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Evaluation of Softness from the Stability Constants of Metal-ion Complexes*1

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Utilizing the dual parameter equation we derived previously, we have evaluated quantitatively softness or class (b) character of metal ions on the basis of the original criteria of soft-hard classification, *viz.*, the stability of metal-ion complexes. Various softness parameters proposed so forth have been proved insufficient to describe softness quantitatively, although they are useful for a rough classification of metal ions into soft and hard acids. Discussion is also given concerning origin of softness, especially from the viewpoint of its closs correlation with the solvation effect.

The general idea of classifying acids and bases into class (a) and (b) (hard and soft) acids and bases has been proposed,[2] according to which hard acids prefer to coordinate with hard bases and soft acids with soft bases. This concept is based on the general trend in inorganic stability constants, that is, some acids (hard) form stable complexes in the sequence F>Cl>Br>I, while others in I>Br>Cl>F. This classification has been shown to be useful even in organic chemistry, although prediction remains qualitative, owing to the lack of quantitative scales for the acid or base strength.

Attempts were made to calculate the softness quantitatively from the fundamental properties of elements such as ionization potentials and ionic radii.[3-7] It has been claimed that a certain dual parameter scale is inevitably required in order to express the acid or base strength completely.[8,9]

The purpose of the present work is to determine the softness of metal ion on the basis of the original criteria for the soft-hard classification, utilizing the dual scale equation proposed before.[4] The most commonly used criterion for the soft-hard classification is the stability constants of halogeno-complexes. The concept of softness recently seems to be more or less subjective. The present attempt would make objective evaluation possible.

The dual parameter scale proposed by the authors is as follows.[4] One parameter X is closely related to "hardness" or the electronegativity, and another parameter Y to "softness." With these parameters, the log of stability constants of metal-ion complexes, log K,*2 is expressed well for hard-hard complexes and, to a lesser extent, for soft-soft complexes by the equation

$$\log K = \alpha X + \beta Y + \gamma \qquad (1)$$

where α and β are the dual basicity parameters of a ligand corresponding to X and Y, respectively, and γ is a constant determined for each ligand. The instability constants of hard-hard complexes are mainly determined by αX term and there is a good linear correlation between X and log K.[4] However, the correlation between Y and log K of soft-soft complexes was less satisfactory. It was, therefore, suggested that if one can adjust Y values, Eq. (1) will be much improved for stability constants.[4] Thus, we attempted to improve Y values using the dual parameter equation of the form of Eq. (1) and the regularities found among log K of halogeno-complexes of metal ions.

Results

Procedure for the Derivation of Softness Parameters, Y'. The stability constants of metal-

*1 A part of this work has been referred elsewhere.[1]

1) M. Misono, *Shokubai (Catalyst)*, **9**, 252 (1967).

2) a) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963). b) S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.*, **12**, 265 (1958).

3) R. S. Nyholm, Proceeding of the Third International Congress on Catalysis, Amsterdam, 1964, p. 25, North-Holland, Amsterdam (1965).

4) M. Misono, E. Ochiai, Y. Saito and Y. Yoneda, *J. Inorg. Nucl. Chem.*, **29**, 2685 (1967).

5) R. J. P. Williams and J.D. Hale, *Structure and Bonding*, **1**, 249 (1966).

6) G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

7) A. Yingst and D. H. McDaniel, *Inorg. Chem.*, **6**, 1067 (1967).

8) J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954); **78**, 1819 (1956).

9) R. S. Drago and B. B. Wayland, *ibid.*, **87**, 3571 (1965).

*2 The stability constant, K, is the equilibrium constant of $M^{n+}+mL \rightarrow ML_m^{n+}$. In the previous paper,[4] K was the equilibrium constant of the reverse reaction, that is, the instability constant. Therefore, log K in the present paper is equal to pK in the previous paper.

