included. The relative efficiencies of the gases in the three systems seem to follow the same order. It is not possible to extend the comparison to a detailed picture of the transfer of energy with the order of accuracy obtainable at present.

Solvent Effects on $n \rightarrow \sigma^*$ Transitions of the Bases, Water, Ammonia, Hydrogen Sulfide and Phosphine

By D. P. Stevenson, G. M. Coppinger and J. W. Forbes

It is shown that the quartz and near vacuum ultraviolet absorption bands of water, ammonia, hydrogen sulfide and phosphine in water solution show a "blue shift" relative to the location of these absorption bands in the vapor or in aprototropic solvent solution spectra. The magnitudes of the blue shifts are approximately equal to the heats of solution at ~25° of these hydrides or bases in water. It is suggested that an upper limit to the concentration of such base molecules in water solution that are not engaged in hydrogen bond complexes with the water solvent can be estimated from the ratio of the absorptivity of the water solution to that of the vapor or aprototropic solvent solution at a particular wave length. It is shown that the effect of small concentrations of water on the spectrum of ammonia in otherwise dry diethyl ether are compatible with this suggestion.

It is generally accepted that the lowest energy (longest wave length) electronic excitation process of such substances as ammonia, water, phosphine, hydrogen sulfide, hydrogen chloride and the alkyl derivatives of these substances is associated with the promotion of a non-bonding electron from a 2p or 3p level of the most electronegative atom to an anti-bonding orbital, *i.e.*, the transition is of the type $n \rightarrow \sigma^*$.[1,2] Stated in other terms, the optical electron for the longest wave length ultraviolet absorption band of such substances is one of the unshared electron pair with which the base properties of these substances are associated. Rather naive considerations[3] suggest that if an unshared electron pair of a base is involved in hydrogen bond formation there should be a significant blue shift of the associated electronic absorption band. That is, hydrogen bonding should markedly lower the energy level of the non-bonding electrons while having relatively small effect on the energy level of the anti-bonding orbital. To the extent that this conclusion is valid, one may further conclude that spectrophotometric observations of the $n \rightarrow \sigma^*$ absorption band of such bases in various solvents should provide a means of distinguishing the degree of specific solvation of bases in prototropic solvents from the non-specific solvation as Brealey and Kasha[3] have suggested for the solvent effects on $n \rightarrow \pi^*$ transitions.

Direct evidence of the general validity of the concept of a dramatic blue shift of $n \rightarrow \sigma^*$ absorption bands accompanying solution of a base in a prototropic solvent is provided by a comparison of the spectrophotometric behavior of water vapor with that of liquid water. Wilkinson and Johnston[4] have described the absorption spectrum

of water vapor for wave lengths in the range of 1450 to 1850 Å. From their Fig. 3 one finds the absorptivity of water vapor to be 162 and 22 l./mole cm. at 1800 and 1850 Å., respectively. Ley and Arends[5] reported measurements on the absorption spectrum of liquid water in the range 1820–1985 Å.; at 1824 Å. and 1850 Å. they report $A = 0.11$ and 0.04 l./mole cm., respectively. This decrease in the absorptivity of water that accompanies its condensation corresponds to a ~150 Å. blue shift of the long wave length edge of the absorption band. Such a wave length shift in the vicinity of 1800 Å. corresponds to ~13 kcal./mole stabilization in the liquid phase of the orbital carrying the optical electron.

Ley and Arends[6] reported on the absorption spectrum of ammonia in hexane ($1900 \leq \lambda \leq 2100$ Å.) and ammonia in water ($1820 \leq \lambda \leq 2020$ Å.) where the absorptivities are in the range from 2000 to 50 l./mole cm. Their results for the hexane solution spectrum of NH_3 coincide with the envelope of the minima of the vibronic bands of the ammonia vapor spectrum reported by Tannenbaum, *et al.*,[7] while the *aqua* ammonia absorption band is displaced about 120 Å. to the *blue* from that of the hexane solution.

The present authors have measured the absorptivities of solutions of ammonia in water and in dry diethyl ether with the results shown as curves I and II of Fig. 1. In the region of overlap between our measurements of the *aqua* ammonia spectrum and those of Ley and Arends,[6] the absorptivities agree to about 50% corresponding to a difference of 10 to 20 Å. at constant absorptivity. The ether solution spectrum coincides more or less with the smooth curve through the ammonia vapor band spectrum.[7] In the region of overlap between our ether solution observations and those of Ley and Arends on hexane solutions, we find perhaps a 10

(1) R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

(2) A. D. Walsh, *J. Chem. Soc.*, 2260, 2296 (1953).

