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THE CONCEPT OF HARD AND SOFT ACIDS AND BASES AND NUCLEOPHILIC DISPLACEMENT REACTIONS

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If we consider a simple ionic equilibrium,

$$N^{(-)}+M^{+} \rightleftharpoons MN$$

the free energy change ΔF is given by

$$\Delta F = -RT\ln K = E_N{}^s - D_{MN} - E_M{}^s \tag{1}$$

where $E_N{}^s$ is the energy required (including entropy of solvation) to remove an electron from N^- (in solution), $E_M{}^s$ the gain in energy on adding an electron to M^+ (in solution), and D_{MN} the dissociation energy of compound MN. The order of equilibrium constants for the combination of a series of ligands with a given metal M is therefore determined by the changes in $E_N{}^s$ and D_{MN}.

In general, when a series of ligands from the same group of the Periodic Table is considered *e.g.*

$F^{(-)}$, $Cl^{(-)}$, $Br^{(-)}$, $I^{(-)}$
$RO^{(-)}$ $RS^{(-)}$ $RSe^{(-)}$ $RTe^{(-)}$
R_3N R_3P R_3As

increases in D_{MN} (ΔD_{MN}) are accompanied by (approximately linear) increases in $E_N{}^s$ ($\Delta E_N{}^s$). This follows[1] from the tendency of D_{MN} to increase with D_{H-N} provided that N is more electronegative than M, *i.e.*

$$D_{MN} = kD_{H-N} + \text{const.}$$

as shown by data in Fig. 1. Also $E_N{}^s$ for a given series increases (almost linearly) with D_{HN}, *i.e.*

$$D_{HN} = k'E_N{}^s + \text{const.} \quad (k' \text{ is the slope of Fig.2})$$

as shown in Fig. 2. Consequently for each series of ligands we have

$$D_{MN} = kk'E_N{}^s + \text{const.}$$

and

$$RT\ln\frac{K_1}{K_2} = (kk'-1)\Delta E_N{}^s \tag{2}$$

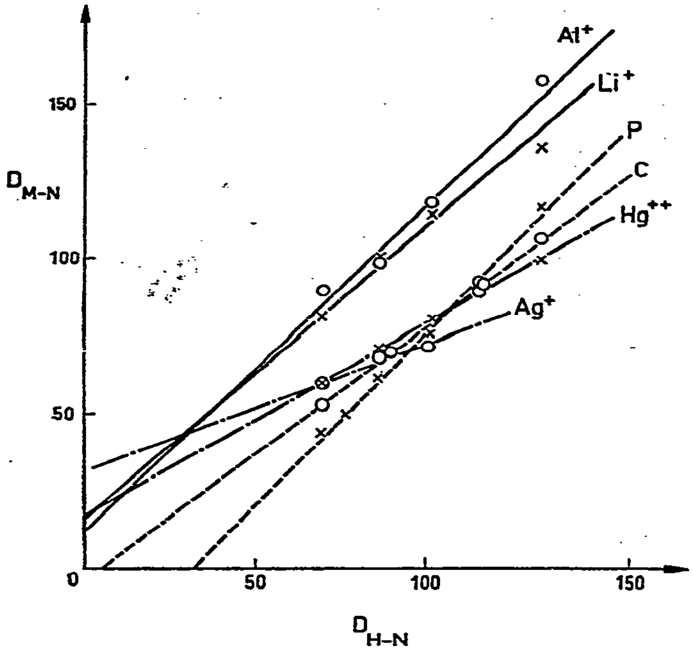


Fig. 1. The relationship between the dissociation energies of M–N bonds, where M is Al^+, Li^+, P^{3+}, C, Hg^{2+}, and Ag^+, and the corresponding bonds formed by the ligand N and hydrogen. N = halogen.