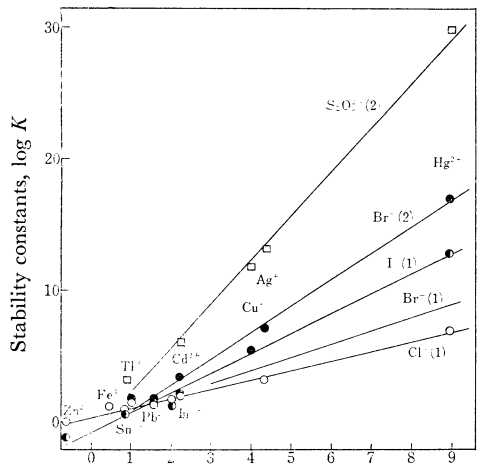

Fig. 1. Regularity among the stabilities of soft-soft complexes.
Log of stability constants of several soft ligand complexes are plotted against those of bromo-complexes. Numbers in parentheses indicate coordination numbers.

ion complexes with various soft ligands, log K, are plotted against those of bromo-complexes for several metal ions in Fig. 1. A fairly good regularity is found among these stability constants. In this figure two apparent trends should be noted: (i) soft metal ions have large log K values ($Hg^{2+}>Cd^{2+}>Zn^{2+}$), and (ii) soft ligands have steep slopes ($I^->Br^->Cl^-$). The trends are well interpreted with the softness sequences and are also expected from the βY term of Eq. (1), suggesting that this type of equation holds among these complexes.

Usefulness of a dual scale equation like Eq. (1) and the regularity in Fig. 1 demonstrated for these complexes prompted us to estimate the softness upon these bases. X values have already been proved to be satisfactory as the hardness parameter in Eq. (1). Thus, if one can choose such Y values that the equation gives satisfactorily the observed log K values, they may be considered to be good softness parameters. In order to avoid confusion, Y', α', β' and γ' will be used hereafter for the new parameters. Then the equation is written as

$$\log K = \alpha' X + \beta' Y' + \gamma' \qquad (2)$$

where X values are common to Eq. (1). From $\beta' Y'$ term which is obtained by the substraction of $\alpha' X + \gamma'$ from log K value, the softness of each metal ion can be estimated with the following procedure.

1) The log K of chloro-complexes is taken, to a first approximation, as Y' value respectively as follows: Hg^{2+}(7.2), Tl^{3+}(6.5), Ag^+(3.8), Cu^+(3.5), Cd^{2+}(2.1), In^{3+}(1.9), Fe^{3+}(1.6), Pb^{2+}(1.6), Sn^{2+}(1.6), Tl^+(1.2) and Zn^{2+}(1.0). Since there are linear correlations among the stability constants of halogeno-complexes (Fig. 1), the stability constants of any halogeno-complexes may be used as the basis for Y' values. Here, chloro-complexes are chosen, simply because a good number of reliable stability constants are available and they give Y' values whose magnitude is better to handle. When there is no experimental log K value of chloro-complex, estimation is made from log K of other halogeno-complexes, considering the regularity in Fig. 1.

2) By the method of least squares, α', β', and γ' are then calculated by Eq. (2) for several soft ligands, including different coordination numbers.

3) Improved Y' values are tentatively obtained from the slopes in log $K-\alpha' X-\gamma'$ *vs.* β' plots (Fig. 2).

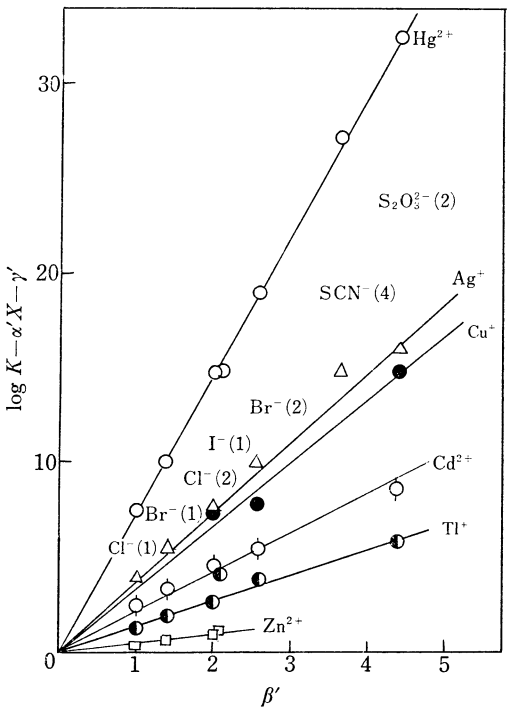

Fig. 2. log $K-\alpha' X-\gamma'$ *vs.* β' plot.

