

Cation–inert gas atom interactions: A look into charge transfer energetics

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Abstract. The charge-transfer energetics of interactions in a series of closed-shell cation–inert gas pairs is studied by using a model based on the electronegativity equalization principle. These results are compared with those obtained from SCF calculations carried out at the STO-3G level. A model interaction potential is tested for these systems. The possible effect of an additional electrostatic factor in the charge transfer process is investigated.

Keywords. Ion–atom interactions; charge transfer in hard–hard interactions; semi-empirical ion–noble gas atom potential; SCF calculations on cation–inert gas systems.

1. Introduction

Empirical concepts like electronegativity (Sanderson 1951, 1952) and hardness (Pearson 1973) have proved to be extremely useful in chemistry. These simple parameters have successfully correlated and systematized a vast array of chemical facts. It is not surprising therefore that there has been considerable activity in recent years for obtaining a better theoretical understanding of these empirical concepts. Thus the negative value of the so-called Mulliken absolute electronegativity, $\chi_A [= \frac{1}{2}(I + A)]$, has been identified with the chemical potential ($-\mu$) of the electrons, $-\mu$ having much the same significance as the thermodynamic chemical potential (Parr *et al* 1978; Donnelly and Parr 1978). Similarly, the absolute hardness of an atom (η) has been identified with the second derivative of the electronic energy $E(N)$ with respect to the number of electrons at fixed nuclear charge (Z). Thus,

$$\eta_A = \frac{1}{2}(\delta^2 E(N)/\delta N^2)_Z \approx \frac{1}{2}(I - A), \quad (1)$$

in the finite difference approximation of the 2nd derivative. The analysis made by Parr and Pearson (1983) could retrieve a number of salient features of the hard-soft-acid-base (HSAB) principle on the basis of these ideas.

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It is well known that hard-hard interactions are predominantly ionic and Parr and Pearson (1983) have provided some kind of rationale for it. Such interactions would not be expected to lead to any sizable degree of charge transfer. Later, it was very correctly argued by Nalewajski (1984) and Nalewajski and Koninski (1984) that there are additional electrostatic effects in hard-hard interactions over and above what had been included in Parr and Pearson's (1983) model (PP) and there are situations when these "additional" interactions could become important. We may conjecture that the PP model is adequate when the acid and the base are of exactly comparable hardness. If one of the pair, say the acid, is very much harder than the base (which is also very hard in the conventional scale of hardness), an *asymmetry* is created in their *mutual deformability*, thereby calling into play additional electrostatic effects (the coupling terms in Nalewajski's model). The present paper investigates some hard-hard interactions of this kind.

2. The systems

Our model acids are closed-shell ions (like $\text{Li}^{(+)}$, $\text{Be}^{(+2)}$, $\text{B}^{(+3)}$, etc.) and our model bases are inert gas atoms. The possibility of interaction between a hard acid like the $\text{Li}^{(+)}$ ion and an inert gas atom (which are hard bases in the usual scale of hardness) leading to the formation of so-called polarization complexes is well known. The particular case of the $\text{Li}^{(+)}$:He pair has been well-studied experimentally as well as theoretically (Polark-Dingels *et al* 1982; Lorentz and Conklin 1972; Tatewaki *et al* 1984). However, little seems to be known about interaction profiles in acid base pairs like $\text{Li}^{(+)}$:Ne; $\text{Be}^{(+2)}$:He/Ne; $\text{B}^{(+3)}$:He/Ne; $\text{C}^{(+4)}$:He/Ne. These interaction profiles are of interest on several counts, viz., interpretation of the results of beam scattering experiments, physisorption of inert gas atoms on alkali halide crystals, study of mobility of ions through inert gases, and so on. In the present context, these ion-atom pairs provide us with interesting models of hard acid hard base pairs with a pronounced degree of asymmetry in the relative hardness of the acid with respect to that of the base. Our main purpose will be to study:

- (i) the actual pattern of charge transfer and its energetics in asymmetric hard-hard interaction;
- (ii) the approximate stability order of the polarization complexes formed;
- (iii) equilibrium internuclear separation in the polarization complexes. A basic aspect of this study will be to evaluate the quantitative utility of parameters like absolute hardness, electronegativity, etc. which can be used to study some of the features mentioned (i-iii).

2.1 Method A

The approximate equilibrium internuclear separation (r_e) in a series of cation-inert gas complexes have been determined by performing minimal basis set LCAO-MO-SCF calculation at the STO-3G level. These r_e values are reported in table 1. The experimental value of equilibrium internuclear separation is available only for the $\text{Li}^{(+)}$:He pair. Our minimal basis set result for Li-He $^{(+)}$ agrees well with the corresponding experimental r_e value (Polark-Dingels *et al* 1982; Lorentz and Conklin 1972) or the accurate theoretical values predicted by the

Table 1. Comparison of the equilibrium internuclear separation in the $A^{+n}:\text{He}$ or Ne complexes calculated by two different methods.