(3) Based on the discussion of the effect of solvent polarity on the location of $n \rightarrow \pi^*$ absorption bands. H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952); G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

(4) R. G. Wilkinson and H. L. Johnston, *J. Chem. Phys.*, **18**, 190 (1950).

(5) H. Ley and B. Arends, *Z. Physik. Chem.*, **B6**, 240 (1929).

(6) H. Ley and B. Arends, *ibid.*, **B17**, 177 (1932).

(7) E. Tannenbaum, E. M. Coffin and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953).

Å. red shift for the ether solution absorption band that may be due to experimental error.

Ley and Arends[8] reported measurements of the absorption spectrum of hydrogen sulfide in hexane and water solutions. We have measured the hydrogen sulfide vapor spectrum with the results shown as curve III of Fig. 1. The measurements of Ley and Arends in hexane solution in the vicinity of 2300 Å. are shifted perhaps 15 Å. to the blue from our vapor spectrum.

We have also measured the absorption spectrum of hydrogen sulfide in aqueous 0.01 N and 0.1 N H_2SO_4 solution with the results shown as Curve IV of Fig. 1. The dilute acid was used as a solvent for the measurement of the aqueous hydrogen sulfide spectrum when we found very large apparent deviation from Beer's law in measurements of water solutions. For example, we found the apparent absorptivity of a 1.5×10^{-3} M H_2S in water solution to be 135 l./mole cm. at 2300 Å. while at this wave length the apparent absorptivity of a 1.3×10^{-4} M solution in water was found to be 390 l./mole cm. The difficulty is clearly due to dissociation of the H_2S; HS^- has a strong absorption band with $\lambda_{max} = 2300$ Å. and $A_{max} \cong 5000$ l./mole cm.[8] In the acid solutions the dissociation is suppressed completely and no apparent deviation from Beer's law was found at either acid concentration.

The water solution absorption band of H_2S is shifted about 50 Å. to the blue relative to the vapor band, corresponding to about 4 kcal./mole stabilization of the non-bonding electron (unshared pair) orbital.

Curves V and VI of Fig. 1 show the results of measurements of the absorption spectra of phosphine in the vapor state and in water solution respectively. We have been able to find no previously reported quantitative measurements of the electronic absorption spectrum of this substance. Further, we found no evidence of the diffuse bands Cheesman and Eméleus[9] reported for the 2200–2300 Å. region. The absorption band of PH_3 in water appears to show a small 30 Å. blue shift from the position of the band in the vapor spectrum (corresponding to 2 kcal./mole).

The reader may have noted that the energy equivalents of the blue shifts of the absorption bands of the four substances, H_2O, NH_3, H_2S and PH_3, in water solution relative to vapor or non-polar solvents parallel in excellent fashion the tendency of the four substances to associate in the liquid phase as measured by the departure of the Trouton's constants of the substances from those of the corresponding iso-electronic rare gas or non-polar hydride. Similarly, the energy equivalent of the blue shift is approximately equal to the heat of solution of the "base" in water in those cases where the heats of solution are known. The data pertinent to these conclusions are summarized in Table I.

In order to show the potential utility of the data in Fig. 1 for the discussion of the specific solvation of bases in prototropic solvents, $i.e.$, for the discussion of hydrogen bond formation, we will focus
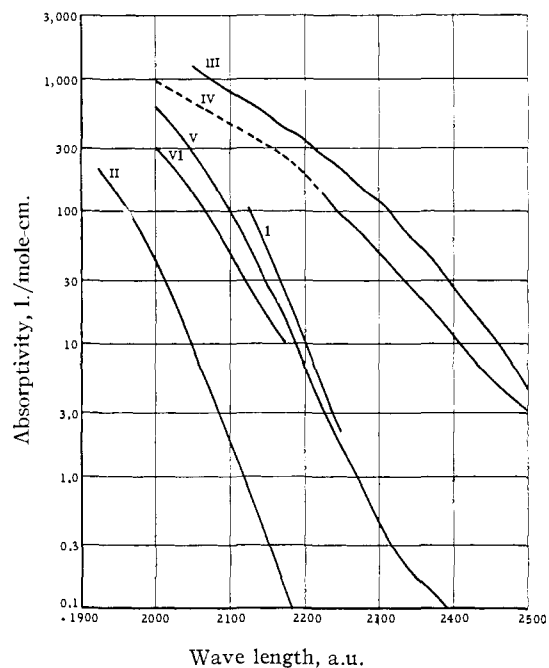
(8) H. Ley and B. Arends, Z. $Physik$. $Chem$., **B15**, 311 (1932).

