[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LOUISIANA POLYTECHNIC INSTITUTE]

Raman Spectra of Formamide-N-d_2 and of Formamide in Concentrated Hydrochloric Acid

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The Raman spectra of $HCOND_2$ and of $HCONH_2$ in concentrated hydrochloric acid have been run. A partial interpretation of the spectra is given. It is shown that there is a considerable amount of coupling between the various types of vibrations so that it is sometimes difficult to pick out corresponding lines in $HCONH_2$ and $HCOND_2$. The spectrum in concentrated HCl exhibits an unusually diffuse and double band in the ν(C–H) region. This is interpreted as due to Fermi resonance between ν(C–H) and the stretching vibrations of hydrogen in $-NH_3^+$.

Introduction

The interpretation of the spectrum of formamide is of particular importance since it is the simplest of the amides, and data from formamide are important in extending the interpretation to more complicated amides and peptides. The Raman spectrum of formamide has been studied extensively by the Graz group,[3] by Rao[4] and by Saksena.[5] The infrared spectrum of formamide has been studied by Lecomte and Freymann,[6] by Evans[7,8] and by Miyazawa,[9] the latter also having studied the infrared spectrum of formamide-N-d_2, a few lines of which had been found by Evans.[7] The Raman spectrum of formamide-N-d_2 is reported for the first time, as is the Raman spectrum of formamide in concentrated hydrochloric acid.

Experimental Methods

The Raman spectrum of formamide in concentrated hydrochloric acid was run photographically on the Gaertner spectrograph at the University of Michigan using the 4358 Å. Hg-line of a Toronto arc as the exciting line and the argon lines for frequency determination. The Gaertner spectrograph gave a dispersion of 213 cm.$^{-1}$ per mm. at 4700 Å. wave length. The powerful light source enabled exposure times of 5 minutes to 1 hour to be used. The Raman spectrum of formamide-N-d_2 was run photographically in our own laboratories using an Applied Research Laboratories Raman Spectrograph, the 4358 Å. Hg-line of General Electric Type H-11 lamps as the exciting line and the lines of an iron arc for wave number measurement. The Applied Research Laboratories spectrograph gave a dispersion of 105 cm.$^{-1}$ per mm. at 4700 Å. wave length. The weak light source made exposure times of 1 to 24 hours necessary. Because of rapid hydrolysis of formamide by concentrated hydrochloric acid it was necessary to run this Raman spectrum at −9° and to give exposure times of less than 30 minutes. Under these conditions no appreciable hydrolysis took place since the Raman bands of formic acid could not be detected. For comparison purposes the spectrum of formic acid in concentrated hydrochloric acid also was run at −9°. The infrared spectra of formamide and formamide-N-d_2 have been run on a Beckman IR-2 infrared spectrophotometer using a NaCl prism and NaCl cells. In our infrared measurements we actually had a saturated solution of NaCl in formamide. During the infrared measurements it was found necessary to keep the formamide-N-d_2 film from exposure to the air, since rapid exchange with atmospheric moisture took place and we would then obtain the spectrum of ordinary formamide.

Materials.—Formamide was prepared by the ammonolysis of ethyl formate, several vacuum distillations, fractional freezing and a final vacuum distillation in an all-glass apparatus free from ground glass joints. A commercial product also was purified and found to give a spectrum identical with the prepared formamide. It was found necessary to purify the formamide immediately before use because of its tendency to darken on standing.

Formamide-N-d_2 was prepared from purified formamide by mixing the formamide with an equal volume of D_2O,[10] holding at 100° for several hours and removing the water by vacuum distillation. This procedure was repeated four times and the formamide-N-d_2 was purified by three vacuum distillations, the last in an all-glass apparatus free from ground glass joints. It was necessary to separate a small amount of ammonium formate during the vacuum distillation. This fact, along with our subsequent observation of the rapidity of isotope exchange in this case, makes us suggest to subsequent workers that the exchange should be done more rapidly and at a lower temperature. Because of the danger of isotopic exchange, no attempt was made to purify the formamide-N-d_2 by fractional freezing. The Raman lines of ordinary formamide could not be detected in the Raman spectrum of formamide-N-d_2. Reagent grade concentrated hydrochloric acid was used without purification.

