Acidity and Catalytic Activity of Metal Ions

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In Lewis's definition, acid-base properties are defined as the acceptance and donation of an electron pair to form a covalent bond. Accordingly, as a first approximation, the acidity may be expected to increase with the electronegativity or the electron-accepting power. According to the definition proposed by Iczkowski and Margrawe,[1] the electronegativity of a metal ion (χ_i) is related to its charge (Z) and to its successive ionization potential (I) in the following way;

$$\chi_i = (\partial I / \partial Z)$$

The successive ionization potential of a metal ion can be approximately expressed in a quadratic equation of its charge (Z); the electronegativity of a metal ion with a charge (Z) is generally given in the following form;

$$\chi_i = a + 2bZ = (1 + 2bZ/\chi_0)\chi_0$$

where χ_0 is the electronegativity of the neutral atom ($Z=0$) given by Pauling, and where the calculated values for $b/\chi_0 (=b/a)$ are approximately unity. A generalized electronegativity of the metal ion can then be found as follows[2];

$$\chi_i = (1 + 2Z)\chi_0$$

In a previous paper,[2] it was shown that the values of χ_i evaluated from the above equation made possible a rough prediction of the acidity and the catalytic activity of the solid surfaces.

In this paper, we have tried to apply this parameter to the catalytic behaviour of metal ions. It is well known that the most familiar process associated with the metal ion acidity is the ionization (hydrolysis) of the aquo-ion; it is frequently expressed as follows;

$$\mathrm{M(H_2O)}_m{}^{\alpha+} + \mathrm{H_2O} \rightleftharpoons [\mathrm{M(H_2O)}_{m-1}\mathrm{(OH)}]^{(\alpha-1)+}] + \mathrm{H_3O^+}$$

This process implies that the equilibrium shifts to the right as the acidity of the central metal ion increases. Figure 1 shows the correlation between the equilibrium constant of this process ($\mathrm{p}K_a$) and the electronegativity of the metal ion (χ_i). This correlation demonstrates that the acidity of the coordinating water, including ion-dipole hydration, increases with the electron-withdrawing power of the central metal ion.

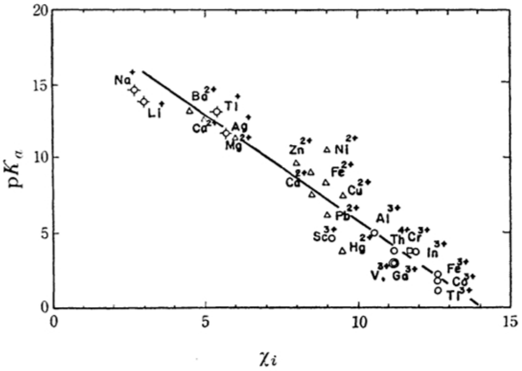

Fig. 1. Acid ionization constants for aqueous metal ions at 25°C.

It is generally accepted that a reaction catalyzed by a metal ion involves the formation of an intermediate species between the metal ion and the reactant, and that this intermediate formation process is generally very rapid. A typical example is the proton-catalyzed halogenation of ketones; the rate-determining step in this reaction has been accepted to be the cleavage of the α-C–H bond of the ketone-proton complex. The characteristics of the metal ion in the halogenation of ketones are similar to those of the proton. Accordingly, it may be expected that the acidity of the α-C–H bond will increase with the electron-withdrawing power of the coordinated metal ion; that is, the coordinated metal ion will draw electrons away from the α-C–H bond toward the carbonyl group, facilitating the removal of the α-hydrogen by a basic species, and the negative charge left on the conjugate base would be spread over a number of atoms, including the coordinated metal ion, to stabilize the conjugate anion rather than being confined to a single carbon atom.

Pedersen[3] has found the following activity sequence of the metal ion for the bromination of 2-carbethoxy cyclopentanone; $\mathrm{Cu^{2+} > Ni^{2+} > La^{3+} > Zn^{2+} > Pb^{2+} > Mn^{2+} > Cd^{2+} > Ca^{2+} > Ba^{2+} > H^+}$.

Figure 2 plots the logarithm of the specific rate constant against the electron-withdrawing power (χ_i), showing a rough parallelism between the catalytic activity and the χ_i parameter, except for $\mathrm{Be^{2+}}$ and $\mathrm{Al^{3+}}$.

The decarboxylation of certain keto-carboxylic

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[1] R. P. Iczkowski and J. L. Margrawe, *J. Am. Chem. Soc.*, **83**, 3541 (1961).

[2] K. Tanaka and A. Ozaki, *J. Catalysis*, **8**, No. 1 (1967).

[3] K. Pedersen, *Acta Chem. Scand.*, **2**, 252, 385 (1948).

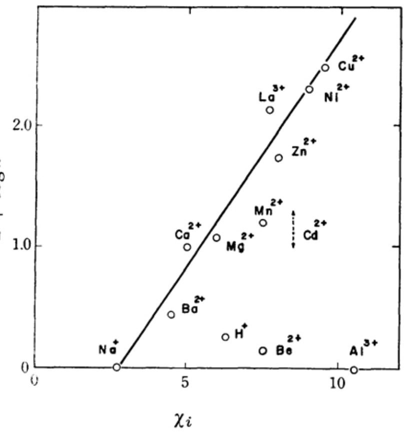
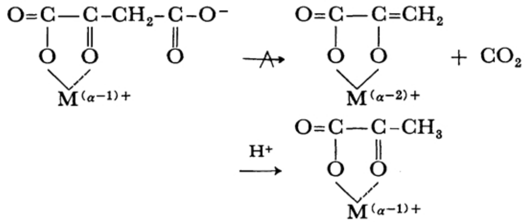


Fig. 2. Catalptic effects of metal ions for the bromination of 2-carbethoxy cyclopentanone at 18°C.

acids is also catalyzed by metal ions. The mechanism of the decarboxylation of oxalo-acetic acid can be represented as follows;



In the decarboxylation of carboxylic acid, RCOOH, it is well known that the reactivity of the carboxylic acid is strongly affected by the electron-attracting properties of the substituent in the R group. The role of the coordinated metal ion is very similar to this electron-attracting substituent in the R group. Figure 3 shows the correlation between the first-order rate constant for the decarboxylation of oxalo-acetic acid obtained by Speck[4] and the electron-withdrawing power of the coordinating metal ions.