(9) G. H. Cheesman and H. J. Eméleus, J. $Chem$. Soc., 2847 (1932).

Fig. 1.—Segments of the quartz region ultraviolet absorption spectra of ammonia, hydrogen sulfide and phosphine: curve I, NH_3 in dry diethyl ether; curve II, NH_3 in water; curve III, hydrogen sulfide vapor; curve IV, hydrogen sulfide in dilute sulfuric acid; curve V, phosphine vapor; curve VI, phosphine in water. All measurements were made with a Cary Model 14 ultraviolet spectrophotometer. The dotted portion of IV from Ley and Arends, ref. 8 of text.

attention on ammonia. $Aqua$ ammonia usually is discussed[10] in terms of the two equilibria

$$NH_{3(free)} + H_2O \rightleftarrows NH_4OH \qquad (1)$$

$$NH_4OH \rightleftarrows NH_4^+ + OH^- \qquad (2)$$
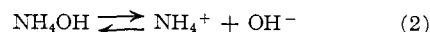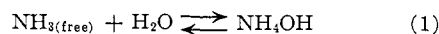
and over the years the conclusion of Moore and Winmill[11] that the equilibrium constant for (1), K

TABLE I

BLUE SHIFTS vs. TROUTON'S CONSTANT AND HEATS OF SOLUTION[a]

	ΔS vap. (b.p.), e.u.	$-\Delta H$ sol., kcal./mole	"Blue shift," kcal./mole
CH_4	17.51	.....	..
NH_3	23.28	+ 8.28	~10
H_2O	26.04	+10.51	~13
Ne	17.54	+ 1.9[b]	..
SiH_4	18	.....	..
PH_3	18.82	?	~ 2
H_2S	20.97	+ 4.6	~ 4
Ar	17.85	+ 2.7[b]	..

[a] ΔS vap. and ΔH sol. (in H_2O) from N.B.S. Circular No. 500. [b] W. Latimer, "Oxidation Potentials," 2nd Ed., Prentice–Hall, New York, N. Y., 1952, p. 367.

$= \dfrac{[NH_4OH]}{[NH_3]}$, is approximately equal to 1, has been generally accepted. It is not clear to the authors what structural concept should be associated with "free" ammonia molecules that have been assumed to constitute about 50% of the ammonia in the

(10) See for example, N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford Press, New York, N. Y., 1950, pp. 880–881.

(11) T. S. Moore and T. F. Winmill, J. $Chem$. Soc., **107**, 1635 (1912).

aqueous solutions. However, it seems reasonable to assume that the implication of "free" is that such molecules are not specifically solvated but are simply subjected to the forces of the general dipolar environment of the medium, water. If "free" has this meaning, then it seems reasonable to assume that the spectral behavior of such "free" ammonia molecules would be very like that of ammonia molecules in diethyl ether solution, where there are the strong general dipolar forces associated with the C–O bonds but no possibility of specific solvation such as is implied in the formula NH_4OH.[12]

Subject to the assumptions indicated in the previous paragraph, one can conclude that the absorption spectrum of *aqua* ammonia, as given by Curve II of Fig. 1, is the sum of two quantities

$$A_{(aq.\ NH_3)} = (1 - \alpha) A_{NH_3} + \alpha A_{NH_4OH} \qquad (3)$$

where α is the fraction of the dissolved ammonia in the form of NH_4OH, *i.e.*, specifically solvated, A_{NH_4OH} is the absorptivity of NH_4OH at the wave length λ, and A_{NH_3} is the absorptivity of "free" ammonia molecules and is to be taken equal to that of a diethyl ether solution at λ. Since αA_{NH_4OH} is of necessity a positive quantity, we have from (3) for the fraction of free ammonia molecules, $1 - \alpha$, the inequality

$$(1 - \alpha) \leq \frac{A_\lambda(aq.\ NH_3)}{A_{NH_3}} = 0.005\ (2100 \leq \lambda \leq 2200\ \text{Å.}) \qquad (4)$$

and the conclusion that less than 0.5% of the ammonia in water solutions is "free."

