one can infer by analogy that regular behavior is to be expected.

Because of the frequent ease with which reaction rates can be measured as a function of mineral acid concentration, because of the present considerable accuracy of the empirical criterion of mechanism and the probability that it will become more accurate with the passage of time, kinetic response to changing acid concentration deserves a restoration of status as a criterion of mechanism.

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Structure of Salts of N,N-Dimethylacetamide and N,N-Di(n) butylacetamide¹

By W. D. KUMLER

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The infrared spectra of N.N-dimethylacetamide, N.N-di(n) butylacetamide, their hydrochlorides and deuteriochlorides have been measured. The spectra are interpreted on the assumption that the proton goes to oxygen.

Introduction

Pauling² calculated that the basic dissociation constant of amides would be 1×10^{-20} if the proton goes to nitrogen and commented "the value for the base constant 1×10^{-20} is so small as to be without significance, except to show that the amides do not form salts with acids by adding a proton to the amino group." This calculation did not take into account the inductive effect of the carbonyl group O

which should be considered. The pK_a of CH_3-C-

NH₂ can be estimated by analogy to be 5.0 from the Н

values for acetic acid, 4.76; glycolic, 3.83; acetoacetic, 3.38; ammonium ion, 9.25; and hydroxyammonium ion, 5.96. The corresponding K_b for \cap

 CH_3 - \ddot{C} - NH_2 without resonance would be 10^{-9} . Since acetamide has 21 kcal. resonance energy the $K_{\rm b}$ of the compound would be $RT \ln 10^{-9}/21,000 =$ $10^{-24.3}$, a smaller value than that above, making N-protonation in amides even more unlikely.

It has been concluded from a number of n.m.r. studies³⁻⁷ that the proton goes mainly on oxygen in agreement with this calculation, but some of these studies6,7 have found a fast proton ex-

(1) Presented in part at the 137th National Meeting of the American Chemical Society at Cleveland, Ohio, April, 1960.

(2) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Third Edition, 1960, p. 281.

(3) W. D. Phillips, J. Chem. Phys., 23, 1363 (1955).
(4) H. S. Gutowsky and C. H. Holm, *ibid.*, 25, 1228 (1956).

(5) G. Fraenkel and C. Niemann, Proc. Natl. Acad. Sci., 44, 688 (1958).

(6) A. Berger, A. Loewenstein and S. Meiboom, J. Am. Chem. Soc., 81, 62 (1959).

(7) G. Fraenkel and C. Franconi, ibid., 82, 4478 (1960).

change on nitrogen but with the concentration of the N-protonated species undetectably small.

Other studies using ultraviolet and infrared⁸⁻¹⁰ and dissociation constant¹¹ data have concluded the proton goes on the nitrogen.

Since the previous evidence was on urea or unsubstituted or monosubstituted amides with one or more hydrogens on the nitrogen, it was of interest to measure N-disubstituted amides where only one proton or deuteron would be present in the hydrochloride or deuteriochloride.

Results

The spectra of N,N-dimethylacetamide and N,Ndi(n) butylacetamide, together with their hydrochlorides and deuteriochlorides shown in Fig. 1, indicate that the spectra of the salts are quite different from those of the free amides particularly in the 4.0 to 6.5 μ region. Conclusions from the infrared spectra, including our own, that the proton goes to nitrogen have been based largely on the assumption that the band around 6 μ in the salts arises from a carbonyl vibration.

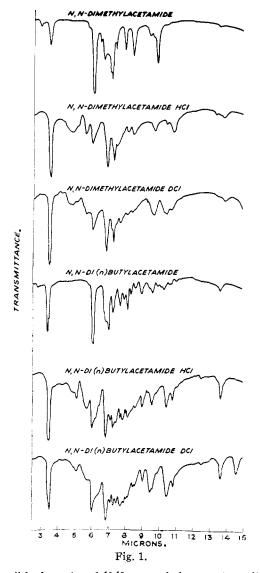
While it is probably an oversimplification to consider any single vibration of a pair of atoms in the -CO-NH system as being exclusively re-

(8) S. Mizushima, T. Simanouti, S. Nagakura, E. Kuratani, M. Tsubol, H. Baba and O. Fujioka, ibid., 72, 3420 (1950). We have repeated this work on N-methylacetamide and like these workers find a band at 2695 Å. in 5 N HCl. However, when the compound was carefully purified as reported by Bello (J. Bello, J. Phys. Chem., 60, 1341 (1956)) no band was found. The band therefore results from an impurity and gives no evidence that the proton is on nitrogen in the salt of N-methylacetamide.

