[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Infrared Absorption of Crystalline and Liquid Hydrazine Monochloride and Monobromide[1-3]

BY J. C. DECIUS AND D. P. PEARSON[4]

RECEIVED OCTOBER 24, 1952

The infrared absorption spectra of N_2H_5Cl, N_2D_5Cl, N_2H_5Br and N_2D_5Br in the crystalline state have been obtained in the region from 3 to 25 μ. Certain regions of these spectra were also studied at liquid air temperatures and also in the liquid state at about 95°. A very broad N–H or N–D stretching region of complex structure has been observed. The results are discussed in terms of the effect of N–H—N hydrogen bonding.

The infrared absorption of N_2H_5Cl as an emulsion has been reported previously by Lieber, Levering and Patterson[5] for the range 2 to 15 μ. The Raman spectra of N_2H_5Cl and N_2D_5Cl in aqueous solution were studied by Edsall,[6] and by Edsall and Scheinberg.[7] The X-ray diffraction of N_2H_5Cl has been obtained by Williams,[8] who found the crystal to be orthorhombic with $a = 21.99$, $b = 12.60$, and $c = 4.44$ A., the space group is C_{2v}^{19} with sixteen molecules per unit cell.

According to Halford's tables,[9] this means that the site symmetry is C_1, hence all fundamental frequencies should appear in both infrared and Raman spectra. If intermolecular coupling is completely neglected, there should appear five frequencies in the hydrogen stretching region (3200–3400 cm.$^{-1}$), four H–N–H deformation frequencies roughly between 1400 and 1600 cm.$^{-1}$, four $-NH_3^+$ or $-NH_2$ group bending frequencies in the 1000 to 1200 cm.$^{-1}$ region, an N–N stretching mode probably below 1000 cm.$^{-1}$ and a torsional mode at a considerably lower frequency. One might also expect to observe translational or rotational modes of the entire $N_2H_5^+$ unit in the lower frequency range, say below 750 cm.$^{-1}$.

Experimental

Preparation of Materials.—The N_2H_5Cl was prepared from 100% hydrazine hydrate (The Matheson Co.) and C.P. hydrochloric acid in stoichiometric amounts, the precipitation being effected by partially evaporating the water over concd. H_2SO_4 in a vacuum desiccator. N_2D_5Cl was prepared by dissolving N_2H_5Cl in 99% D_2O (Norsk Hydro-Elektrisk Kvaelstofaktieselskab) and evaporating over P_2O_5; five such recrystallizations were carried out. The N_2H_5Br was obtained through the courtesy of Professor M. B. Williams; N_2D_5Br was prepared analogously with N_2D_5Cl.

Preparation of Samples for Infrared Absorption.—Thin films of the various salts were made by melting a few milligrams of the dried material between NaCl or KBr windows on a hot-plate. These were then allowed to cool to room temperature or were maintained at about 95° for the liquid phase experiments employing an electrically heated copper block provided with openings for the insertion of the windows. A few low temperature absorption curves were recorded using a cell similar to that described by Wagner and Hornig.[10]

Infrared Spectrometer.—A Model 12-C Perkin–Elmer instrument was employed, with LiF, NaCl and KBr prisms available for appropriate ranges of the spectrum. This instrument has been modified for double-beam operation, utilizing the principle introduced by Savitzky and Halford,[11] but retaining the use of a thermocouple rather than a Golay detector.

Experimental Results

The infrared transmission spectra of the various compounds in various physical states are depicted in Figs. 1 and 2. More precise values of the positions of the transmission minima, hereinafter referred to as absorption maxima or peaks, can be obtained from Table I. The transmission curves below 700 cm.$^{-1}$ are corrected for the presence of stray light of shorter wave lengths.

