau\delta\omega$ were evaluated in the same manner as described above.

Aqueous hydrochloric acid[11] was added to NMF and NMA in our studies of the acid hydrolysis.

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(11) At the time of the experiments we were unaware of the fact that the activation energy depends upon the concentration of the acid.

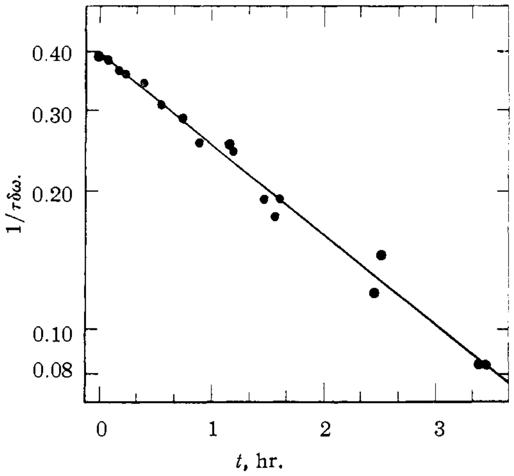


Fig. 2.—The rate of acidic hydrolysis of N-methylformamide as determined from measurements of the H_3O^+ concentration *via* its effect upon the NH proton exchange rate. $[H_3O^+]$ is proportional to $1/\tau\delta\omega$, the log of which is plotted against time. The slope of the least squares straight line gives a pseudo first order rate constant for the hydrolysis of 1.26×10^{-4} sec.$^{-1}$.

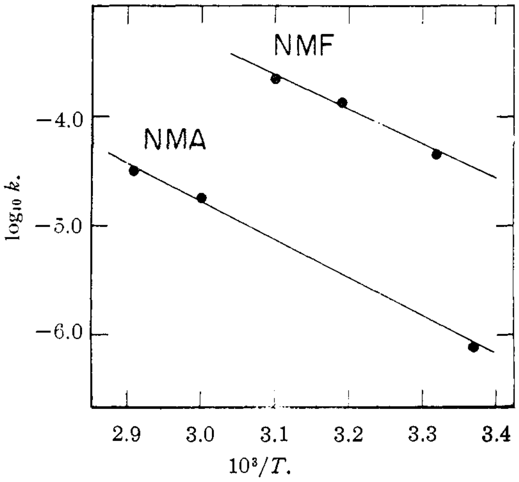


Fig. 3.—Temperature dependence of the rate of acid hydrolysis for N-methylformamide (NMF) and N-methylacetamide (NMA). The plots of log k *versus* the reciprocal temperature $10^3/T$, where k is the pseudo first order rate constant, have slopes corresponding to activation energies of 13 ± 3 and 15 ± 3 kcal. mole^{-1} for the hydrolysis of NMF and NMA, respectively.

Too much acid could not be added, otherwise the doublet would "recover" too slowly, the rate expressions would be complicated, and also the N-methyl proton resonance signal would be weakened. With the amounts of acid added, the amide concentration may be regarded as constant throughout the reaction, at least within the errors inherent in measuring $\delta\omega_e$ and $\delta\omega_\infty$. Hence the hydrolysis reaction will be pseudo first order in the acid concentration, represented by $-d[H_3O^+]/dt = k\cdot[H_3O^+]$. Moreover, τ_N, the mean lifetime of the NH proton with respect to chemical exchange, is proportional to $1/[H_3O^+]$. Therefore, a plot of log $(1/\tau\delta\omega)$ *versus* time should be a straight line, the slope of which gives us the value of the rate constant k. Such a plot for the case of NMF at 313°K. is shown in Fig. 2 as an example. The values of k thus obtained at three different temperatures for NMF and NMA are collected in Table III. These k's actually include the amide concentration, or some function of it, *e.g.*, $k = k_h[\text{amide}]$; however, to a good enough approximation, the concentration of amide was the same in the experiments at different temperatures. Thus, a plot of log k *versus* $10^3/T$ should be a straight line with a slope corresponding to the activation energy for the hydrolysis. This is shown to be the case in Fig. 3 from which activation energies for the acid hydrolysis of NMF and NMA were estimated to be 13 ± 3 and 15 ± 3 kcal. mole^{-1}, respectively. These values are in the same range as those for other amides,[10] though no data for NMF and NMA seem to be available in the literature for direct comparison.

TABLE III

SPECIFIC RATE CONSTANTS[a] FOR THE ACID HYDROLYSIS OF THE AMIDES

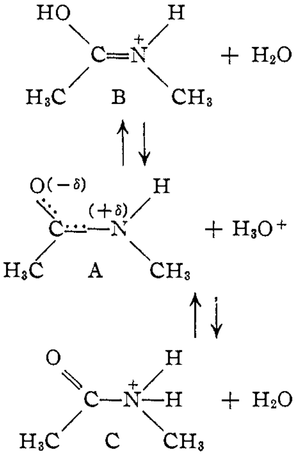
	N-methylformamide			N-methylacetamide		
Temp., °K.	301	313	323	297	333	343
$k \times 10^4$, sec.$^{-1}$	0.47	1.3	2.2	0.008	0.18	0.34

[a] The k's are actually pseudo first order rate constants; *i.e.*, $k = k_h[\text{amide}]$ where [amide] was effectively the same in the experiments on each compound.

