situation is very complicated and involves assumptions concerning the mechanism of the reaction, the above considerations should be regarded as giving qualitative support to the Brönsted theory and not as proving the validity of the Brönsted equation.

Summary

1. Reaction velocity measurements of the hydrolysis of methyl acetate, catalyzed by 0.1 and 0.2 *M* hydrochloric acid at 25 and 35° in dioxane–water mixtures covering a range of concentration of dioxane from 0 to 90% by weight have been made.

2. The relative activity coefficient of methyl acetate in these dioxane–water mixtures has been determined by vapor pressure measurements.

3. The reaction velocity constant was found to be proportional to the acid concentration in all mixtures in moderately dilute acid solution.

4. As a first approximation, the activation energy was found to be independent of the solvent composition.

5. From Brönsted's equation, the activity coefficient of the transition complex was computed and found to vary with solvent composition in a manner similar to the variation of the activity coefficient of hydrochloric acid in these mixtures. A similar result was found for the variation of these quantities in salt solutions. These conclusions are evidence for the validity of the Brönsted theory.

NEW HAVEN, CONN. RECEIVED MARCH 13, 1941

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

The Relative Strengths of Acids and Bases

BY E. C. LINGAFELTER

In presenting a generalized theory of acids and bases, Lewis[1] has suggested that it is impossible to arrange acids or bases in a single monotonic order of strength, which would hold for neutralizations by all bases or acids under all conditions. Luder, in his recent review on the electronic theory of acids and bases,[2] implies that such an order should be possible. However, if we consider the various factors which affect the strength of the bond between an acid and a base, it is evident that such an order should not be possible.

Luder states that "according to Lewis' theory, the strength of an acid corresponds to its tendency to accept an electron-pair from a base. The strength of a base corresponds to its tendency to donate an electron-pair to an acid." More correct statements would be: (a) The strength of an acid corresponds to the strength of the bond which it can form with a base, or (b) the strength of an acid corresponds to the decrease in free energy upon formation of a bond with a base.

The interatomic forces in such an acid–base neutralization compound involve not only the bonding forces of the covalent bond, but also electrostatic forces which depend upon the magnitude and separation of charges, and the presence or absence of dipole moments in either acid or base.

Pauling[3] has pointed out the variation in the strengths of bonding orbitals of different types. Since the factors contributing to bond strength can vary more or less independently, the relative strengths of a series of bases may depend on the particular acid used in making the comparison. That this is the case, can be shown by a brief consideration of some equilibrium constants.

The equilibrium constant

$$K = \frac{\text{(neutralization compound)}}{\text{(acid) (base)}}$$

is a measure of the strength of the acid or base. In Table I are given the equilibrium constants at 25°[4] for the reactions

$H^+ + \text{base} = \text{neutralization compound}$

$Ag^+ + 2(\text{base}) = \text{neutralization compound, and others.}$

Thus, using H^+ for our reference acid, we find: $CN^- \sim NH_3 > SO_3^=$ while for Ag^+: $CN^- > SO_3^= > NH_3$. The difference is even more striking if we consider the effect of the charges of the bases.

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[1] G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[2] Luder, *Chem. Rev.*, **27**, 547 (1940).

[3] Linus Pauling, "The Nature of the Chemical Bond," Chap. III, Cornell University Press, Ithaca, N. Y., 1939.

[4] Equilibrium constants for the metal-complexes and for HCN, NH_4^+ and HSO_3^- are taken from Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938. The relative strengths of HCl, HBr, and HI are from Hantzsch and Weissberger, *Z. physik. Chem.*, **125**, 251 (1927).