Before entering upon a detailed interpretation of the spectra, several rather obvious generalizations may be made. The transmission curves of the chlorides and bromides are very similar, with the peaks of the latter shifted to a frequency lower by about 15 cm.$^{-1}$ on the average. The breadth of the N–H stretching region is remarkable; it apparently extends all the way from 2602 to 3261 cm.$^{-1}$. In order to achieve good resolution of this region, it was necessary to employ a much thinner film than was needed through the rest of the spectrum. The bands in this region were further sharpened by cooling the sample to approximately the temperature of liquid air.

The most notable differences between the transmission curves in the crystalline and liquid states are the broadening of the bands and shift to lower frequencies upon melting. Another notable change was observed in the neighborhood of 500 cm.$^{-1}$, where a relatively narrow absorption for the crystalline phase is replaced by a broader absorption with no peak down to below 425 cm.$^{-1}$. Somewhat similar changes occur to the absorption maxima found at about 1745 and 1970 cm.$^{-1}$ in crystalline N_2H_5Cl.

Interpretation

The Hydrogen Stretching Region.—This region is characterized by the very complex and broad absorption shown in Fig. 1. Although five distinct absorption maxima might be expected in the absence of symmetry, the separation and number of the peaks is larger than may reasonably be

---

(1) Presented at the Northwest Section Meeting of The American Chemical Society in Corvallis, Oregon, June 21, 1952.

(2) Published with the approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 221, School of Science, Department of Chemistry.

(3) This research was supported in part by a grant-in-aid from the General Research Funds of the Graduate School, Oregon State College.

(4) Some of the material of this paper is taken from a thesis submitted by David P. Pearson in partial fulfillment of the requirements for the Degree of Master of Science.

(5) E. Lieber, D. R. Levering and L. J. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

(6) J. T. Edsall, *J. Chem. Phys.*, **5**, 225 (1937).

(7) J. T. Edsall and H. Scheinberg, *ibid.*, **8**, 520 (1940).

(8) M. B. Williams, private communication, Oregon State College.

(9) R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

(10) E. L. Wagner and D. F. Hornig, *ibid.*, **18**, 296 (1950).

(11) A. Savitzky and R. S. Halford, *Rev. Sci. Instruments*, **21**, 203 (1950).

