

[CONTRIBUTION FROM DEPARTMENT OF PHYSICS, UNIVERSITY OF FLORIDA]

The Infra-red Spectra of Ammonium Halides¹

BY DUDLEY WILLIAMS

As a result of Reinkober's investigations^{1a} of the infra-red absorption and reflection spectra of ammonium salts in the solid state and in solution, it is frequently stated² that the characteristic oscillation frequencies of cations are increased on transition from solid to solution. This change in frequency is the reverse of the usual change for anions. As the ammonium group has nine fundamental frequencies³ (four of them distinct) and as Reinkober gives results for only two bands, it appeared that further work might be desirable before the above-mentioned increase in frequency could be definitely established even for the ammonium group. The solution work of Reinkober is summarized in Table I.

The object of the present investigation was to obtain additional data on the ammonium frequencies by absorption measurements with the hope of gaining further information on the changes taking place in the 3.2μ and 5.8μ bands when the salts are dissolved. By means of a rock-salt prism spectrometer the transmission spectra of the solvent and of the solutions were studied over the range 2μ to 8μ . A preliminary study showed the changes in NH_4^+ frequencies with concentration to be small as compared with the changes accompanying the solid-to-solution transition, and hence saturated solutions were taken in order to ensure sufficient absorption near 5.8μ . Fluorite absorption cells of approximately 0.02 mm. thickness were used. The samples of powdered salts for comparison with the solutions were prepared by a gaseous reaction between ammonia and hydrogen fluoride, hydrogen chloride, and hydrogen bromide. The mean diameters of these particles varied between 2 and 10 microns in the various samples, and consequently thin absorbing layers had to be used on account of scattering. The powders were deposited directly upon a fluorite or rock-salt plate and were then heated in order to drive off any occluded gases.

The absorption of these powder samples was similar to that of the samples Reinkober prepared by sublimation. No entirely satisfactory powder samples of ammonium iodide were obtained, and hence the data for this material are incomplete.

The results for the solutions obtained are shown in Fig. 1. The dotted curves indicate the transmission of water, well-known bands appearing at 3.0 , 4.7 and 6.15μ . The solid curves represent the transmission of the solutions as indicated. Three major differences between solvent and solution curves are at once apparent: (1) an enormous increase in absorption on the long-wave length side of the 3μ water band, (2) a small increase in absorption near 5.7μ , and (3) an additional band near 7μ . The increased absorption in these regions probably arises primarily from the oscillations of the ammonium group. Another marked effect is observed in the neighborhood of the 4.7μ associational water band; the appearance of this band varies with the solute. In the fluoride curve, the associational band apparently is shifted to shorter wave lengths and is not separated from the ammonium absorption in this region. In the chloride and bromide curves, the maximum appears at longer wave lengths, while in the iodide curve this band is apparently no longer separated from the ammonium band near 5.7μ . Although the shift in the position of the 4.7μ band produced by the presence of these solutes is in general agreement with previous work⁴ on alkali halide solutions, the magnitude of the shifts is much larger in the case of the ammonium compounds. The appearance of the transmission curves is also in fair agreement with the curves published by Reinkober.

In obtaining an estimate of the positions of the absorption bands arising from the ammonium group in solution, one might select only the actual absorption maxima appearing in the curves (as was done by Reinkober), a procedure giving satisfactory results only for the 7μ band (which is not near the characteristic water bands), or one may assume that the water spectrum is unchanged by the presence of the solute and calculate "relative

(1) Original manuscript received June 24, 1940.

(1a) O. Reinkober, *Z. Physik*, **3**, 323 (1920); **35**, 179 (1926).

(2) F. G. Rawlins and A. M. Taylor, "Infra-red Analysis of Molecular Structure," Cambridge, 1929, p. 57; C. Schaefer and F. Matossi, "Das ultrarote Spektrum," Verlag Julius Springer, Berlin, 1930, p. 370.

(3) H. R. Mills and A. C. Menzies, *Proc. Roy. Soc. (London)*, **149A**, 407 (1935).

(4) E. Ganz, *Z. physik Chem.*, **33**, 163 (1936); E. K. Plyler and E. S. Barr, *J. Chem. Phys.*, **6**, 316 (1938); T. N. Gautier and D. Williams, *Phys. Rev.*, **56**, 616 (1939).