Similar reasoning applied to the data on the vapor and water solution spectra of water, phosphine and hydrogen sulfide leads to the conclusion that less than 0.2% H_2O, 50% PH_3 and 42% H_2S are "free" in water solution at about 25°.

In order to ascertain that the decrease in absorptivities associated with change of solvent from ether to water in the case of ammonia is appropriately attributable to specific complex formation, obser-

(12) By the formula, NH_3OH, we imply an "outer complex" in the sense of Fig. 2 of the definitive paper of R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

vations were made of the effect on the ammonia spectrum of the addition of water to diethyl ether solutions of ammonia. There were measured the optical densities at 2125, 2150 and 2175 Å. (1.0 cm. cell), of ether solutions of NH_3 with various concentrations of water. As may be seen in Table II, the presence of 5 to 10 ml. of H_2O per liter of ether causes a large reduction in the effective absorptivity of the ammonia solutions at these wave lengths.

TABLE II

EFFECT OF H_2O ON THE SPECTRUM OF NH_3 IN DIETHYL ETHER

C^0 (NH_3), M		0.0139	0.0139	0.139
C^0 (H_2O), M		0.0000	.0334	.555
O.D. (1 cm.)	2125	1.460	.686	.585
	2150	0.695	.332	.286
	2175	0.327	.147	.132
$<D/D_0>$			0.455 ± 0.012	0.406 ± 0.005
K			3.4 ± 0.1	2.6 ± 0.1

If one assumes the optical density of each of these solutions is proportional to the concentration of "free" ammonia in the solution, one can calculate an apparent association constant for the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4OH\ (\text{in ether}) \qquad (5)$$

from the expression

$$K = \frac{[1 - D/D_0]}{(D/D_0)[H_2O]} \qquad (6)$$

since the total NH_3 concentration in the solution is small compared with the water concentration. As may be seen in the last line of Table II, the spectral data give ~ 3 l./mole for the (NH_3—H_2O) association constant in the ether solution. Such a value for the association constant would imply that considerably less than 1% of the ammonia in water solution is free, if the association constant were independent of solvent. Clearly the results of the measurements on the effect of water on the spectrum of the ether solution of ammonia are completely compatible with the interpretation given above of the difference between the spectra of the water and the ether solutions of ammonia.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

The Oxidation of Oxalate Ion by Peroxodisulfate. II. The Kinetics and Mechanism of the Catalysis by Copper(II)[1]

BY EPHRAIM BEN-ZVI[2] AND THOMAS L. ALLEN

RECEIVED MAY 20, 1961

The oxidation of oxalate ion by peroxodisulfate is strongly catalyzed by copper(II), but the catalysis is subject to inhibition by molecular oxygen. An investigation has been made of the kinetics of the catalyzed reaction in the absence of oxygen. The rate law is first-order in peroxodisulfate, zero-order in oxalate, and half-order in the catalyst. A free-radical chain mechanism, involving oxidation of copper to the terpositive state, is postulated for the reaction. It is shown that copper does not take part in the chain-initiating step. Reduction of copper to the unipositive state probably does not occur.

In the first part of this series[3] it was shown that copper(II) is a very effective catalyst for the oxi-

(1) This work was assisted by a research grant from the National Science Foundation.

(2) Abstracted in part from the Ph.D. Dissertation of Ephraim Ben-Zvi, University of California, Davis, 1960.

(3) T. L. Allen. *J. Am. Chem. Soc.*, **73**, 3589 (1951).

dation of oxalate ion by the $S_2O_8^=$ ion,[4] and a brief study of the kinetics of the copper-catalyzed re-

(4) In common usage $S_2O_8^=$ is persulfate. Under the "1940 Rules" [W. P. Jorissen, H. Bassett, A. Damiens, F. Fichter and H. Rémy, *ibid.*, **63**, 889 (1941)] and in *Chemical Abstracts* it is designated peroxydisulfate. In the "Definitive Rules for Nomenclature of Inorganic Chemistry," *ibid.*, **82**, 5523 (1960)] it is peroxodisulfate.