(9) M. Davies and L. Hopkins, Trans. Faraday Soc., 53, 1563 (1957).

(10) E. Spinner, Spectrochim. Acta, 95 (1959), and J. Phys. Chem. 64. 275 (1960).

(11) J. T. Edward, H. S. Chang, K. Ajatis and R. Stewart, Can. J. Chem., 38, 1518 (1960).



sponsible for a band,^{12,13} nevertheless such a vibration can be considered mainly responsible. Katritzky and Jones¹⁴ have pointed out it is just as logical if not more so to assume the band around 6 μ in amide salts arises mainly from the C—N vibration as to assume it arises mainly from a C—O vibration, since acetamidine hydrochloride has a strong band at 5.95 μ which has been assigned to a N—C— N and NH₂ modes by Davies and Parsons¹⁵ and to the former mode by Mecke and Kutzelnigg.¹⁶ To be considered also is the fact that the n.m.r. workers are unanimous in the view that the n.m.r. evidence strongly supports O-protonation. Let us therefore see if a logical interpretation of our infrared data can be given in terms of O-protonation.

In N,N-dimethylacetamide hydrochloride there are bands at 4.85, 5.65 and 6.02 μ with shoulders at

(12) R. D. B. Fraser and W. C. Price, Nature, 170, 490 (1952).

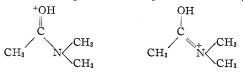
(13) R. D. B. Fraser and W. C. Frice, Proc. Roy. Soc. (London),
 141B, 66 (1953).

(14) A. R. Katritzky and R. A. Y. Jones, *Chemistry & Industry*, in press (1961); also, A. R. Katritzky, private communication.

(15) N. Davies and A. N. Parsons, Z. physik. Chem. N.F., 20, 34 (1959).

(16) R. Mecke and W. Kutzelnigg, Spectrochim. Acta, 16, 1216 (1960).

4.25 and 5.20 μ (see Fig. 1). The whole range from 3.20 to 5.90 μ is lowered so absorption is greater in this region. If the proton is on oxygen



the resulting resonating forms would have bands arising from an $\stackrel{+}{=} \stackrel{+}{OH} \leftrightarrow -OH$ stretch, an $\stackrel{+}{=} \stackrel{+}{OH} \leftrightarrow$ -OH bend, a C= $\stackrel{+}{=} \stackrel{-}{O} \leftrightarrow$ C--O- stretch and a C= $\stackrel{+}{N} < \leftrightarrow$ C--N < stretch.

Two absorptions that disappear in the deuterium salt that are present in the hydrochloride are the band at 5.65 μ and the whole background absorption between 3.70 and 5.50 μ that caused this region to absorb more in the hydrochloride than in the deuteriochloride by 5 to 15 transmission % units. These same changes took place with the salts of N,N-di(n)butylacetamide and these absorptions must therefore involve a motion directly associated with hydrogen. Presumably the broad absorption between 3.20 and 5.50 μ is associated with the $\stackrel{+}{=}$ OH \leftrightarrow —OH stretch and the band at 5.65 μ with the banding motion of this group. This group is

the bending motion of this group. This group is undoubtedly strongly hydrogen bonded in the solid salt so it is not surprising that the absorption due to the stretching mode is broad and occurs at longer wave length than OH stretching motions usually occur. The presence of the plus charge would also tend to shift the absorption to longer wave lengths, just as a plus charge on nitrogen shifts the N-H vibration to longer wave length.¹⁷

It would also be expected that the strong hydrogen bonding would shift the OH bending mode to shorter wave length and indeed the band at 5.65μ is at shorter wave length than the OH in plane deformation frequency of aliphatic alcohols, which occurs around 7.1 to 7.7 μ .¹⁸

The band at 6.02 μ in the hydrochloride is at nearly the same place, 6.05 μ , in the deuteriochloride and it appears reasonable to assign these bands to the C=N< \leftrightarrow C-N< stretch, since a band occurs at 5.95 μ in acetamidine hydrochloride,^{15,16} in which compound there does not seem

to be much choice but to assign the band to this group. The spectra from 4.0 to 5.3 μ also is nearly the same in both salts, since both have the broad band

at 4.85 μ with shoulders at 4.25 and 5.20 μ . What is responsible for this band is uncertain. The vibration of the carbon-oxygen bond in the C=

OH \leftrightarrow C—OH group has not been accounted for, but it seems unlikely that this can account for the absorption in this region since the carbonyl usually absorbs around 6 μ and resonance with C–OH with contribution of a carbon single bonded oxygen would be expected to move it to longer wave length.