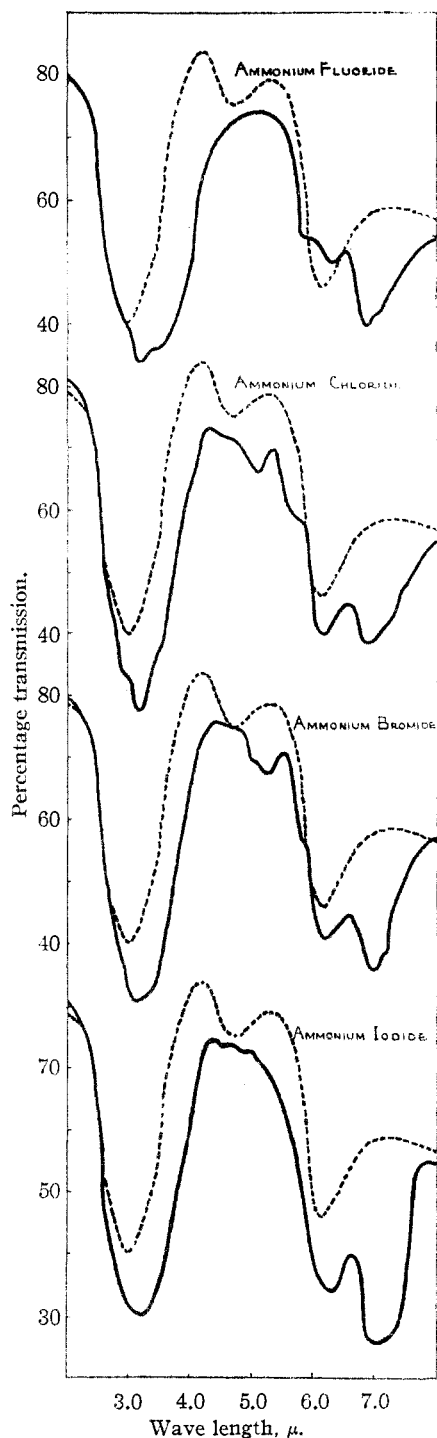


Fig. 1.—The infra-red transmission spectra of aqueous solutions of ammonium halides.

absorption factors" as in previous work on solutions.⁵ Although the solvent spectrum is obviously modified by the presence of the ammonium compounds, it was decided to employ the latter

(5) D. Williams and L. Decherd, *THIS JOURNAL*, **61**, 1382 (1939).

method, since the ammonium band near 5.8μ produces no separate maximum in the solution curve itself. It should be noted, however, that the curves giving "relative absorption factors" show maxima not only at the wave lengths of ammonium absorption but also in spectral regions in which the solvent absorption is modified.

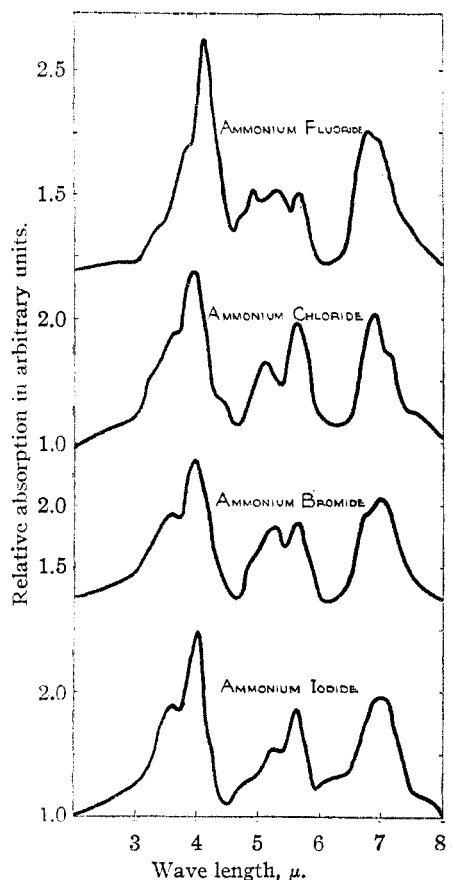


Fig. 2.—The absorption of ammonium halide solutions compared with that of water.