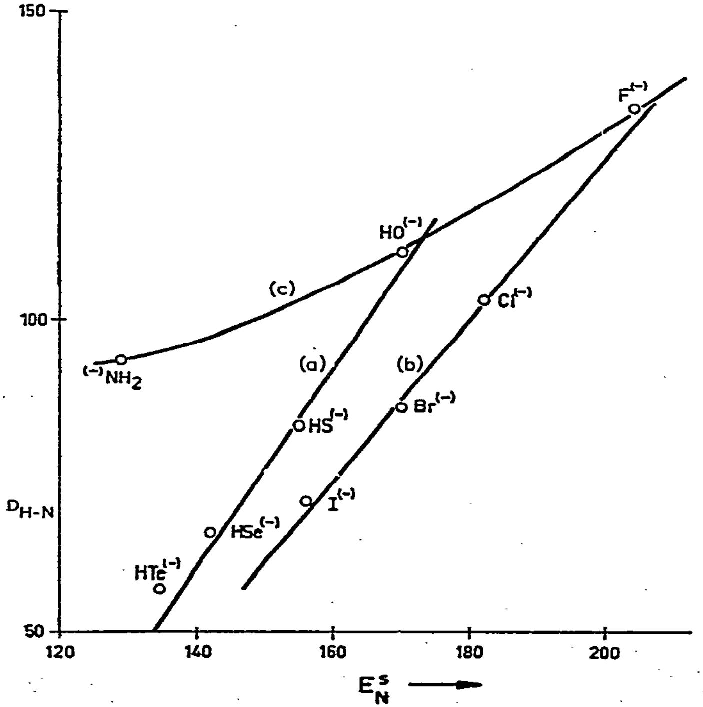


Fig. 2. The relationship between the H–N dissociation energies and solution electron affinities, $E_N{}^s$.

Thus in general we have two orders depending on the magnitude of k (which depends on the nature of M) and k' (which depends on the ligand series considered), *i.e.*

A. Order ($kk' > 1$, *i.e.* $\Delta D_{MN} > \Delta E_N$)	B. Order ($kk' < 1$, *i.e.* $\Delta D_{MN} < \Delta E_N$)
$F^- > Cl^- > Br^- > I^-$	$I^- > Br^- > Cl^- > F^-$
$RO^- > RS^-$	$RS^- > RO^-$

Order A is characteristic of a hard metal since it tends to combine preferentially with hard bases (*e.g.* F^-, OR^-), order B being characteristic of a soft metal[2]. Since the constant k' is similar for these two ligand series, these orders will define soft and hard behaviour, in the same way as A and B metals are defined in the Chatt-Ahrland-Davis classification[3]. A given order is however not usually obtained if the two series are combined, since the $D_{H-N}-E_N$ lines for the two series do not coincide (Fig. 2), as shown by the following data:

1) $F < Cl < Br < I < OH < RS$	$MeHg^+$ equilibria[4]
2) $F < Cl < Br < OH < I < RS$	S_N2 displacement on carbon[5]
3) $F < OH < Cl < Br < I < RS$	Ag^+ equilibria[4] Pt^{II} displacements[6]

These orders differ in the relative position of OH^- since bond energy changes are more important for this ligand (*vide infra*).

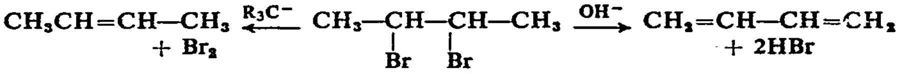
For a wider comparison, the soft–hard classification will depend on the particular series of ligands chosen (*i.e.* on the magnitude of k'). Referring to Fig. 2, it is noted that kk' may be less than 1 when ligand series (c) is considered, whereas $kk' > 1$ for series (a) and (b). For example, for proton neutralisation (in water) we have

$F^- > Cl^- > Br^- > I^-$ and $RO^- > RS^-$ *i.e.* "hard" orders

but

$R_3C^- \gg F^-$ *i.e.* "soft" order.

The order $F^- > R_3C^-$ can be observed only for combination with very hard acids (*e.g.* Al^{3+}) where bonding is largely electrostatic. That R_3C^- is very soft is shown by the preferential reaction at soft electrophilic centres[7], *e.g.*



$$\underset{+\,Br_2}{CH_3CH{=}CH{-}CH_3} \xleftarrow{R_3C^-} CH_3{-}\underset{Br}{CH}{-}\underset{Br}{CH}{-}CH_3 \xrightarrow{OH^-} \underset{+\,2HBr}{CH_2{=}CH{-}CH{=}CH_2}$$

The significant feature* is that

$$\left[\frac{k_{R_3C^-}}{k_{HO^-}}\right]_{Br} > \left[\frac{k_{R_3C^-}}{k_{HO^-}}\right]_{H}$$

showing R_3C^- to be a very soft nucleophile relative to HO^-.