TABLE I

EQUILIBRIUM CONSTANTS FOR FORMATION OF NEUTRALIZATION COMPOUNDS

Base Acid	H^+	Ag^+	Cu^+	Hg^{++}
CN^-	2.5×10^9	2.6×10^{18}	1×10^{16}	2.5×10^{41}
NH_3	1.8×10^9	1.7×10^7		
$SO_3^=$	1×10^7	3.3×10^8		
Cl^-	weak		3.4×10^5	9×10^{15}
Br^-	weaker		8.3×10^5	4.3×10^{21}
I^-	weakest		7.1×10^8	1.9×10^{30}

The constants for CN^- and $SO_3^=$ should decrease relative to that of NH_3 in changing from H^+ as reference acid to Ag^+ (which shows a higher coordination number) because of the unfavorable repulsion of the charged bases. However, we find that the change is in the opposite direction.

Another comparison may be made, using the bases Cl^-, Br^-, I^-, CN^- and the acids H^+, Cu^+, Hg^{++}. Here, using H^+ for our reference acid we find: $CN^- > Cl^- > Br^- > I^-$; using Cu^+: $CN^- > I^- > Br^- \sim Cl^-$; and using Hg^{++}: $CN^- > I^- > Br^- > Cl^-$.

In both sets of data considered, we see that there is a reversal of relative strength of some of the bases upon changing the reference acid. Therefore there can be no single monotonic order of base strengths which would be applicable to all cases.

Summary

1. A consideration of the forces involved in the neutralization of an acid and a base, as defined by Lewis, indicates that it is not possible to arrange acids or bases in a single monotonic order of strength.

2. A consideration of a series of equilibrium constants, taken from the literature, shows definitely that bases cannot be so arranged, and that, by changing the reference acid, a reversal of relative base strength can in some cases be observed.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Photochemistry of Acetamide in Water Solution

BY DAVID H. VOLMAN

Evidence has been presented by Gopala Rao and Dhar,[1,2] that the formation of ammonia in the soil from amino acids is mainly an oxidative de-amination, accelerated by sunlight. Thus it has been shown that aqueous solutions of amino acids photolyze in the presence of various photosensitizers. Likewise, it has been shown that amides are hydrolyzed in aqueous solution with the formation of the corresponding ammonium salt, when exposed to sunlight in the presence of photosensitizers.[3] Hence, it has been postulated that the process of ammonification of nitrogenous compounds in the soil may be mainly photochemical in tropical countries, taking place under the influence of sunlight.[3]

It was believed that a study of the photochemical reaction involved in the ultraviolet region of absorption would be of value in elucidating the mechanism for the photosensitized reaction.

The experiments reported herein on the ultraviolet photolysis of acetamide are found to give results which may be compared with those obtained by Rao and Pandalai[3] on the photosensitized reaction. Data on the variation of the quantum yield with temperature and concentration are given. In addition, analyses on the gaseous products obtained in the acetamide solution photolysis, and experiments with propionamide and butyramide, are reported.

Experimental Method

The solutions of amide in water were irradiated by a parallel ultraviolet light beam obtained from a mercury lamp (Hanovia Alpine) through a quartz lens of $f = 10$ cm. At a constant distance a quartz cell of 10-cm. length and 83-ml. volume was placed in the path of the light beam.

Quantum yields were obtained by comparing the reaction with the photodecomposition of monochloroacetic acid in the somewhat crude way described by Weizmann, Bergmann and Hirshberg.[4] A second cell containing a monochloroacetic acid solution was placed behind the first cell described above. The difference between the amount of monochloroacetic acid decomposed in the second cell when the first cell contained (a) water, and (b) the investigated solution could be used to calculate the number of quanta absorbed in the solution. The quantum yield of 0.32 for the monochloroacetic acid hydrolysis at 25° recently reported by Smith, Leighton and Leighton[5] was used.

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(1) Rao and Dhar, *J. Indian Chem. Soc.*, **10**, 699 (1933).

(2) Rao and Dhar, *ibid.*, **11**, 617 (1934).

(3) Rao and Pandalai, *ibid.*, **11**, 623 (1934).

(4) Weizmann, Bergmann and Hirshberg, THIS JOURNAL, **58**, 1675 (1936).

(5) Smith, Leighton and Leighton, *ibid.*, **61**, 2299 (1939).