The curves showing the relative absorption of the solutions are given in Fig. 2. The absorption maxima near 7μ are well defined in all the curves, while less intense bands near 5.65μ are also found in every curve. These maxima probably arise from the vibrations ν_4 and ν_2 , respectively. The interpretation of the curves between 3μ and 5.5μ is by no means as simple. In this region intense bands appear near 3.9μ and 5.2μ , while there is evidence for less intense bands at 3.6μ in all curves except the fluoride where corresponding apparent absorption appears at 3.8μ . It is possible that the maxima at 3.9μ and 5.2μ may be due to the absorption produced by ammonium hydroxide molecules formed by hydrolysis, as

Plyler and Gordy⁶ have observed broad regions of increased absorption near 3.65μ and 5.2μ in aqueous solutions of hydroxides and of the hydrolyzing salts which yield hydroxide molecules in solution. The discrepancy between the position of the maximum as reported by Plyler and Gordy and the position obtained in the present work may arise from the better resolution obtainable with the fluoride instrument or from differences in thickness of the absorbing layers employed. It should be noted that the absorption observed for hydroxide solutions consists of broad regions of absorption rather than sharp bands. Hence the position of the transmission maximum for water may have a marked influence on the wave length of the apparent maximum absorption caused by the hydroxides. With the thin cells used in the present work the maximum water transmission appears at 4.2μ rather than at 3.8μ as in the thicker cells used by Plyler and Gordy. Another factor involved is the effect of the solute on the broad 4.7μ water band. As a result of the complicating factors involved in the region between 3 and 5.4μ , it is impossible from the present work to ascertain the positions of the bands arising from the ammonium frequencies ν_1 and ν_3 .

TABLE I

Salt	Solid state, cm. ⁻¹		Aqueous solution, cm. ⁻¹	
	ν_1	ν_3	ν_1	ν_3
NH ₄ F	3115	1505	2800	1470
NH ₄ Cl	3115	1420	3250	1430
NH ₄ Br	3115	1415	3250	1430
NH ₄ I	3115	1400	3250	1405

TABLE II

Compounds	Frequencies (cm. ⁻¹)		
	$\nu_1 - \nu_3$	ν_2	ν_4
Ammonium Fluoride			
Powder	2940	1800 ^(?)	1490
Solution	1770	1470
Ammonium Chloride			
Powder	3070	1750	1410
Solution	1770	1450
Ammonium Bromide			
Powder	3070	1710	1400
Solution	1770	1430
Ammonium Iodide			
Powder
Solution	1770	1430

^o This band is exceedingly weak in the infra-red.

(6) E. K. Plyler and W. Gordy, *J. Chem. Phys.*, **2**, 470 (1934).

In Table II are listed the absorption frequencies observed for the powdered salts and for the frequencies ν_2 and ν_4 in solution. It will be observed that the results of Reinkober are corroborated for ν_4 , *i. e.*, the ammonium chloride and bromide frequencies are increased, while the fluoride frequency is decreased. The same general result will be noted in the case of ν_2 , although in this case the change for ammonium fluoride is scarcely beyond the limit of experimental error. The explanation of the peculiar behavior of ammonium fluoride may possibly be found in the strong tendency of fluorine to form associational bonds through hydrogen. The ammonium ion frequencies in the four halide solutions are nearly constant (the variation in ν_4 possibly arising as a result of experimental error or of the use of rather concentrated solutions). In the crystals these frequencies are lower for the chloride and bromide, and probably the iodide, but higher for the fluoride. This difference is presumably due to a difference in crystal structure and nature of inter-ionic bonds. Ammonium chloride, bromide, and iodide have the cesium chloride structure, which is not favorable to hydrogen bond formation, whereas ammonium fluoride, with the wurtzite structure, contains hydrogen bonds from the ammonium ion to each of the four surrounding fluoride ions.

The hydrolysis and association mentioned above prevent the drawing of any conclusions concerning the effects of solution on ν_1 and ν_3 . Hydrogen bonds between ammonium ions and water molecules are probably formed in the solution. However, the effect of such hydrogen bonding is to produce marked changes in the OH valence vibrations of water and also in the NH valence vibrations of the ammonium group. Since the bands produced by these vibrations overlap, no definite conclusions can be drawn.

Summary

The infra-red transmission of aqueous solutions of the ammonium halides has been measured and compared with the transmission of the powdered salts. The results obtained in the 7μ region are in essential agreement with Reinkober's results. However, this author's interpretation of the solution spectra near 3.2μ seems open to question. The present study indicates that the 7μ and 5.8μ bands are shifted to shorter wave lengths in the solid-to-solution transition except in the case of

fluoride, but no definite conclusions can be reached concerning variation in the ammonium bands near 3.2 μ because of hydrolysis effects. Evidence for

changes in the associational structure of the solvent is found in the 4.7 μ region.