Results

Our infrared wave numbers were accurate only in the 700 to 1800 cm.$^{-1}$ region because we were limited to a NaCl prism. In this region for liquid formamide our results are in agreement with those of Evans[7] and will not be relisted.

In the region 700 to 1800 cm.$^{-1}$ our measurements on the infrared spectrum of formamide-N-d_2 agree very closely with those of Miyazawa[9] except that we did not detect the weak band observed by Miyazawa at 1493 cm.$^{-1}$ and we observed a very, very weak band at 762 cm.$^{-1}$ rather than the 710 cm.$^{-1}$ reported by Miyazawa[9] (750 cm.$^{-1}$ by Evans[7]). It is also of interest to note that our 1112 cm.$^{-1}$ band is of much smaller intensity than the one reported by Miyazawa at 1115 cm.$^{-1}$. Our Raman results are given in Table I.

The failure to observe bands in the 600 cm.$^{-1}$ region and in the 2400 cm.$^{-1}$ region in $HCOND_2$ is presumably due to their extreme weakness rather than to their absence. The most striking feature in the spectrum of formamide in concentrated hydrochloric acid is the broadening of all bands and the extreme broadening and doubling of the 2900 cm.$^{-1}$ band. This effect is not observed in the spectrum of formic acid in HCl.

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[1] We wish to acknowledge receipt of a Frederick Gardner Cottrell Grant from Research Corporation making the research possible.

[2] We appreciate coöperation from the Chemistry Department of the University of Michigan where a portion of this work was done.

[3] Most completely by L. Kahovec and H. Wassmuth, *Z. physik. Chem.*, **B48**, 70 (1940).

[4] A. L. S. Rao, *J. Indian Chem. Soc.*, **18**, 337 (1941).

[5] B. D. Saksena, *Proc. Indian Acad. Sci.*, **11A**, 53 (1940).

[6] J. Lecomte and R. Freymann, *Bull. soc. chim.*, **8**, 612 (1941).

[7] J. C. Evans, *J. Chem. Phys.*, **22**, 1228 (1954).

[8] J. C. Evans, *J. phys. radium*, **15**, 314 (1954).

[9] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **76**, 821 (1955).

[10] The D_2O was 99.7% from Stuart Oxygen Company

TABLE I

OBSERVED RAMAN WAVE NUMBERS (CM.$^{-1}$) AND INTENSITIES[11]

HCOOH in concd. HCl (25%) −9°	$HCONH_2$ liquid 25°	$HCONH_2$ 25% in H_2O 25°	$HCONH_2$ in concd. HCl (25%) −9°	$HCOND_2$ liquid 35°
182(0)				
697(2)	604(2)	608(2)	600(2)	
1059(1)				
	1093(4)	1096(5)	1091(4)	914(2)
				1120(1)
1203(2)	1312(7)	1332(8)	1332(4)	1345(6)
1397(6)	1390(10)	1392(10)	1374(10)	1397(6)
	1598(2)	1608(3)	1609(2)	
1714(8)	1678(4)	1693(3)	1709(3)	1667(1)
	1704(sh)			
	2766(1)			
2949(10)	2889(6)	2906(5)	2921?	2902(2)
			3016? (bsh)	
~3401(bvs)[12]	3300 to 3500 (bvs)	~3400(bvs)	~3390(bvs)	

Discussion

The diffraction data of Ladell and Post[13] have shown that in the crystalline state the C–N bond has about as much double bond character as does the C–O bond. This double bond character has been attributed to the resonating forms

$$H(C::O):NH_2 \text{ and } H(C:O^-)::NH_2^+$$

The formamide molecule should then be planar and have twelve fundamental vibrations. Using the frequencies[14] of liquid formamide, the more certain assignments are given in Table II. These assignments agree with those of Evans[7] and Miyazawa.[9]