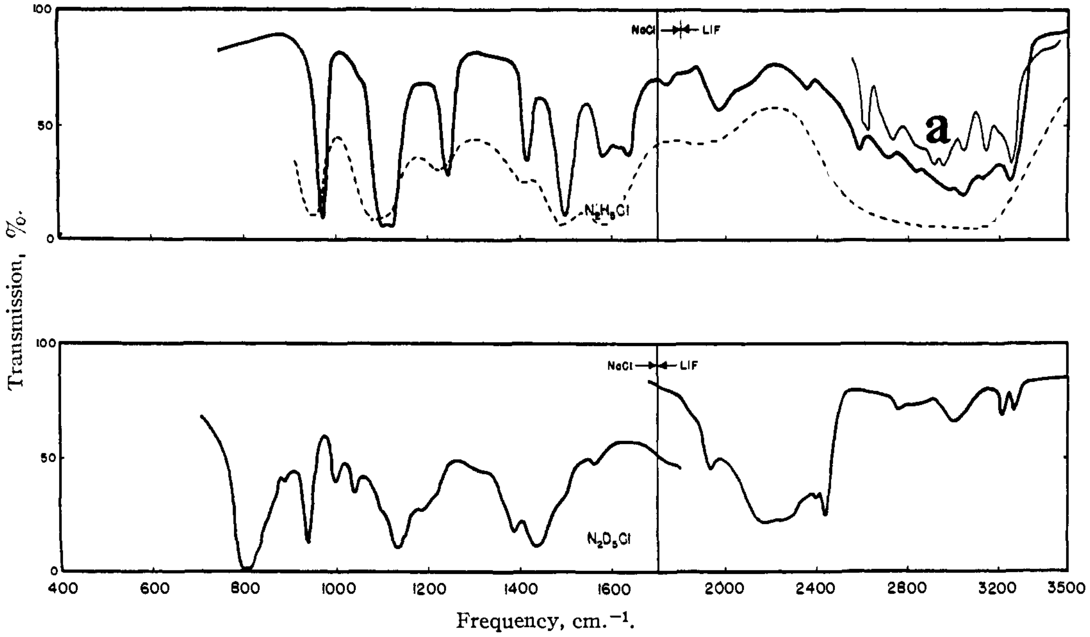

Fig. 1.—The infrared transmission of N_2H_5Cl (upper curve) and N_2D_5Cl (lower curve): broad line, solid, 25°; thin line (a), solid, approx. —190°; dotted line, liquid, 95°.

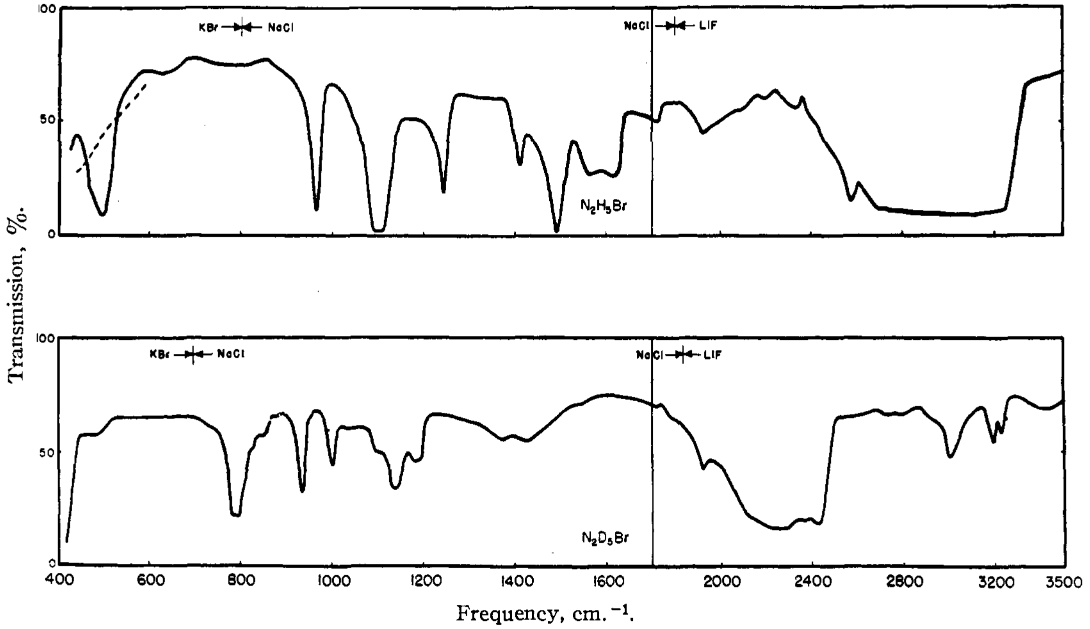

Fig. 2.—The infrared transmission of N_2H_5Br (upper curve) and N_2D_5Br (lower curve): broad line, solid, 25°; dotted line, liquid, 95°.

expected on the basis of a free molecule potential function, and presumably intermolecular potential terms connected with hydrogen bonding play an important role here. In this connection it is interesting to note the absorption in this same region exhibited by the deuterated compound. If it can be assumed that the peaks are due to $N_2D_4H^+$ ions present because of a small percentage contamination with ordinary hydrogen, then, as pointed out by Hiebert and Hornig[12] the frequencies will be influenced by the equilibrium crystalline field, but not appreciably by coupling terms between the displacement of the N–H bond and the N–D bonds of the neighboring ions, owing to the large frequency difference. It is gratifying that the observed number of peaks in the $N_2D_4H^+$ case does not exceed five. Presumably the more complex spectrum of $N_2H_5^+$ is due to intermolecular coupling with consequential splitting.