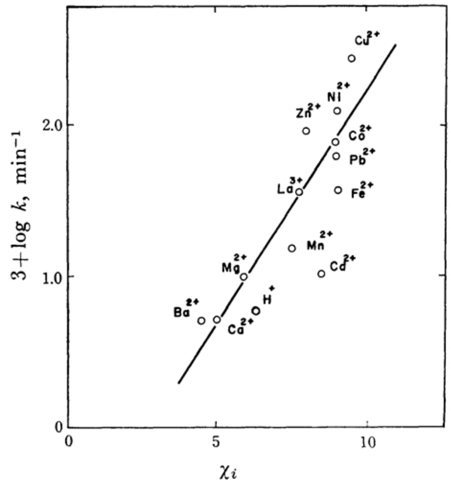
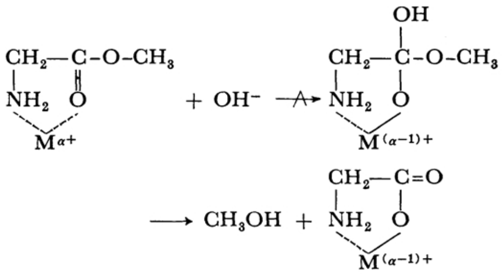


Fig. 3. Catalytic effects of metal ions for the decarboxylation of oxaloacetic acid.

Kroll[5] visualized the mechanism of metal ion catalysis for the hydrolysis of an amino-acid ester as follows;



In this mechanism, the role of the metal ion is similar to that in other reactions discussed above; the correlation with the χ_i parameter is shown in Fig. 4.

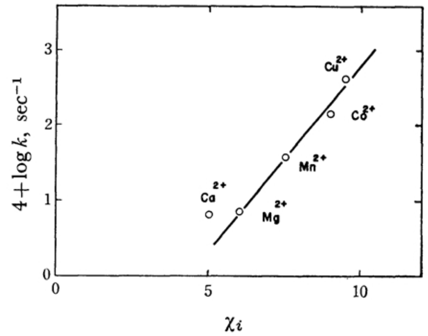


Fig. 4. Catalytic effects of the divalent ions for the hydrolysis of glycine methyl ester.

On the basis of the above examples, the kinetic mechanism of metal ion catalysis, and probably of hydrogen ion catalysis, can generally be given as follows;

$$R + M^{\alpha+} \underset{K}{\rightleftharpoons} X \xrightarrow[k]{} \text{Products}$$

where R is the reactant, M is the metal ion, and X is the intermediate complex. The reaction rate, therefore, is;

$$r = \frac{kK(\mathrm{R})(\mathrm{Mo})}{1+K(\mathrm{R})}$$

$$(\mathrm{Mo}) = (\mathrm{M})+(\mathrm{X})$$

where k is the catalytic rate constant for the rate-determining step and where K is the pre-equilibrium constant between the metal ion and the reactant. The $K(\mathrm{R})$ term usually being sufficiently small to neglect, $K(\mathrm{R}) \ll 1$, the reaction rate can be written as follows;

$$r = kK(\mathrm{R})(\mathrm{Mo})$$

The catalytic activity of the metal ion has been

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[4] J. F. Speck, *J. Biol. Chem.*, **178**, 315 (1948).
[5] H. Kroll, *J. Am. Chem. Soc.*, **74**, 2036 (1952).

usually discussed in connection with the tendency to form intermediate complexes, *i.e.*, the value of the pre-equilibrium constant (K). However, the above equation implies that the effect of the metal ion on the rate constant, k, can not be ignored.

If the inductive effect caused by the electron-withdrawing power of the coordinated metal ion on the catalytic rate constant (k) is expressed in a way similar to that of an organic substituent,[6] the rate constant is formulated in a logarithmic form with the electron-withdrawing power of the metal ion (χ_i) as follows;

$$\log (k/k^*) = \rho_i \chi_i$$

where k^* and k are the rate constant for the reference ion and the catalyst ion respectively, and where ρ_i is a constant.

The stability of the complex is strongly affected by the basicity of the ligand and the acidity of the metal ion; if this is extended to the stability between the metal ion and the reactant, the pre-equilibrium constant, K, would be given as follows;

$$\log (K) = a\chi_i + b$$

The apparent catalytic activity of the metal ion (k_a) can then be described as follows;

$$\begin{aligned}\log (k_a) &= \rho_i \chi_i + a\chi_i + b + \log (k^*)\\ &= \alpha\chi_i + \beta\end{aligned}$$

where α and β are the constants.

This equation reveals that the catalytic activity will increase linearly with the χ_i parameter; the observed relationship between the activity and the χ_i parameter seemingly support the above expectation.

The authors wish to thank Professor Kenzi Tamaru of the Department of Chemistry of The University of Tokyo for his helpful discussions.

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[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Co., New York (1940); R. W. Taft Jr., *J. Am. Chem. Soc.*, **24**, 2729, 3120 (1952).