Repeating the above procedure one can get the most reasonable value of Y' for each metal ion. Iteration was not actually continued, since the agreement of the second Y' with the first ones was good enough. The final Y' values are Hg^{2+} (7.3), Tl^{3+} (6.0), Ag^+ (3.8), Cu^+ (3.3), Cd^{2+} (2.0), In^{3+} (1.8), Sn^{2+} (1.8), Pb^{2+} (1.6), Fe^{3+} (1.4), Tl^+ (1.3), and Zn^{2+} (0.7). Linearity of the plots in Fig. 2 is significantly improved compared to that in Fig. 1, which provides a good support for Y' as a good softness parameter which is based on the original criteria for the soft-hard classification. Additional Y' values are determined in a similar manner, using only log K of halogeno-complexes, as follows: Au^+ (10.9), Au^{3+} (9.4), Pt^{2+} (6.9), Pd^{2+} (5.6), Co^{2+} (1.2) Fe^{2+} (0.3) and Mn^{2+} (0.0). Although these values might be less reliable because of the limited number

Table 1. Calculated and observed stability constants of metal-ion complexes

	Y'[b]	OH^-		Stability Constants, log K[a] NH_3		pyridine		Br^-		I^-		$S_2O_3^{2-}$	
		calcd	obsd										
Na^+	0	−1.3	−0.5										
Ag^+	3.8	2.7	2.3	2.9	3.2	1.9	2.0	4.3	4.3			13.7	13.0
Cu^+	3.3											11.5	11.7
Tl^+	1.3							0.8	0.9	0.9	0.7	2.6	3.1
Mg^{2+}	0	2.5	2.6	0.6	0.2								
Ca^{2+}	0	1.4	1.3	0.0	−0.2								
Fe^{2+}	0.3	4.1	3.9	1.8	1.4	0.7	0.7						
Ni^{2+}	1.7	5.4	4.6	3.3	2.8	1.7	1.8					3.7	1.0
Cu^{2+}	1.9	6.0	6.5	3.8	4.2	1.9	2.5	1.5	~0				
Zn^{2+}	0.7	4.5	4.4	2.2	2.4	1.0	1.0	−0.1	−0.6	−0.7	−1.3	2.6	3.1
Cd^{2+}	2.0	5.3	2.3?	3.4	2.7	1.8	1.3	1.8	2.2	2.0	2.3	6.1	5.8
Hg^{2+}	7.3	9.4	10.3	8.8	8.8	5.3	5.1	9.1	9.0	12.9	12.8	29.5	29.7
Fe^{3+}	1.4	11.1	11.8					0.9	0.5				
In^{3+}	1.8	9.8	10.3					1.4	2.0	1.2	1.2		
Number of log K data used for calculation		17		13		8		9		6		7	
α'		1.50		0.89		0.41		−0.01		−0.12		0.12	
β'		0.59		0.90		0.60		1.40		2.08		4.40	
γ'		−2.79		−2.50		−1.29		−0.97		−1.63		−3.31	

a) The values on the left part of each row are those calculated by $\log K=\alpha' X+\beta' Y'+\gamma'$ and those on the right are the observed ones, which are the same as in the previous paper[4] except for some revision and supplements using data in Ref. 14. The values for $S_2O_3^{2-}$ are the overall instability constants of $M(S_2O_3)_2^{(n-4)+}$. Other values are of mono-coordinated complexes.

b) Since very few log K values have been reported for the complexes of less soft metal ions, such as Fe^{2+}, Co^{2+} and Cu^{2+}, Y' was estimated from $Y'=2.8Y-6.2$ which is found to hold approximately between Y and Y'. Y' was put to zero when $2.8Y-6.2$ became negative. This estimation seems sufficient for log K calculation, becuase $\beta' Y'$ term in Eq. (2) contributes little in these cases.