Although the arrangement of the sixteen $N_2H_5^+$ ions in the unit cell is not known, it is natural to assume that hydrogen bonds between the $-NH_3^+$ group of one ion and the nitrogen of the $-NH_2$ group of another ion play an important role in de-

---

[12] G. L. Hiebert and D. F. Hornig, *J. Chem. Phys.*, **20**, 918 (1952).

Table I

Infrared Absorption Maxima of Hydrazine Monochloride and Monobromide (Cm.$^{-1}$)

s = strong, m = medium, w = weak, n = narrow, b = broad, u = unresolved

N_2H_5Cl			N_2H_5Br		N_2D_5Cl	N_2D_5Br
Solid, −190°	Solid, 25°	Liquid, 95°	Solid, 25°	Liquid, 95°	Solid, 25°	Solid, 25°
			495 sb	430 vb		415
	973 sn	950 sb	965 sn		790 s,u	780 s,u
	1101 sb	1080 s,u	1095 sb		805	795
	1124 sb	1100	1100 sb		940 sn	932 sn
	1246 sn	1225 mb	1243 sn		1000 mn	998 mn
	1417 mn	1405 mb	1410 sn		1041 mn	1045 w
	1500 sn	1495 sb	1491 sn		1100 m	1095 m
	1584 mb	1595 sb	1568 mb		1133 sn	1135 s
	1638 mb		1615 mb		1155 m	
	1745 wb		1725 wb		1190 m	1185 m
	1970 mb	1900 wb	1930 mb		1385 s	1375 m
	2350 w		2330 w		1434 s	1420 m
					1563 w	1550 w
2617 sn	2602 sn		2575 sn		1930 sn	1925 sn
2727 sb	2716 sb		2690		2170 sb	
2903 s?	2903 s?	2600–3200 s,u				
2950 s?	2950 s?					2250
3034 sn	3034 sn		s,u		2390 sn	2370 sn
3141 sn	3150 sn				2440 sn	2430 sn
3253 sn	3261 sn		3250		2745 w	2730 w
					2830 w	2810 w
					2985 w	3000 w
					3205 w	3195 w
					3250 w	3230 w

termining the structure.[13] The close similarity of the N_2H_5Cl and N_2H_5Br spectra tends to eliminate the possibility of hydrogen bonding to the halide ions, since bromide ion would not be expected to be able to participate in such bonding.

The Bending and Deformation Region.—As will appear below, there is good reason to believe that the relatively sharp absorption at 973 cm.$^{-1}$ in N_2H_5Cl is essentially a N–N stretching mode. Excluding this frequency, there remain peaks in N_2H_5Cl at 1101, 1124, 1246, 1417, 1500, 1584 and 1638 cm.$^{-1}$; 1745 may be excluded since it apparently disappears in the liquid phase and is therefore in all probability a combination with a lattice mode. For a completely unsymmetrical free $N_2H_5^+$ ion, one would expect to observe four bending and four deformation modes, the former occurring at lower frequencies than the latter. If the $-NH_3^+$ group is nearly degenerate, two of the bending and two of the deformation modes would be only slightly split. The peaks at 1101 and 1124 appear almost unresolved, but work with some thinner samples indicated the definite existence of separate maxima. If these peaks are then assigned to the nearly degenerate $-NH_3^+$ bending modes, there is no difficulty in finding the corresponding $-ND_3^+$ frequency, namely, 790–805 cm.$^{-1}$.

As far as the remaining frequencies in this region are concerned, it is not possible to assign them in detail aside from pointing out that the three highest (1500, 1584, 1638 cm.$^{-1}$) are probably deformation (H–N–H) rather than bending (H–N–N) modes. Also in this region the total number of peaks does not exceed that predicted by site symmetry selection rules.