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* There are unfortunately exceptions to this soft and hard definition.

It is to be noted that H^+ is not the hardest acid, since in the complex or compound it is less electron deficient than a proton. A small electron density produces considerable soft character (*e.g.*, the hydride ion is a very soft base).

Kinetic Processes[8]

In a displacement reaction, the nucleophilic order will depend in a similar manner on the relative values of ΔD_{NM} and $\Delta E_N{}^s$ and also on the extent of bond formation between the nucleophile N^- and electrophilic centre X. Consider the following displacement reaction involving a transfer of charge of ze from N^- to the electrophile XY,

$$N^- + XY \rightleftharpoons \overset{(1-z)-}{N} --- \overset{(\Delta-z)+}{X} --- \overset{\Delta-}{Y} \rightarrow NX + Y^-$$

The rate constant k is given by

$$-RT\ln k \equiv \Delta F^* = \alpha E_N{}^s - \beta D_{XN} + f(XY) \tag{3}$$

For a given electrophile, we may assume that the change in energy, $f(XY)$ is constant. Now $\alpha \rightarrow 1$, $\beta \rightarrow 1$, when $z \rightarrow 1$ and $\alpha \rightarrow 0$, $\beta \rightarrow 0$ when $z \rightarrow 0$. For intermediate values, we consider that $\alpha > \beta$ since the D_{MN} term includes inter electronic repulsions in the NXY bond, which are very important in transition states.

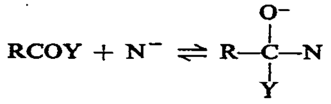
These considerations lead to the following situations:

a) When $\alpha \rightarrow 1$, the rate order will follow the thermodynamic order as given by equation (1). This may be the hard or soft order depending on the values of D_{XN}.

b) When $\alpha \rightarrow 0$, we have zero selectivity (limiting S_N1).

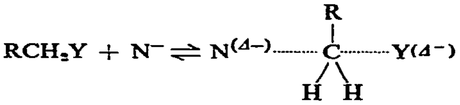
c) For small values of α ($\alpha < 0.5$), the βD_{XN} term is relatively small, and the rate changes follow $E_N{}^s$, *i.e.* the order for soft acids.

We reach the important conclusion therefore that the soft or hard behaviour is determined not only by the values of $E_N{}^s$ and D_{XN}, but also by the extent of bond formation in the transition state. This is shown by the rate orders frequently observed for acylation (I) and alkylation (II).



$$RCOY + N^- \rightleftharpoons R-\overset{\overset{O^-}{|}}{\underset{\underset{Y}{|}}{C}}-N$$

(I)



$$RCH_2Y + N^- \rightleftharpoons N^{(\Delta-)} \cdots C(R)(H)(H) \cdots Y^{(\Delta-)}$$

(II)

$F^- > Br^-, I^-$	$I^- > Br^- > Cl^- > F^-$
$RO^- > RS^-$	$RS^- \gg RO^-$

With this added proviso, electrophiles can be divided into soft and hard as shown by the following examples.

Soft electrophiles	*Hard electrophiles*
$R_1R_2R_3CY$, R_1R_2PY, RSY, Br–Y	R_1R_2POY, RCOY, RSO_2Y
H–Y ($\alpha \to 0$)	HY ($\alpha \to 1$)

Since the nucleophilic order depends on the degree of bonding in the transition state (by changing k of equation 2), a common order of increasing nucleophile or ligand softness cannot be established. Variations in different orders will follow the kinetic equation given above. As an example we compare, in Fig. 3, the stability constants for combination with[4] CH_3Hg^+ with the rate constants for displacement at a complex[6] of Pt^{II} by a series of nucleophiles.

