[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

The Infrared Absorption Spectra of Some N-Bromoacetamides[1]

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The infrared absorption spectra of N-bromoacetamide and five α-halogen N-bromoacetamides have been determined on samples in the solid state and as dilute solutions in carbon tetrachloride. Lithium fluoride and sodium chloride prism spectrometers were used to scan the region from 1 to 15 μ. Tentative assignments have been made for several of the observed bands. Spectroscopic evidence indicates that the molecules exist in the keto form and are associated through N–H...O bridges in the solid state. It has been possible to relate the intensity of the N–H fundamental band at 2.93 μ to the brominating activity of the N–Br bond.

Introduction

While much spectroscopic work has been done on the amide group as an integral part of proteins and other biologically important compounds, considerably less data are available on the spectra of simpler amides. Buswell, Rodebush and Roy[3] have conducted a thorough spectroscopic study of acid amide association in the near infrared region. Recently, many amides and N-substituted amides have been extensively studied in the 6μ region by Lenormant.[4–6] His results have rather definitely established the keto form as being predominant in the solid state. Thus Lenormant[7] has also confirmed the previous assignment of bands in the 3μ region to N–H fundamental vibrations by substituting deuterium for the hydrogens on the nitrogen atom and observing a consequent shift in these bands to around 4μ. Richards and Thompson[8] have conducted the most detailed spectroscopic study of the amides thus far and have been able to interpret their data from a consideration of the keto form and its resonance dipolar structure. Senti and Harker[9] have conducted an X-ray analysis of the crystal structure of acetamide and found it to exist only in the keto form. They also concluded that the molecule was planar with respect to the carbon, nitrogen and oxygen atoms; and that the molecules are associated into ring polymers through N–H···O bridges. Kumler and Porter[10] also concluded from dipole studies on several amides that no enol form was present. These conclusions concerning the structure of the amides have been further substantiated by investigations of their Raman spectra.[11]

Very little work of a spectroscopic nature has been done on the α-halogen acetamides and none is reported for the N-halogen amides. Wittek[12] has reported the Raman spectra of trichloroacetamide, and Lenormant[13] has studied several α-chloroacetamides in the 6μ region.

Experimental

A Perkin–Elmer model 12C spectrometer fitted with a sodium chloride prism was used to obtain the spectra in the region from 2 to 15 μ. Measurements were made on a fused sample of the compound pressed between sodium chloride plates. A Perkin–Elmer model 12B spectrometer fitted with a lithium fluoride prism was used to obtain the spectra in the region from 1 to 4 μ. Measurements were made on dilute solutions in carbon tetrachloride. The particular cell length and concentration used is indicated on each spectrogram. The compounds are all rather hygroscopic and presented a small amount of absorption due to water present as an impurity. The resulting absorption bands were of weak intensity and identical in character to those in the background arising from atmospheric water vapor and whatever moisture may have been present in the solvent. These bands have not been plotted and the region observed for them (from 2.56 to 2.76 μ) has been represented with a broken line. A rather strong peak presented by the solvent in the region from 3.14 to 3.28 μ was not conveniently subtracted from the background and this region has also been represented by a broken line.

The N-bromoacetamide was supplied by the Arapahoe Chemical Company of Boulder, Colorado, and was used without further purification. All of the N-bromoacetamide derivatives were prepared and carefully purified in this Laboratory using methods previously described.[14]

Discussion

The Spectra.—The spectrogram of the sodium chloride region for each compound is presented in Fig. 1 and several of the tentative assignments for absorption bands in this region are given in Table I. The intense band at 3.20μ is precisely the position of a hydrogen-bonded fundamental N–H valence vibration (1ν). The fact that this band is sharp and definite on the short wave length side indicates that there is no contribution from a hydrogen-bonded O–H group which would present an absorption band at about 3.00 μ.