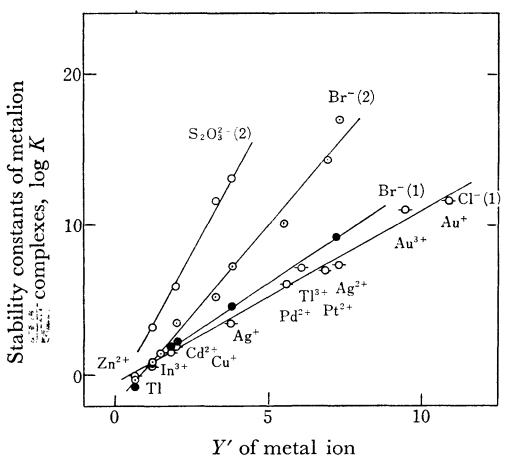

Fig. 3. Stability of metal-ion complex as a function of softness parameter, Y'.
Numbers in parentheses are the same as in Fig. 1.

of reported log K, satisfactory linear correlation of new parameters, Y', with log K values of soft-soft complexes is obtained as demonstrated in Fig. 3. This good correlation is comparable with that of X with log K of hard-hard complexes.[4] A part of the deviation from the straight line found in Fig. 3 may be due to the minor contribution from $\alpha' X$ term in Eq. (2). Some of the calculated log K values by Eq. (2) are given in Table 1 for several metal-ion complexes. The results for the complexes of ligands with considerable softness are given in this table. For hard ligand complexes, the agreement between the calculated and the observed log K values[4] was as good as the present one. Agreements between the calculated and the measured log K in this table are excellent as a whole. Remarkable improvements in agreement are observed especially for I^- and $S_2O_3^{2-}$($\beta'>1$). As for the magnitude of β there is little change; both β and β' follow the softness sequence and are linearly correlated with $n_{P:}$, the reactivity index of a nucleophile for the displacement reaction of Pt^{2+}-complex.[10]

10) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *J. Amer. Chem. Soc.*, **87**, 241 (1965).

Discussion

Comparison of Y′ with Other Softness Parameters. The proposed parameter Y' thus obtained semi-empirically on the basis of the original criteria for the soft-hard classification, may reasonably be considered as a quantitative expression of softness (see Figs. 1 and 2). It seems of interest to compare such various parameters proposed for the quantitative expression of softness of metal ion, as R(N),[3] R(W),[5] Y,[4] α/β[7] and $E_n^=$,[6] with the present parameter Y' and look into the physical meaning of softness. All of these parameters are useful as rough criteria for the soft-hard classification of metal ions, although a few exceptions are always inevitable.

However, it is apparent that the correlations are only qualitative. If one plots these parameters against Y', only fair correlations are obtained for $E_n^=$ and Y, and rather poor ones for R(N), R(W) and α/β. This means that the approximation used for the derivation of the parameters previously proposed are too simple for quantitative use.

Origin of Softness. The soft-hard classification is based on the fact that, reviewing inorganic stability constants in *aqueous* solution, metal ions fall into two distinct groups: those which form halogeno-complexes whose stability order is (i) F>Cl>Br>I, and (ii) I>Br>Cl>F. This situation, however, contrasts with that observed in the gas phase, where the sequence of molecular stability is always found to be MF_2>MCl_2>MBr_2>MI_2. This obviously demonstrates the importance of solvent effect, that is, the change in solvation state during the complex formation. Klopman[6] has recently derived his softness parameter as the difference between the bond energy and the desolvation energy accompanying complex formation. The bond energy consists of electrostatic and charge-transfer interaction energies. In his treatment, the extent of softness of metal ion depends on how much the bond energy overcomes the energy loss due to desolvation. We have previously discussed the bond energy of coordination and the soft-hard properties, dividing the total bond energy into electrostatic, σ-bond and π-bond energies.[4] In this treatment the heat of solvation was assumed to be proportional to the electronegativity X, since the bond energy of metal ion to aquo ligand is mainly correlated to the αX term.