| Ion A^{+n} | Atom B | Polarization complex $(\text{AB})^{+n}$ | Equilibrium intermolecular separation (r_e) calculated by | | Mulliken overlap population in the complex | r_e values available in the literature |
|------------------|-----------|-----------------------------------------------|---------------------------------------------------------------------|------------------------------|-----------------------------------------------------|---------------------------------------------------|
| | | | Method A (\AA) | Method B (\AA) | | |
| Li^+ | He | $(\text{LiHe})^+$ | 1.955 | 1.915 | 5.07×10^{-2} | 1.95 ^a , 1.9 ^b |
| Li^+ | Ne | $(\text{LiNe})^+$ | 1.547 (1.724) ^c | 1.963 | 9.74×10^{-2} (8.86×10^{-2}) | – |
| Be^{+2} | He | $(\text{BeHe})^{+2}$ | 1.644 | 1.586 | 0.1038 | – |
| Be^{+2} | Ne | $(\text{BeNe})^{+2}$ | 1.524 | 1.634 | 0.1434 | – |
| B^{+3} | He | $(\text{BNe})^{+3}$ | 1.433 | 1.457 | 0.2627 | – |
| B^{+3} | Ne | $(\text{BNe})^{+3}$ | 1.459 | 1.505 | 0.1895 | – |

^aPolark-Dingels *et al* (1982), ^bTatewaki *et al* (1984), ^c values in parentheses correspond to the second minimum (higher energy).

STO-CI calculation of Tatewaki *et al* (1984). For the other interacting pairs, no data is available for comparison. The STO-3G results, however, reveal certain interesting trends in the computed r_e values. Thus, with Li^{+1} and Be^{+2} as the hard acids, the equilibrium internuclear separations in the polarization complexes formed with Ne are predicted to be uniformly smaller than in the He-complexes. This trend is reversed in the complexes formed with B^{+3} . The $\text{Li-Ne}^{(+)}$ system shows two minima, the global one corresponding to a shorter internuclear separation of $r_e = 1.547 \text{ \AA}$ and a shallower one at $r_e = 1.724 \text{ \AA}$. The energy difference between the two minima is only 0.002 a.u. $\text{C}^{(+4)}:\text{He}$ or $\text{C}^{(+4)}:\text{Ne}$ systems do not show any minima at all.

2.2 Method B

We also attempted to fit the r_e values to a much simpler relation proposed by Stevenson:

$$r_e^{\text{AB}^{+n}} = r_A(+n) + r_B - \lambda |\chi_A(+n) - \chi_B| \quad (2)$$

where λ is a parameter. For a fixed value of $\lambda = 0.095$, the predicted values are reported in table 1. These values show some degree of agreement with SCF results. Nevertheless, certain anomalies do appear when one compares the Ne-complexes with their He-counterparts (e.g. $\text{Li-He}^{(+)}$ and $\text{Li-Ne}^{(+)}$). A more detailed analysis of bonding in these complexes seem to be necessary in order to attain better understanding of the trend exhibited by the $r_e(\text{SCF})$ values.

3. Bond population in polarization complexes

One may be prone to enquire about the magnitudes of bond populations in these polarization complexes. In table 1 we have therefore reported Mulliken overlap population (q_{AB}) at $r = r_e$ in all the complexes studied. The q_{AB} values exhibit the following trends:

- (i) For a given inert gas (He/Ne), an increase in the hardness of the acceptor ion leads to an increase in the overlap population.
- (ii) The highest overlap population (0.2627) is obtained with the hardest acid-base pair studied (i.e. in $B^{(+3)}:He$)
- (iii) Except with B^{+3} , overlap population in the Ne-complexes is uniformly higher than in the corresponding He-complex.

One can not fail to see that the trend exhibited by the q_{AB} values is in conformity with the pattern displayed by the SCF- r_e values (table 1). Thus, a higher overlap population is seen to be associated uniformly with shorter r_e values. The generally small overlap population points to a very weak covalent binding in these complexes. This is understandable as hard-hard interactions are expected to be predominantly ionic. The little covalency that appears must be the result of polarization of the base (B) by the acid (A), the latter being very much harder than the base ($\eta_A \gg \eta_B$). That $C^{(+4)}:He$ or $C^{(+4)}:Ne$ systems do not appear to form stable polarization complexes at all, points to the fact that beyond a certain critical level of asymmetry in the mutual polarization of the acid and base, chemical binding may not take place.

4. Degree of charge transfer

The actual degree of charge transfer ($\Delta q_{B \rightarrow A}$) from the base (B) to the acid (A) can be calculated by invoking the electronegativity equalization principle (e.e.p.) for the "atoms" in "molecules", and at the simplest level of approximation is given by

$$\Delta q_{B \rightarrow A} = \frac{(\chi_A - \chi_B)}{2(\eta_A + \eta_B)} = \Delta q^{e.e.p.} \quad (3)$$

These ' Δq ' values for the cation-inert gas systems are reported in table 2. For comparison, we have also reported the Δq values predicted by our SCF calculations. We call these Δq^{SCF} . Perusal of table 2 immediately reveals that except for

Table 2. Calculated values of net charge transfer ($\Delta q_{B \rightarrow A^{+n}}$) from the inert gas atom to the ion and the charge transfer stabilization energies under different approximations.