TABLE I

GENERAL ASSIGNMENT OF BANDS IN THE SODIUM CHLORIDE REGION

Band, μ	Assignment
3.20 to 3.22	N—H valence (1ν)
5.83 to 6.11	C═O valence (1ν)
6.88 to 7.05	C—N valence (1ν)
7.74 to 8.26	N—H group rocking
7.35 to 7.70	C—H deformation (1δ)

The spectrogram of the lithium fluoride region for each compound is presented in Fig. 2 and several of the tentative assignments are given in Table II. In the spectra for this region it will be noted that as the concentration increases the fundamental N–H valence vibration at 2.93μ broadens but does not shift a measurable amount. Hence there is no

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[2] du Pont Predoctoral Fellow in Chemistry, 1950.

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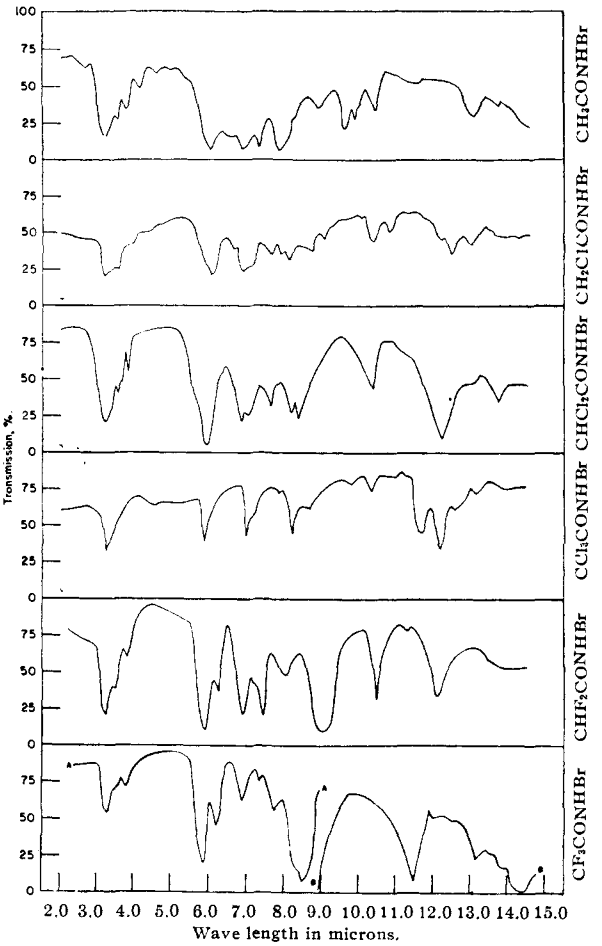

Fig. 1.—Infrared absorption spectra of indicated compounds in the rock-salt region. Fused sample between sodium chloride plates: A, thin sample; B, thick sample.

indication of association through hydrogen bonding taking place in the range of concentrations studied.

TABLE II

GENERAL ASSIGNMENT OF BANDS IN THE LITHIUM FLUORIDE REGION

Band, μ	Assignment
1.50 to 1.52	N—H valence (2ν)
1.70 to 1.72	C—H valence (2ν)
1.90 to 1.92	C=O valence (3ν)
2.93	N—H valence (1ν)
2.96 to 3.08	C=O valence (2ν)
3.32 to 3.38	C—H valence (1ν)

Correlation of Band Intensity.—The most intense band in the lithium fluoride region is the N–H fundamental at 2.93μ. It has been possible to relate the absorption coefficient for this band to the brominating activity of the N–Br bond. The absorption coefficient, a, may be defined as

$$\ln (I_0/I) = aCL$$

where $\ln(I_0/I)$ is the optical density, C is the molar concentration and L is the cell length in centimeters.