The heat of complex formation, $M^{n+}+mL^- \rightarrow ML_m^{(n-m)+}$(L=F, Cl, Br and I) is equal to the difference between the heat of M-L bond formation and the desolvation energy. Since the latter is roughly equal, with opposite sign, to the solvation energies of M^{n+} and L^-, the stability sequence for a given metal ion, either F>Cl>Br>I or F<Cl<Br<I, may be determined by the change in M-L bond energy relative to that in solvation energy of L^- from F to I.

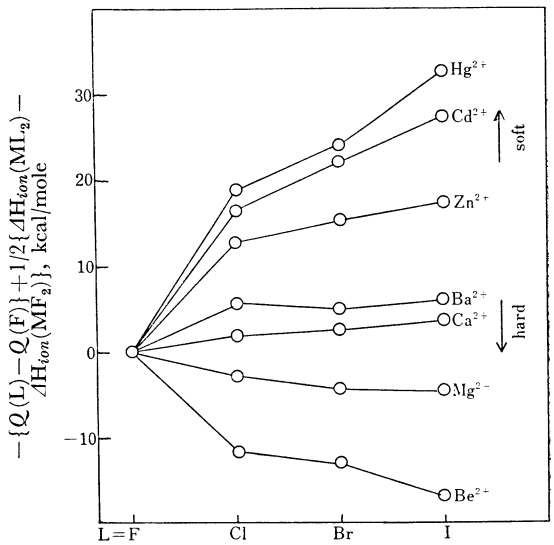

Fig. 4. The change in metal-halogen bond energy from F to I relative to the change in the heat of hydration of halide ion.
Q(L): Heat of hydration of halide ion (L^-).
Q(F): Heat of hydration of fluoride ion.
$\Delta H_{ion}(ML_2)$: Heat of reaction of M^{2+}(gas)+$2L^-$(gas)→ML_2(gas).

In Fig. 4, this situation is demonstrated for some metal ions. The coordinate represents the difference between the changes among halogens from F to I in M-L bond energies and those in solvation energies of L^- by refering to fluoride ion in both cases. In contrast to the M-L bond energy which is approximated by half of the heat of the reaction of $M^{2+}+2L^- \rightarrow ML_2$ in the gas phase, F>Cl>Br>I, the desolvation energy of L^- suggests a favorable order for the stable complex formation (F<Cl<Br<I). It may be stated, therefore, that the main factor to determine the stability sequence of metal-halogeno complexes is how much the decrease in M-L bond energy in F, Cl, Br, I series is compensated by the decrease in desolvation energy in the same series. Thus Hg^{2+} and Cd^{2+} are soft, because their M-L bond energies decrease more moderately than those of metal ions such as Be^{2+} and Ca^{2+}.

Roughly speaking, both the solvation energy and

Table 2. Calculated stability constants of the complexes of methylmercuric ion, CH_3Hg^+ by Eq. (2) and the observed values

	OH^-	Ac^-	NH_3	pyridine	Cl^-	Br^-	I^-
calcd[a]	12.9	4.0	10.6	5.9	5.9	7.4	10.4
obsd[b]	12.8	4.4	10.5	6.1	5.9	7.6	10.3

a) Calculated using X=6.52 and Y'=5.35 together with α', β' and γ' in Table 1.
b) Taken from Ref. 15.

Table 3. Calculated reactivity indices by Eqs. (3), (4) and (5) and reported values

		Ac^-	pyridine	Cl^-	Br^-	OH^-	NH_3	I^-	$S_2O_3^{2-}$ [a]
n	calcd	1.48	2.51	2.79	3.63	5.00	4.40	5.15	6.67
	reported[b]	2.72	3.6	3.04	3.89	4.20	—	5.04	6.36
E_n	calcd	0.57	0.98	1.12	1.45	1.92	1.71	2.06	2.65
	reported[c]	0.95	1.20	1.24	1.51	1.65	1.84	2.06	2.52
H	calcd	6.86	4.56	−0.5	−2.1	20.0	10.5	−4.6	−2.8
	reported[c]	6.46	7.04	−3.0	−6.0	17.5	11.2	−9.0	3.6

a) The values of α', β' of $S_2O_3^{2-}$ are estimated as $\alpha'=0.06$ and $\beta'=2.50$ for mono-coordinated complexes, from those of dicoordinated ones considering the dependency of α' and β' of other ligands on the changes in the coordination number.
b) Taken from Ref. 11.
c) Taken from Ref. 8.