TABLE II

VIBRATIONAL ASSIGNMENTS

Class	Form	$HCONH_2$, cm.$^{-1}$	$HCOND_2$, cm.$^{-1}$
a′	$\nu_a(NH_2)$	3330	2530
a′	$\nu_s(NH_2)$	3190	2360
a′	$\nu(CH)$	2889	2902
a′	$\nu_a(OCN)$	1680	1670
a′	$\delta(CH)$	1390	1397
a′	$\nu_s(OCN)$	1311	1342
a′	$\delta(OCN)$	602	507
a″	$\pi(CH)$	1051	1048

The remaining four vibrations belong to the amide hydrogens. The work of Edsall and Scheinberg[15] on CH_3ND_2 fixed $\delta(NH_2)$ at 1614 cm.$^{-1}$ in CH_3NH_2 and 1212 cm.$^{-1}$ in CH_3ND_2. A band is observed in the infrared and Raman of $HCONH_2$ at 1600 cm.$^{-1}$ and this band disappears on deuteration. A band appears at 1221 cm.$^{-1}$ in the infrared spectrum and one at 1115 cm.$^{-1}$ in the infrared and Raman spectra of $HCOND_2$. The 1221 cm.$^{-1}$ band gives a better wave number ratio (1.31 as compared with 1.44 for the 1115 cm.$^{-1}$ band) and agrees more closely with the value observed by Edsall and Scheinberg,[15] but was not observed in the Raman spectrum while the 1600 cm.$^{-1}$ band appeared in the Raman. The 1115 cm.$^{-1}$ band in $HCOND_2$ might also correspond to the 1093 cm.$^{-1}$ band in $HCONH_2$. A similar situation was observed by Otvos and Edsall[16] in the Raman spectra of $CO(NH_2)_2$ and $CO(ND_2)_2$. In these compounds, the 1604 (4b) cm.$^{-1}$ band disappears on deuteration and bands appear at 1201 (1b) cm.$^{-1}$ and 1164(1) cm.$^{-1}$. The 1164(1) cm.$^{-1}$ band in $CO(ND_2)_2$ might be interpreted as arising from the 1167(4) cm.$^{-1}$ band in $CO(NH_2)_2$. However, this latter interpretation is not reasonable since the 1164 (1) cm.$^{-1}$ band is observed to be depolarized while the 1167(4) cm.$^{-1}$ band is polarized. The substitution of two ND_2 groups for the two NH_2 groups of urea should eliminate the almost D_{3h} symmetry of the heavy groups (O and the two NH_2) and should not result in the change of a band from polarized to depolarized. It must be concluded that the 1164 cm.$^{-1}$ band of $CO(ND_2)_2$ does not correspond to the 1167 cm.$^{-1}$ band of $CO(NH_2)_2$. The formamide spectrum is so similar to that of urea that it is reasonable to assume that the 1115 cm.$^{-1}$ band of $HCOND_2$ does not correspond to the 1093 cm.$^{-1}$ band of $HCONH_2$. This leaves the 913 cm.$^{-1}$ band of $HCONH_2$ as corresponding to the 1093 cm.$^{-1}$ band of $HCONH_2$. Additional data or normal coördinate calculations are necessary to decide the relationship between 1221 and 1115 cm.$^{-1}$ of $HCOND_2$ and 1600 cm.$^{-1}$ of $HCONH_2$.

Although the 1093 cm.$^{-1}$ band probably consists mostly of planar rocking of the NH_2 hydrogens, the 1.20 ratio between 1093 cm.$^{-1}$ and 913 cm.$^{-1}$ shows that other vibrations must be contributing.

The out-of-plane NH_2 vibrations (wagging and torsional) cannot be assigned with any reasonable certainty from our data.