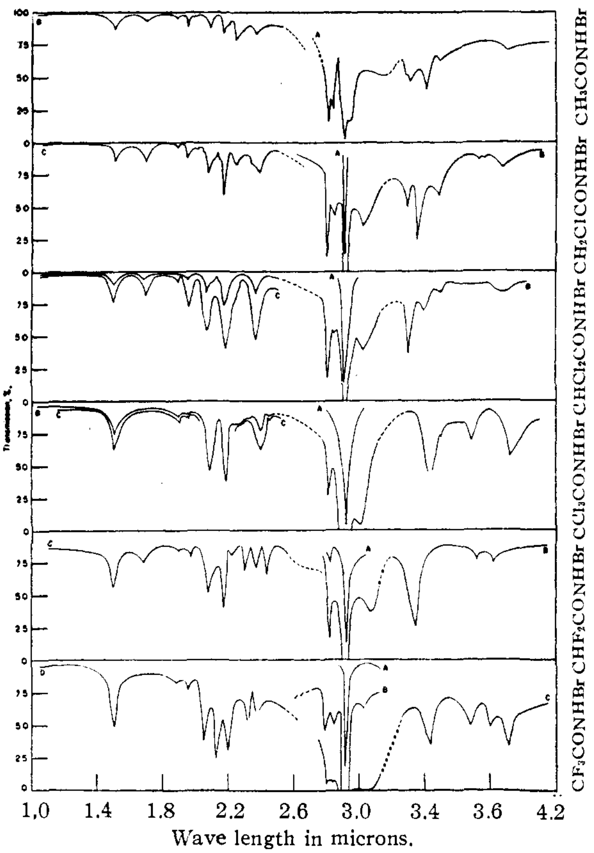

Fig. 2.—Infrared absorption spectra in the lithium fluoride region. Samples of CCl$_4$ solution.

CH$_3$CONHBr, A, 0.0017 M in 10 cm. cell
B, 0.01 M in 10 cm. cell
CH$_2$ClCONHBr A, 0.001 M in 4 cm. cell
B, 0.01 M in 4 cm. cell C, 0.01 M in 5 cm. cell
CHCl$_2$CONHBr A, 0.0017 M in 4 cm. cell
B, 0.017 M in 4 cm. cell C, 0.017 M in 10 cm. cell
CCl$_3$CONHBr A, 0.003 M in 4 cm. cell
B, 0.03 M in 4 cm. cell C, 0.03 M in 10 cm. cell
CHF$_2$CONHBr, A, 0.001 M in 5 cm. cell
B, 0.01 M in 5 cm. cell C, 0.05 M in 5 cm. cell
CF$_3$CONHBr A, 0.0006 M in 5 cm. cell
B, 0.006 M in 5 cm. cell C, 0.03 M in 5 cm. cell
D, 0.12 M in 5 cm. cell

Park and others[14] have reported on the brominating activity of these N-bromoacetamides. They observed that in the bromination of toluene varying amounts of ring and side chain bromination occurred depending on the nature of the α-carbon group. In interpreting their results they assumed that the mechanism of ring bromination was by way of a positive bromine atom. In other words, in some cases a heterolytic cleavage of the N–Br

TABLE III

ABSORPTION COEFFICIENT FOR THE N-H BAND AT 2.93μ AND THE PERCENTAGES OF RING AND SIDE CHAIN BROMINATION OF TOLUENE

α-Carbon group	Absorption coefficient	Per cent.	
		Ring	Side chain
-CF$_3$	250	88	12
-CH$_2$Cl	220	82	18
-CHF$_2$	174		
-CHCl$_2$	128	62	38
-CCl$_3$	117	17	83
-CH$_3$	106	0	100

bond was more likely to occur than in others. It is evident from Table III that the greater the absorption coefficient for the band at 2.93μ the greater is the amount of heterolytic cleavage of the N–Br bond and subsequent ring bromination. No bromination studies have been conducted with N-bromodifluoroacetamide but it might be expected to give a slightly less amount of ring bromination than N-bromomonochloroacetamide. Thus, it may be possible to predict in a qualitative manner the chemical activity of an N-bromoacetamide from spectroscopic studies.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Organotin Compounds Containing an Azo Linkage