⁽¹⁷⁾ P. J. Stone, J. C. Craig and H. W. Thompson, J. Chem. Soc., 52 (1958).

⁽¹⁸⁾ L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1958, pp. 216-220.

There are humps on the long wave length side of the 6μ band, and it seems quite possible that these arise from the carbon-oxygen stretching vibration

in the C=OH \leftrightarrow C-OH group.

Although one can come close to the frequencies of the bands in the 4.0 to 5.3μ region by adding frequencies of some of the longer wave length bands, it seems unlikely that the intensity of these combination bands would be as great as those observed. Also, in N,N-dimethylacetamide itself one can add up low frequency bands in the same way which should give bands in this region if this is a factor, but there is no evidence of any absorption at all in this region in the free amide. Since we know of no reason why the salts should behave differently from the free amide with respect to combination bands, we are at a loss to account for the bands in this region.

There is a new band in the deuterochloride at

7.72 μ which evidently arises from the $-D = D \leftrightarrow -O = D$ bending mode, since the ratio of the frequency of the band that disappeared in the hydrochloride to the frequency of this band is 1770 cm.⁻¹/1295 cm.⁻¹ = 1.37.

The spectra of N_N -di(n)butylacetamide and its hydrochloride and deuteriochloride in the 4.0 to 6.5 μ region are similar to those of the dimethyl compound. Thus, the free amide has a narrow band at 6.10 μ due to the carbon absorption and no additional bands down to 4.0μ . The hydrochloride has a broad band at 6.05 μ with shoulders at 6.25 and $6.45~\mu,$ a band at $5.70~\mu,$ one at $5.10~\mu$ with shoulders at 4.80 and 4.25 $\mu.$ The deuteriochloride has a band at 6.05 μ with shoulders at 6.30 and 6.50 μ , a band at 5.15 μ with shoulders at 4.85 and 4.30 μ . The band at 5.70 μ in the hydrochloride has virtually disappeared in the deuteriochloride so this can be attributed to the OH band. The whole region from 3.70 to 5.50 μ in the hydrochloride gives evidence of more absorption than it does in the deuteriochloride so this is attributed to the OH stretch. The shoulders at 6.30 and 6.50 μ in the spectra of the salts are attributed to the carbon-oxygen

stretch in the C==OH \leftrightarrow C--OH group.

The general similarity of the spectra of the salts of N,N-di(n) butylacetamide with that of N,N-di(n)

dimethylacetamide in the region 4.0 to 6.5 μ is a reason for considering that the same kind of protonation, namely O-protonation, is present in both cases.

The greater complexity of the spectra from 7 to 9 μ in the N,N-di(*n*)butylacetamide and its salts presumably arises from the increased modes possible in the butyl groups compared to methyl.

The strong band at 14.62 μ in the deuterium salt of N,N-(di(*n*)butylacetamide which is not present either in the hydrochloride or the free amide is apparently associated with an $\stackrel{+}{=}$ OD bending mode, perhaps an out-of-plane mode. There is an indication of a similar band off scale in N,N-dimethylacetamide deuterochloride for the curve decreased 10 transmittance % units from 14.7 to 15.0 μ , suggesting a band beyond 15 μ .

Experimental

The salts were made by passing dry HCl or dry DCl into a benzene solution of the amide. The salts precipitated and the benzene and excess HCl or DCl were removed under vacuum. The resulting white solids were very hygroscopic. The equivalent weights were determined by quickly removing a portion from a stoppered tube and titrating with base. The equivalent weights are given in Table I.

TABLE	I
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Compound	Equivalent Obsd.	weight Theor.
N,N-Dimethylacetamide HCl	122	123.4
N,N-Dimethylacetamide DCl	124	124.4
N,N-Di(n)butylacetamide HCl	208	207.8
N,N-Di(n)butylacetamide DCl	207	208.8

An attempt was made to measure the salts in KBr but the spectra always showed the presence of water. By making up mulls in a dry-box kept free of moisture by circulating nitrogen over molecular sieves it was found that spectra using Nujol or perfluorokerosene could be obtained that gave no evidence of the presence of water.

The spectra were measured on a Perkin-Elmer model 21 recording infrared spectrophotometer with a sodium chloride prism.

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