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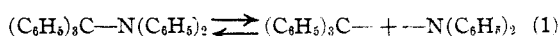
RECEIVED JANUARY 2, 1942

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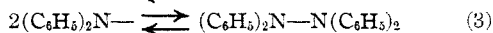
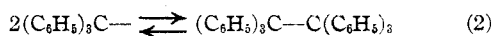
Divalent Nitrogen. II. The Action of Nitric Oxide on Pentaphenylethane¹

BY HENRY SONNEBORN, III, AND F. Y. WISELOGLE

There is abundant qualitative evidence that the compound triphenylmethyldiphenylamine undergoes reversible dissociation in solution at 100° giving triphenylmethyl and diphenylnitrogen radicals (Eq. 1).² Since each of these radicals can dimerize reversibly forming symmetrical com-



pounds (Eqs. 2, 3), the triphenylmethyldiphenylamine at 100° is also in equilibrium with hexa-



phenylethane and tetraphenylhydrazine. In analogous systems the unsymmetrical product generally predominates and it is of considerable interest to evaluate the factors responsible for the stabilization of such unsymmetrical molecules with respect to their symmetrical counterparts.³ A determination of the equilibrium constant for each reaction would make possible a direct calculation of the heat of dissociation which may be taken as the strength of the bond ruptured.⁴ While the heat of dissociation of hexaphenylethane is known,⁵ considerable experimental difficulties

would arise in measuring the equilibrium constants for the other reactions due, for the most part, to the thermal instability of the diphenylnitrogen radical.⁶

A quantity closely related to and generally paralleling the bond strength is the activation energy for the dissociation; this energy is calculated from the rate of dissociation measured at different temperatures. Activation energies for the dissociation of hexaphenylethane⁷ and tetraphenylhydrazine⁶ already have been determined and some time ago we set out to determine the activation energy for the dissociation of triphenylmethyldiphenylamine. We hoped to measure the rate of dissociation by capturing the triphenylmethyl radicals with oxygen in the presence of pyrogallol and measuring the uptake of oxygen. Although this reagent has proved ideally satisfactory for studying rates of dissociation of polyarylethanes,⁸ oxygen and pyrogallol were inapplicable in this case. The quantity of oxygen consumed corresponded, approximately, to one mole per mole of triphenylmethyldiphenylamine in agreement with our expectations. The rate of absorption greatly exceeded that predicted, however, and did not follow the first order law, a requisite behavior if the dissociation reaction had been the rate controlling step.^{2b}

Since oxygen appeared to be excluded as a reagent for studying the rate of dissociation of triphenylmethyldiphenylamine,⁹ we have turned to other possible radical capturing substances. Nitric oxide has been shown to react rapidly and

(1) From a dissertation submitted by Henry Sonneborn, III, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Johns Hopkins University. A portion of this paper was presented before the Division of Organic Chemistry at the St. Louis meeting of the American Chemical Society, April 7-11, 1941. We are indebted to the Hynson, Westcott and Dunning Research Fund for a grant-in-aid covering a part of the cost of this research. Paper I, see ref. 6.

(2) (a) Wieland, *Ann.*, **361**, 200 (1911); (b) Cain, Dissertation, "The Free Diphenylnitrogen Radical," The Johns Hopkins University, 1939.

(3) Pauling and Wheland, *J. Chem. Phys.*, **1**, 374 (1933).

(4) It is important to distinguish between the bond strength as defined here and the bond energy as defined by Pauling. The latter "represents not the amount of energy required to break one bond in a molecule, but instead the average amount required to break all the bonds" of a similar type when the molecule is disrupted into atoms. Only for a diatomic molecule are the bond strength and the Pauling bond energy identical. There is considerable experimental evidence, however, that for carbon-carbon single bonds the two quantities are approximately the same except where radicals are stabilized due to resonance. L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, pp. 53, 58.

(5) Ziegler and Ewald, *Ann.*, **473**, 163 (1929); Preckel and Selwood, *This Journal*, **63**, 3397 (1941).

(6) Cain and Wiselogle, *ibid.*, **62**, 1163 (1940) (paper I of this series).

(7) Ziegler, Orth and Weber, *Ann.*, **504**, 131 (1933).

(8) (a) Ziegler, Ewald and Seib, *ibid.*, **504**, 182 (1933); (b) Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 354 (1936); (c) Bachmann and Osborn, *ibid.*, **5**, 29 (1940); (d) Witten and Wiselogle, *ibid.*, **6**, 584 (1941).

(9) We have subsequently learned that pyrogallol rapidly attacks the undissociated triphenylmethyldiphenylamine liberating a triphenylmethyl radical. By substituting basic oxidation inhibitors, e. g., *p*-phenylenediamine, for pyrogallol first order rate constants were obtained.