The Region below 1000 Cm.$^{-1}$.—For N_2H_5Cl, this region may be expected to include the N–N stretch, a torsional vibration and the lattice modes. In agreement with Edsall and Scheinberg,[7] we assign 973 cm.$^{-1}$ (which shifts only to 940 cm.$^{-1}$ in N_2D_5Cl) as the N–N stretch. In the experimentally available infrared region, down to about 400 cm.$^{-1}$, only one additional strong absorption was found, namely, the peak at 495 cm.$^{-1}$ in N_2H_5Br (which shifts to ≤ 410 cm.$^{-1}$ in N_2D_5Br). This absorption must be assigned either to internal torsion of the $N_2H_5^+$ ion or to a lattice mode. Because of

Table II

Fundamental Frequencies of N_2H_5Cl and N_2D_5Cl

Mode	N_2H_5Cl Infrared[a] solid, 25°	Liquid, 95°	Raman[b] aqueous solution	N_2D_5Cl Infrared[a] solid, 25°	N_2D_5Cl Raman[b] aqueous solution
N–N	973	950	965	940	943
$-NH_3^+$ bend	1101	1080	1107	790	
	1124	1100		805	838
Bend	1246	1220	1274	1000	989
Bend	1417	1405	1424	1100	1098
Deformation	1500	1495	1533	1133	1158
Deformation	1584				
Deformation	1638	1600	1632	1190	1198
Stretch ($-NH_3^+$)	2716		2692		2176
Stretch ($-NH_3^+$)	2950		2983	2170	
	3034				
Stretch ($-NH_2$)	3150		3197–3219	2390	2354
Stretch ($-NH_2$)	3261		3286–3309	2440	2410

[a] This research. [b] Edsall,[6] Edsall and Scheinberg.[7]

---

[13] Note added in proof.—Since this manuscript was submitted, X-ray studies by Sakurai and Tomiie, *Acta. Cryst.*, **5**, 293 and 289 (1952), have independently confirmed this viewpoint.

the very marked change in the distribution of intensity in this region upon melting (Fig. 2) it seems more reasonable to interpret this as a lattice mode, possibly involving rotation of the $N_2H_5^+$ ion as a rigid unit.

Comparison with the Raman Spectrum.—Although the available Raman data on N_2H_5Cl and N_2D_5Cl refer to aqueous solution, it is nevertheless interesting to compare the data as is done in Table II.

Although the agreement between the infrared and Raman frequencies is not complete, it is perhaps as close as may be reasonably expected in view of the difference in the physical states. Aside from the hydrogen stretching region, the largest differences occur between 1246 and 1274 and between 1500 and 1533.

Acknowledgment.—The assistance of Mr. Bruce Hunter and Mr. Harry Nelson in certain phases of this work is gratefully acknowledged.

CORVALLIS, OREGON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Rates of Ionization of Pseudo Acids.[1] IV. Relation between Rates and Equilibria

BY RALPH G. PEARSON AND ROBERT L. DILLON[2]

RECEIVED DECEMBER 11, 1952

If the logarithms of the rate constants for ionization of pseudo acids are plotted against the logarithms of the corresponding equilibrium constants, the best straight line divides the compounds into those with positive rate deviations and those with negative deviations. The greater the ability of a substituent to absorb the negative charge generated in the carbanion, the greater the negative deviation. As electron absorbers $NO_2 > CO > CN \geq SO_2$. Compounds having the latter two groups as activators show positive deviations. Thus, nitriles and sulfones are characterized by high rates of ionization for a given acid strength and hence high rates of recombination of their carbanions with a proton. This latter factor causes the rate of bromination of nitriles and sulfones to be dependent on the hydrogen ion and bromine concentrations in contrast to nitro and carbonyl compounds. Substitution of a second electronegative group on a monosubstituted compound makes the rate deviation more positive. This is apparently because a second substituent increases the electronegativitity of the central carbon atom to the point where it controls a relatively greater share of the anionic charge. The common activating groups are arranged in the following order (for equilibria, not rates) $NO_2 > CO > SO_2 > COOH > COOR > CN \sim CONH_2 >$ halogen. This order differs from that obtained from hydroxyl acids. There is shown to be no sharp division between normal and pseudo acids and bases (or primary and secondary). There is instead a gradual transition from one to the other.