The HCl Spectra.—The extreme broadening and doubling of the 2900 cm.$^{-1}$ band of formamide on dissolving in concentrated HCl must not be interpreted as meaning that the H-atom on carbon has been greatly changed, since the δ(C–H) band at 1390 cm.$^{-1}$ does not become so diffuse and is not doubled. A reasonable interpretation of these divergent effects can be obtained from the work of Edsall and Scheinberg[15] on methylamine and hydrazine. In CH_3NH_2 bands were observed at 3322 cm.$^{-1}$ and 3382 cm.$^{-1}$, whereas in $CH_3NH_3^+$ a weak diffuse band was observed near 2980 cm.$^{-1}$ which was attributed to the NH_3^+ group. In $^+H_3N–NH_2$ a broad band was found at 2963 cm.$^{-1}$. Our data can be interpreted in the following way: when formamide is dissolved in concentrated hydrochloric acid a proton is captured by the amido nitrogen, forming $HCONH_3^+$. The symmetrical stretching frequency of the hydrogens in $-NH_3^+$ enters into Fermi resonance with the C–H stretching frequency producing a very diffuse double-headed band in the 2900–3030 cm.$^{-1}$ region. The proton capture must involve most of the formamide since the usual C–H stretching band could not be observed. This interpretation is supported by the shift of the carbonyl stretching vibration to higher values (1678 cm.$^{-1}$ in liquid $HCONH_2$,

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[11] Intensities were obtained from microphotometer tracing of the spectra.

[12] Bvs, broad and very strong; bsh, broad shoulder. The Raman bands in the 3400 cm.$^{-1}$ region in the aqueous solutions are chiefly due to the water present. The strong water bands cover up any bands due to other molecules.

[13] J. Ladell and B. Post, *Acta Cryst.*, **7**, 559 (1954).

[14] In the discussion and Table II weighted averages are given.

[15] J. T. Edsall and H. Scheinberg, *J. Chem. Phys.*, **8**, 520 (1940).

[16] J. W. Otvos and J. T. Edsall, *ibid.*, **7**, 632 (1939).

1693 cm.$^{-1}$ in H_2O solution, and 1709 cm.$^{-1}$ in concentrated HCl) in the acid solution. This same shift (to 1709 cm.$^{-1}$ in concentrated HCl) has been observed for the carbonyl frequency by Sannie and Poremski[17] in their study of the Raman spectrum of acetamide in concentrated HCl and indicates that acetamide also takes up a proton to form $CH_3CONH_3^+$ in concentrated HCl. This interpretation of the 1709 cm.$^{-1}$ band had already been made by Sannie and Poremski.[17] Our results show that the 1611 cm.$^{-1}$ band of acetamide[17] does not belong to ν(C–N) of the imino alcohol form of acetamide since the corresponding band in formamide disappears on deuteration.

(17) C. Sannie and V. Poremski, *Bull. soc. chim.*, **6**, 1629 (1939).

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Vibrational Spectra of Phosphite and Hypophosphite Anions, and the Characteristic Frequencies of PO_3^{--} and PO_2^- Groups

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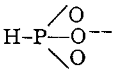
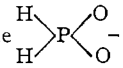
Infrared absorption spectra of the  $H\text{–}P(O)(O)O^{--}$ anion and Raman and infrared spectra of the  $H_2PO_2^-$ anion have been obtained in the solid state and in aqueous solution. All of the expected fundamental vibrations can be reasonably assigned to the observed bands. The PO_2^- symmetric and antisymmetric stretching vibrations in the $H_2PO_2^-$ anion occur at 1050 and 1200 cm.$^{-1}$, respectively. Similar bands are observed at almost the same frequencies for the $(CH_3O)_2PO_2^-$ anion and the Na-salts of nucleic acids. The PO_3^{--} symmetric and asymmetric (degenerate) stretching vibrations of the HPO_3^{--} anion give bands at 980 and 1100 cm.$^{-1}$, respectively. These vibrations in the $CH_3OPO_3^{--}$ anion and in nucleotides in solution at high *p*H seem to give bands at almost the same positions. These are considered to be characteristic frequencies of the PO_2^- and PO_3^{--} groups.