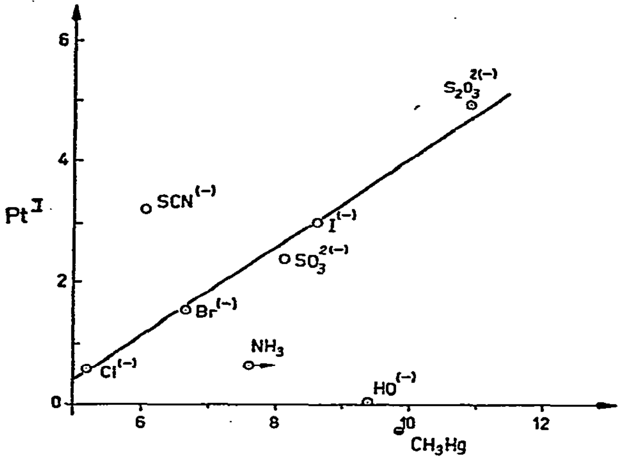


Fig. 3. The relationship between the equilibrium constant for the addition of ligand N to the CH_3Hg^+ cation and the rate of displacement on Pt^{II} complexes[6].

Basic ligands (RO^- and RNH_2) have a relatively greater affinity for $MeHg^+$ than for Pt^{II} since the bond is fully formed in the first case. The β term of equation (3) is therefore relatively small compared with the corresponding term in equation (1). On the other hand, the thiocyanate ion has a greater affinity for Pt^{II} than for CH_3Hg^+, probably because conjugation

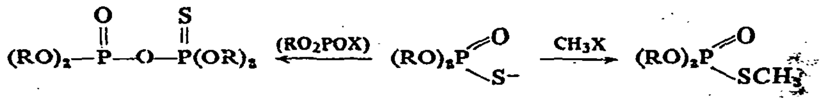
$$^{\ominus}\overset{\frown}{N}{=}C{=}\overset{\frown}{S}\!:\ \longrightarrow XY$$

reduces the activation energy of the kinetic process. A similar high reactivity is observed in S_N2 displacements on carbon[5].

Ambident ions[9]

The reactions of ambident ions also provide exceptions to the simple classification of hard and soft acids and bases. In the following reactions,

$$CH_3CONCS \xleftarrow{CH_3COX} NCS^- \xrightarrow{CH_3X} CH_3SCN$$



$$(RO)_2\overset{O}{\overset{\|}{P}}-O-\overset{S}{\overset{\|}{P}}(OR)_2 \xleftarrow{(RO_2POX)} (RO)_2P{\overset{O}{\underset{S^-}{}}} \xrightarrow{CH_3X} (RO)_2P{\overset{O}{\underset{SCH_3}{}}}$$

the soft electrophile reacts with the soft sulphur atom and the hard electrophile with the hard nitrogen or oxygen atom in agreement with the general principle that soft electrophiles tend to react preferentially with soft nucleophiles and hard with hard. A similar rule was advanced by Kornblum *et al.*[9] for the reactions of nitrite and enolate ions with alkyl halides.

There are however many examples where the simple rule is contradicted[10], *e.g.*

(1) 

$$(RO)_2PO^- + (RO)_2P(O)X \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{P}}(OR)_2$$

(2) $(RO)_2PO^- + (RO)_2PX \rightarrow (RO)_2P-O-P(OR)_2$

The preferential reaction of soft phosphorus in $(RO)_2P{-}O^-$ with hard P in $(RO)_2POCl$, is determined by the high P=O bond energy in the transition state (which resembles the addition intermediate), hence the thermodynamically stable product is obtained. It is possible, however, that the reaction leading to the isomer is reversible, in which case the thermodynamic product is always formed. In reaction(2) the transition state is closer to the reactants, and the greater charge on oxygen relative to phosphorus promotes reaction on the former (particularly in the aprotic or non-polar solvents used).

We conclude therefore that the interpretation of ambident ion action requires a knowledge of the nature of the transition state (in addition to the extent of reversibility of the competing reactions), and that a simple soft and hard rule, although frequently obeyed, is not a general one for this kind of reactant.

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