In a continuation of our studies of pseudo acids we present in this paper some new data on the rates of ionization in water and the acid ionization constants of some substituted nitro and cyano compounds. We have also accumulated all of the available data on rates and equilibria for the simple carbon–hydrogen acids. The standard reaction is

$$HA + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^- + H_3O^+ \qquad (1)$$

where k_1 and $K_a = k_1/k_2$ can generally both be measured. From these k_2, the rate constant for ion recombination, can be calculated.

Experimental

Materials.—1-Chloronitroethane was a sample donated by the Commercial Solvents Corporation. It was purified by dissolving in alkali, extracting with ether and acidifying the aqueous phase with hydroxylamine hydrochloride.[3] The nitro compound thus obtained was fractionated and the product boiling at 37–38° at 20 mm. was used; $n^{25}D$ 1.4235. Hurdis and Smythe[4] report $n^{20}D$ 1.4224.

Ethyl nitroacetate was made according to the literature,[5] b.p. 65° at 2 mm., $n^{25}D$ 1.4229. Ethyl cyanoacetate was made according to "Organic Syntheses," b.p. 198°, $n^{20}D$ 1.4176. Ethyl monobromcyanoacetate was made according to the literature,[6] b.p. 135° at 40 mm.

A sample of malononitrile obtained from the Schwarz Laboratories was recrystallized twice from water, m.p. 31° (literature value 32.1°). Monobromomalononitrile was made according to Hesse,[7] m.p. 62° (literature 65°).

Potassium dinitromethane was made by the procedure of Duden.[8] The product was recrystallized from water. Since the free acid is unstable, the salt was acidified with an equivalent amount of acid just before use.

A sample of nitroacetone was kindly supplied by Dr. May Nilson of this Laboratory, m.p. 46–48° (literature values of 46.5 and 49° have been reported). The compound was stored under ether.

Methods.—The rates of ionization were determined by measuring the rates of bromination using the conductometric method previously described.[1] An open neck conductance cell was used so that mixing of reagents could be done in the cell. An excess of bromine was used and the conductance data plotted as for a first-order reaction. The slowly reacting 1-chloronitroethane was also treated as a zero-order reaction using low concentrations of bromine. The equilibrium resistance was determined sometimes directly on the reaction mixture and sometimes from synthetic mixtures of hydrobromic acid corresponding to the final concentration. The same results were obtained by the two methods.

The conductance method was checked by direct titration of unreacted bromine in the case of 1-chloronitroethane. For ethyl nitroacetate a check was made by adding allyl alcohol followed by potassium iodide so that the amount of bromine reacted could be determined with standard thiosulfate.

Ethyl nitroacetate, ethyl cyanoacetate, nitroaceton, dinitromethane and malononitrile used up two moles of bromine per mole of pseudo acid. Since good first-order kinetics were obtained up to 80% reaction, it was assumed that the second stage of bromination was much faster than the first. This was checked in the case of ethyl cyanoacetate and malononitrile by making the monobrominated derivative and measuring its rate of bromination (see Table III). That the above assumption is not always true has been

---

[1] For previous papers in this series see THIS JOURNAL, 72, 1692, 3594 (1950).

[2] Based on a portion of the Ph.D. dissertation of Robert L. Dillon, Northwestern University, 1951.

[3] This procedure was suggested by Prof. Nathan Kornblum.

[4] E. C. Hurdis and C. P. Smyth, THIS JOURNAL, 64, 2829 (1942).

[5] Rodionov, Mochinskaya and Belikov, *Zhur. Obshchei Khim.*, 18, 917 (1948).

[6] G. Errera and F. Perciabosco, *Ber.*, 33, 2976 (1900).

[7] B. C. Hesse, *Am. Chem. J.*, 18, 728 (1896).

[8] P. Duden, *Ber.*, 26, 3003 (1893).