Introduction

Although accumulating infrared and Raman spectra cover a great variety of compounds, our knowledge of the vibrational spectra of simple phosphorus compounds is still quite limited. Several authors[2-4] have investigated the Raman spectra of phosphite and hypophosphite anions but so far no infrared data seem to be available. In spite of the simple structure of these anions, the assignment of their fundamental frequencies has never been complete. In view of this situation, the infrared absorption spectra of a few salts containing these anions have been investigated. The Raman spectrum of potassium hypophosphite has been reexamined, since previous data on the hypophosphite ion are not in agreement on some points. The results of this study have led to a reasonable assignment of the fundamental frequencies. It is shown that the knowledge thus obtained facilitates the interpretation of the vibrational spectra of other compounds with PO_3^{--} and PO_2^- groups.

Hypophosphite Anion and the PO_2^- Group.—The results of the Raman and infrared measurements for 50% aqueous solution of KH_2PO_2 are given in the first and the second columns of Table I. A thin sheet of solid KH_2PO_2 was prepared in which, fortunately, thin pyramidal crystals were oriented with their axes practically along one direction. It was thus possible to obtain infrared absorption data on solid KH_2PO_2 with polarized radiation. The results are given in the third column of Table I.

Previous authors have reported a Raman line for the $H_2PO_2^-$ ion at about 586 cm.$^{-1}$; it is weak according to Mathieu and Jacques[3] but it is stronger than the 467 cm.$^{-1}$ line according to Hanwick and Hoffman.[4] Hanwick and Hoffman[4] reported another line at 777 cm.$^{-1}$. In the present work, however, no appreciably intense lines could be found near these frequencies on plates which were properly exposed for the other lines. The strong band near 2350 cm.$^{-1}$ was always found to be accompanied by a weaker, depolarized line at 2311 cm.$^{-1}$ which was not reported by the previous authors.

TABLE I

VIBRATIONAL SPECTRA OF THE HYPOPHOSPHITE ANION[a]

Raman, cm.$^{-1}$ KH_2PO_2 aq. soln. (Int.)	(dep. rat.)	Infrared, cm.$^{-1}$ KH_2PO_2 aq. soln.	KH_2PO_2 crystal	Assignment
467 (5)	p(0.74)	469(m)	476(s)	A_1 PO_2 scissor
822 (1)	d?	811(s)	808(s) ‖	B_1 PH_2 rock
924 (7)	d(0.84)	.....	.....	A_2 PH_2 twist
1048(10)	p($\ll$ 0.5)	1042(s)	1046(s) ⊥	A_1 PO_2 sym. stretch
1088 (5)	d(0.94)	1086(m)	1080(w) ⊥	B_2 PH_2 wag
1157 (7)	p(0.71)	1160(s)	1171(s) ⊥	A_1 PH_2 scissor
.....		1180(s)	1230(s) ⊥	B_2 PO_2 anti. stretch
2311 (5)	d?	2314(s)	2312(s) ‖	B_1 PH_2 anti. stretch
2357(10)	p($\ll$ 0.5)	2363(w)	2375(m) ⊥	A_1 PH_2 sym. stretch

[a] s, strong; w, weak; m, medium; ‖, polarized parallel to the long crystal axis; ⊥, polarized perpendicular to the long crystal axis.

In the interpretation of the results, a non-planar structure with C_{2v} symmetry was assumed for the $H_2PO_2^-$ ion[5] (see Fig. 1). There should be nine normal vibrations, and the present assignment of these to the observed bands is given in the last column of Table I.

It is reasonable to take the lowest frequency (467 cm.$^{-1}$) for the PO_2 scissoring motion and the

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[1] Fulbright Travel Grantee. Department of Chemistry, Faculty of Science, Tokyo University, Hongo, Tokyo, Japan.

(2) A. Simon and F. Feher, *Z. anorg. allgem. Chem.*, **230**, 289 (1937).

(3) J. P. Mathieu and J. Jacques, *Compt. rend.*, **215**, 346 (1942).

(4) T. J. Hanwick and P. O. Hoffman, *J. Chem. Phys.*, **17**, 1166 (1949); **19**, 708 (1951).

(5) W. H. Zachariasen and R. C. L. Mooney, *ibid.*, **2**, 34 (1934).