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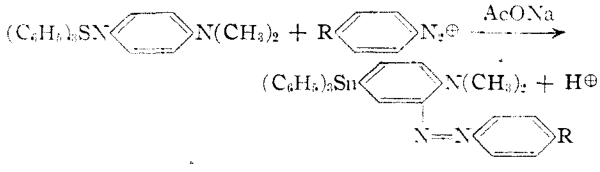
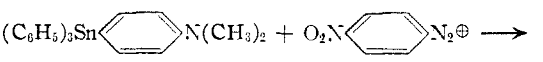
Some organotin compounds containing an azo linkage have been prepared by treating triphenyl-*m*- and triphenyl-*p*-dimethylaminophenyltin with appropriate diazonium salts. Their preparation and replacement of substituents by the diazonium cation in the course of the diazo-coupling reaction are described.

Organometallic compounds of silicon,[1] tin[2] and lead[3] containing an azo linkage have been prepared. It was found[1] that when trimethyl- and triphenyl-*p*-dimethylaminophenylsilane were treated with *p*-nitrobenzenediazonium salt the dye isolated in both cases was 4-dimethylamino-4'-nitroazobenzene. The latter is formed by the replacement of the trimethylsilyl and triphenylsilyl groups by the diazonium cation during the diazo-coupling reaction. Trimethyl- and triphenyl-*m*-dimethylaminophenylsilane, however, showed normal behavior toward diazonium salts, and gave a series of azo dyes in good yields. In contrast with its silicon analog, triphenyl-*p*-dimethylaminophenyltin reacted normally with *p*-nitrobenzenediazonium salt.[2] In order to explore the scope and limitations of this reaction, some additional organotin compounds containing an azo linkage have been synthesized with a view to their examination as carcinogenic agents[2] and for their substantivity as dyes.[1]

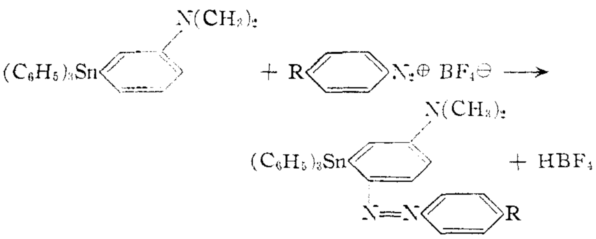
In the method previously reported,[2] triphenyl-*p*-dimethylaminophenyltin reacted with the *p*-substituted benzenediazonium salt in an acetate buffered solution. This method was extended to prepare compounds where R was —Br and —Cl as well as —NO_2 but the yields were very low, and in the case where R was —SO_3H, no reaction took place. Therefore a new method of preparation was sought. An improved procedure was found in the use of *p*-substituted benzenediazonium fluoborates which are stable solids and can be isolated, dried and weighed. A buffered solution was no longer used, and the coupling reaction was carried out in a dioxane–water solution.



It was found that when triphenyl-*p*-dimethylaminophenyltin was treated with *p*-nitro- and *p*-bromobenzenediazonium fluoborate, replacement of the triphenyltin group by the diazonium cation occurred. This result is in agreement with that obtained for the silicon analog. Other examples of replacement of substituents in the diazo-coupling reaction have been reported; the replacement of the carboxyl group during diazo-coupling with 2-hydroxy-1-naphthoic acid and *p*-hydroxybenzoic acid,[4] replacement of halogen and sulfonyl groups in the 1-position of 2-naphthol by the diazonium ion,[5] partial replacement of bromo and carboxyl groups in *p*-substituted dimethylaniline and complete replacement of the trimethylsilyl group in 1-trimethylsilyl-2-naphthol.[1,6]



Triphenyl-*m*-dimethylaminophenyltin coupled in the normal manner with diazonium fluoborates and the azo dyes were isolated in good yields. In preparations where R was –NO_2, –Br or –CO_2H, the reaction was successful, but where R was —$N(CH_3)_2$, no reaction took place. This might be expected as the diazonium ion is an electrophilic reagent, and its cationoid reactivity will be enhanced by electron-attracting and reduced by electron-releasing substituents in the para position on the benzene ring. The structure proof for this series of compounds was carried out by reductive



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