We have not carried out detailed experiments on the alkaline hydrolysis of NMF and NMA, but preliminary runs show that it is considerably faster than the acid hydrolysis. This agrees with the lower activation energies found for the alkaline hydrolysis of other amides.[12]

Discussion

Let us first consider the proton exchange. From their study of the reaction in aqueous acidic solutions of NMA, Berger, *et al.*,[8] proposed that the proton exchange involves the equilibria



(I)

Their conclusion that the equilibrium A ⇄ B does not contribute to the proton exchange ob-

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We added 2 N HCl at 28 and 40° and 3 N HCl at 50° to NMF, and 1 N HCl to NMA at all the temperatures studied. However, the resultant variations in the activation energy should be within our experimental error, as can be seen from the results of B. S. Rabinovitch and C. A. Winkler, *Can. J. Research*, **B20**, 73 (1942).

[12] See for example ref. 10f.

served is supported by the n.m.r. studies of Fraenkel and Niemann[13] which demonstrate that in strong acid not only do the amides exist as form B but also that the NH proton exchange of B is slow. The base catalyzed proton exchange is much faster, about 10^4 times as fast as the acidic exchange at room temperature, and the direct bimolecular mechanism proposed[8] for it is

$$CH_3CONHCH_3 + OH^- \rightleftarrows CH_3CON^-CH_3 + H_2O \quad (II)$$

Evidence bearing upon the mechanism of proton exchange in our experiments on the pure liquids is meager. One might suspect that a trace of moisture could hydrolyze some of the amide and produce enough OH^-, particularly at the relatively high temperatures involved, that the base catalyzed mechanism (II) is rate governing. However, the coalescence temperatures, T_c, were found to be reproducible in different samples and the same exchange rates were found at a given temperature when a sample was cooled from a higher temperature as when it was heated, indicating that any hydrolysis was at thermodynamic equilibrium throughout the temperature range investigated. Moreover, when the data in Fig. 1 for NMA are extrapolated to room temperature, the resulting exchange rate, $R = 1/\tau_N$, is about 5×10^{-3} sec.$^{-1}$ which is very slow in comparison to the base catalyzed rate of about 3 sec.$^{-1}$ found[8] for $[OH^-] \cong 10^{-8}$ in aqueous solution. For these reasons, it is proposed that the exchange mechanism in the pure liquids may involve the bimolecular process

$$2RCONHCH_3 \rightleftarrows RCON^-CH_3 + RCON^+H_2CH_3 \quad (III)$$

The acidic hydrolysis in aqueous solution is a simpler matter, at least in the sense that our results bear more directly upon the reaction mechanism. It is significant that the hydrolysis is much slower than the proton exchange even though the activation energies of the two reactions, for NMF and NMA, do not differ greatly. For example, the data in Fig. 2 give an hydrolysis rate of 10^{-4} sec.$^{-1}$ for NMF and a proton exchange rate, at $t = 0$, of 10 sec.$^{-1}$. This difference is hard to explain on the basis that both rates depend upon $[\text{amide}][H_3O^+]$, but it is compatible with the finding for acetamide[14] that the rate of acidic hydrolysis is proportional to the concentration of its conjugate acid. The difference in exchange and hydrolysis rates is reasonable in terms of the equilibria given in (I), if the N-protonated form, C, of the conjugate acid, which is present in low concentration, is that which undergoes hydrolysis. It is also reasonable in that the hydrolysis requires rupture of the C–N bond which is weaker in C than in the O-protonated form, B.

The base catalyzed reactions in aqueous solution appear to differ mainly in the point at which the OH^- ion attacks the "normal" form of the amide molecule, $RCONHCH_3$. Proton exchange occurs when the attack is at the nitrogen, as in (II).[8] On the other hand, attack at the carbonyl carbon results in hydrolysis.[15] This pattern of attacking two alternative places in a molecule and leading to two alternative processes is similarly found in bimolecular substitution and elimination reactions.

The use of n.m.r. methods to study a reaction as slow as the hydrolysis warrants some comment. The indirect procedure developed is of limited applicability and accuracy. However, some advantage resulted from, in effect, observing exchange and hydrolysis rates simultaneously in the same system, which would not have been possible with conventional methods. Moreover, as is characteristic of n.m.r. experiments in general, the observations did not disturb the system in the ordinary chemical sense. One might have attempted to follow the hydrolysis reaction by measuring the n.m.r. intensities of reactants and products. But the apparent intensities and the accuracy of such a direct procedure are adversely affected by a number of factors.[16,17] Also, in order to have the simple, pseudo first order conditions, the concentrations of products were too small for good n.m.r. detection. It is concluded that n.m.r. rate studies are best made of fast exchange-type reactions but that in some cases it may be worthwhile to employ an indirect procedure such as is described here to study a relatively slow reaction.

Acknowledgments.—The author wishes to express his sincere thanks to Professor H. S. Gutowsky for his continued guidance and valuable discussions throughout the course of this work. His thanks are also due Dr. G. Slomp and Professor P. E. Yankwich for helpful discussions of various aspects of the work. Drs. J. C. Buchta, J. P. Heeschen and R. L. Rutledge contributed to the development of the apparatus.

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(13) G. Fraenke. and C. Niemann, *Proc. Natl. Acad. Sci., U. S.*, **44**, 688 (1958).

(14) See ref. 10g, 11, and papers cited therein.

(15) A detailed discussion of the mechanism for alkaline hydrolysis is given in ref. 10g.

(16) These factors are discussed in detail by H. S. Gutowsky in "Physical Methods in Chemical Analysis," Vol. III, Academic Press, Inc., New York, N. Y., 1956, p. 370 ff.

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