the σ-bond energy linearly depend on X,[4] probably the latter, to a lesser degree. As shown in Fig. 4, the more ionic the M-L bond, the more strongly the bond energy depends on X, resulting in a more negative slope in Fig. 4. In other words, an increase in covalency increases softness. The ability of π-bond formation (back donation) strongly favors the sequence I>Br>Cl>F. The reason why E_n^* of Pd^{2+}, Pt^{2+} and Au^+ are lower than those expected from Y' may be explained by the fact that π-bonding was neglected in E_n^* calculation. Thus, if the decrease in M-L bond energy from F to I of a certain metal ion becomes moderate, by the enhancement of covalency, especially of π-bonding in M-L bond, class (b) character or softness, increases.

Changes in softness may also occur by the solvent effect in the way pointed out by Williams and Hale.[5] Reduction of dielectric constant of solvent decreases the change in the solvation energy from F to I, so that the solvation becomes less important. As a consequence all cations revert to class (a) character as dielectric constants approach unity, that is, for example, in the gas phase.

Some Examples of Applications. The values of softness and hardness, (X, Y'), of CH_3Hg^+, CF_3Hg^+ and $C_3F_7Hg^+$ are calculated by Eq. (2) as (X=6.52, Y'=5.35), (6.79, 5.80) and (6.54, 5.89), respectively. These calculated log K values agree well with the reported ones (Table 2). Y' are large as expected, but it is to be noted that X values are also large. Belluco *et al.*[10] reported poor correlation of the log K of CH_3Hg^+ complexes with n_{Pt}. However, n_{Pt} correlates well with β[4] or β'. This discrepancy is understandable, if one takes into account the considerable hardness of CH_3Hg^+; n_{Pt} and β are determined by softness[4] while log K of CH_3Hg^+ complexes depends on both softness and hardness. The ability of mercuric ion to form strong σ-bond may partly account for the hardness, as σ-bond energy depends on X.[4]

The reactivity indices of a nucleophile in various displacement reactions on carbon, such as n,[11] E_n and H,[8] have been related to the present α' and β' by the formulas

$$n = 2.3\alpha' + 2.6\beta' \quad (3)$$

$$E_n = 0.9\alpha' + 1.0\beta' \quad (4)$$

$$H = 13.2\alpha' - 1.4\beta' \quad (5)$$

n and E_n are the nucleophilic constants (approximately, $n \propto E_n$) and H the basicity of a nucleophile (oxibase scale[12]). The values calculated by the above equations are in fair agreement with the reported values of n and E_n, but not with H (Table 3). Poor argeement for H may not be serious, because H is usually of little importance in the reactivity which depends mostly on n (or E_n). Equations (3) and (4) demonstrate that the reactivity of a nucleophile depends almost equally on hardness α' and softness β'. The ratio of these two coefficients, which gives the relative dependency of the reactivity on hardness to that on softness, is expected to vary from one type of reaction to another. In fact, in the case of the ligand displacement of Pt^{2+} complexes, the reactivity n_{Pt} is mainly controlled by softness.[4] The reactivities for the displacement reactions of CH_3I and CH_3Br by a nucleophile, n_{CH_3I} and n_{CH_3Br}, are determined by both hardness and softness, since they are proportional to E_n.[13]

The authors are indebted to Professor Y. Yoneda for his helpful discussions.

11) C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).
12) R. E. Davis, *ibid.*, **87**, 3010 (1965).
13) R. G. Pearson, H. Sobel and J. Songstad, *ibid.*, **90**, 319 (1968).
14) Chem. Soc. Special Publication, No. 17, Stability Constants of Metal-ion Complexes, London (1964).
15) R. S. Tobias, *Organometal. Chem. Rev.*, **1**, 93 (1966).