Solvation versus Solvolysis

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In the October 1981 issue of *Chem 13 News,* K. J. Laidler, commenting on H. I. Feinstein's earlier article in the May issue on the classification of chemical reactions, objected to that author's use of the term "hydrolysis" to describe such reactions as (1, 2):

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad [1]$$

$$O^{2-} + H_2O \rightarrow 2OH^- \qquad [2]$$

In support of this objection, Laidler cited the etymology of the word hydrolysis (from the Greek words *hydro* or water and *lysis* or splitting) and the recent lUPAC report "Glossary of Terms Used in Physical Organic Chemistry" (3), implying that the term should be employed only to describe reactions in which "a water molecule brings about the splitting of one or more chemical bonds," by which criterion reactions 1 and 2 apparently do not qualify.

The specific definition to which Laidler refers (which actually appears under the heading of solvolysis) reads as follows (3):

> *Generally, a reaction with a solvent [e.g.* H_2O*] or with a lyonuim ion [e.g.* H_3O^+*] or lyate ion [e.g.* OH^-*], involving the rupture of one or more bonds in the reacting solute. More specifically the term is used for substitution, elimination and fragmentation reactions in which a solvent species is the nucleophile.*

Though such a definition may be suitable for organic chemistry, its use in inorganic chemistry would cause havoc as it would literally require that all solvent-induced ionic dissociations, such as:

$$NaCl(s) + (x + y)H_2O(l) \rightarrow Na^+(H_2O)_x + Cl^-(H_2O)_y \qquad [3]$$

$$HCl(g) + (1 + y)H_2O(l) \rightarrow H_3O^+ + Cl^-(H_2O)_y \qquad [4]$$

be classified as hydrolysis reactions.

Indeed, the definition is in many ways at variance with the long-standing definition of solvolysis given in the inorganic acid-base and nonaqueous solvent literature (4). Thus, for example, Sisler defines solvolysis as (5):

> *... a reaction in which the solvent molecule reacts with the solute in such a way that the solvent molecule is split into two parts, one or both of which becomes attached to a solute molecule or ion.*

This process is to be contrasted with solvation (5):

> *... in which a molecule of the solvent attaches itself to a solute species (cation, anion or molecule) by any one of the various chemical bonds, notably ion-dipole. hydrogen bonding or coordinate covalent bonding.*

In short, solvolysis reactions are characterized by the heterolytic cleavage of the solvent molecule itself and not necessarily by the cleavage of the solute species. In contrast, solvation interactions are characterized by the preservation of the integrity of the solvent molecule, while the solute species itself may or may not be heterolytically cleaved.

Heterolysis reactions in solution generally lead to charged fragments or ions. When the solvation interaction fails to cleave the solute, the reaction is simply termed solvation – for example:

$$(CH_3)_2CO(l) + H_2O(l) \rightarrow (CH_3)_2CO\cdots H_2O(aq) \qquad [5]$$

However, when the solvation interaction leads to solute heterolysis and ion formation, as in reactions 3 and 4, one generally talks about ionic dissociation rather than solvation.

Likewise, solvolytic heterolysis of the solvent itself frequently leads to ion formation (e.g., H_3O^+ and OH^-, in the case of water, or NH_4^+ and NH_2^- in the case of liquid ammonia) and these ions generally correspond to the so-called characteristic solvent ions of the solvent-system acid-base definitions (4). If the solute preferentially combines with the characteristic solvent anion, thereby causing an increase in the solvent cation concentration (e.g. H_3O^+ or NH_4^+), the reaction is said to be an acidic solvolysis. Conversely, if the solute preferentially combines with the characteristic solvent cation, thereby causing an increase in the solvent anion concentration (e.g., OH^- or NH_2^-), the reaction is said to be a basic solvolysis.

Typical introductory textbook discussions of acidic and basic hydrolysis arc generally consistent with these definitions. In all cases the water molecule is cleaved and either the free OH^- or free H_3O^+ concentration is preferentially increased. For example:

Acidic Hydrolysis

$$Fe^{3+}(aq) + 2H_2O(l) \rightarrow Fe(OH)^{2+}(aq) + H_3O^+(aq) \quad [6]$$

$$SO_2(g) + 2H_2O(1) \rightarrow SO_2(OH)^-(aq) + H_3O^+(aq) \quad [7]$$

Basic Hydrolysis

$$CO_3^{2-}(aq) + H_2O(1) \rightarrow HCO_3^-(aq) + OH^- (aq) \quad [8]$$

$$CN^-(aq) + H_2O(1) \rightarrow HCN(aq) + OH^-(aq) \quad [9]$$

The sole exception to this statement is the incorrect, but virtually universal, description of the behavior of ammonium salts in water as being due to acidic hydrolysis. This is probably a carryover from the turn of the century when it was thought that the predominant species in ammonia water was NH_4OH. Thus ammonium salts were thought to increase the H^+ (or H_3O^+) concentration via hydrolysis and NH_4OH formation:

$$NH_4^+(aq) + 2H_2O \rightarrow NH_4OH(aq) + H_3O^+(aq) \quad [10]$$

Of course, it is now known that the predominant species in ammonia water is actually the NH_3 molecule itself and that the NH_4^+ ion, like the HCl molecule, decreases the pH via ionic dissociation rather than hydrolysis:

$$NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq) \quad [11]$$

Needless to say, reactions 1 and 2 definitely do qualify as hydrolysis by these definitions.

Unfortunately, however, Feinstein then errs in the opposite direction by incorrectly including several examples of acidic solvolysis under the heading of solvation:

$$SO_3 + 2NH_3 \rightarrow SO_3(NH_2)^- + NH_4^+ \quad [12]$$

$$SO_3 + 2H_2O \rightarrow SO_3(OH)^- + H_3O^+ \quad [13]$$

To the best of my knowledge, the reaction of SO_3 with water has not been thought of as a simple, additive, hydration interaction since the middle of the 19th century and the demise of the dualistic theory, which wrote the reaction as:

$$SO_3 + H_2O \rightarrow SO_3{\bullet}H_2O \quad [14]$$

Though discussions of definitions and classifications are frequently dismissed as pedantic, the above confusion shows that failure to give them proper consideration can often lead to chaos. At their best, definitions and classifications are extremely valuable guides to the study and systemization of factual matter, whereas their neglect, at both the introductory and advanced levels, can lend credibility to the often heard student complaint that descriptive chemistry is little more than a hodgepodge of unrelated facts.

References and Notes

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