| Ion (A^{+n}) | Atom (B) | Amount (Δq) of $B \rightarrow A^{+n}$ charge transfer calculated by | | | Charge transfer stabilization energy ΔE_{CT}^0 (eV) | Additional electro- static factor to be added to ΔE_{CT}^0 (ΔE_{es}) (eV) | Corrected measure of ΔE_{CT} (eV) |
|---------------------|-------------|-------------------------------------------------------------------------------------|--------------------------|-------------------------|----------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|
| | | Method A Δq^{SCF} | Method B Δq^0 | Method C $\Delta q'$ | | | |
| Li ⁺ | He | 0.0606 | 0.3126 | 0.3048 | -5.08 | 1.58 | -3.50 |
| Li ⁺ | Ne | 0.1897 | 0.3317 | 0.3212 | -6.23 | 2.06 | -4.17 |
| Be ⁺² | He | 0.1405 | 0.5110 | 0.4499 | -17.86 | 6.66 | -11.20 |
| Be ⁺² | Ne | 0.3450 | 0.5230 | 0.4630 | -18.64 | 7.31 | -11.33 |
| B ⁺³ | He | 0.3683 | 0.5900 | 0.5403 | -38.43 | 14.30 | -24.13 |
| B ⁺³ | Ne | 0.6220 | 0.5980 | 0.5507 | -39.40 | 14.17 | -25.23 |

$B^{+3};Ne$, $\Delta q^{e.c.p.}$ values predicted by (3) are much larger than the corresponding Δq^{SCF} values. This overestimation is presumably due to the failure of (3) to take into account the “effective” increase in the electronegativity of the neutral inert gas atom (χ_B) in the presence of the positive charges on acceptor ion (A). The acceptor ion, on the other hand, is hardly affected by the neutral inert gas atom. This asymmetry in the mutual deformation has not been taken care of in the derivation of (3) leading to the presently observed large differences among the $\Delta q^{e.c.p.}$ and Δq^{SCF} values. The agreement between Δq^{SCF} and $\Delta q^{e.c.p.}$ values observed for the $B^{(+3)};Ne$ pair is probably fortuitous. These qualitative arguments find a coherent analytical representation in recent papers by Nalewajski (Nalewajski and Koniski 1984; Nalewajski 1984) who argues that (3) is deficient in that the expression for Δq has not been derived from a full second-order expansion of energy $E(N, Z)$ of an atom in a molecule. When this is done one gets a modified expression for Δq (4):

$$\Delta q = \frac{1}{2(\eta_A + \eta_B)} [(\chi_A - \chi_B) + 2(\alpha_B \Delta Z_B - \alpha_A \Delta Z_A)], \quad (4)$$

where $\alpha_A = \frac{1}{2}(\delta\mu_A/\delta Z_A)_N < 0$ and ΔZ_A represents the increase in the effective core charge of the atom A in the molecule A–B due to the presence of its partner B. If the acid and the base are comparably hard $\alpha_B \Delta Z_B \approx \alpha_A \Delta Z_A$, so that (3) holds quite well. But if the hardness of A and B are not at all comparable (although both are hard) as in our present example, the situation becomes quite different. In our case, $\Delta Z_B \gg Z_A$, so that (4) becomes

$$\Delta q \approx \frac{1}{2(\eta_A + \eta_B)} [\chi_A - \chi_B + 2\alpha_B \Delta Z_B] = \frac{1}{2(\eta_A + \eta_B)} (\chi_A - \bar{\chi}_B)$$

where $\bar{\chi}_B = \chi_B - 2\alpha_B \Delta Z_B$ and may be called the electronegativity of B in the molecule AB.

Since $\alpha_B < 0$, $\bar{\chi}_B > \chi_B$ reducing the effective electronegativity difference between A and B. This shows that Δq given by (3) could indeed have been overestimated.

5. Charge transfer energetics

The charge transfer (CT) stabilization energy associated with the formation of heteropolar species (A–B) can be approximately calculated by involving the electronegativity equalization principle. Thus, using the model proposed by Parr and Pearson (1983), we have,

$$\Delta E_{CT}^0 = -\frac{1}{4}(\chi_A - \chi_B)^2/(\eta_A + \eta_B). \quad (5)$$

ΔE_{CT}^0 values calculated by using (5) are reported in table 2. We may note, however, that in the cation–inert gas system the process of electron transfer from the inert gas atom to the cationic acid would lead to the onset of additional electrostatic effects. Therefore, ΔE_{CT}^0 should be corrected by adding a term ΔE_{es} to it where

$$\Delta E_{es} = \frac{\Delta q(n - \Delta q)e^2}{r_{AB}}$$

and Δqe is the net flow of electron density from the inert gas atom B to the cation A^{+n} carrying a net positive charge of magnitude $+ne$, r_{AB} being the distance of

separation between A^{+n} and B. Hence, the corrected value of CT stabilization energy is given by (assuming $e = 1$) (corr = corrected)

$$\Delta E_{CT}^{corr} = \Delta E_{CT}^0 + \Delta E_{es} = -\frac{1(\chi_A - \chi_B)^2}{4(\eta_A - \eta_B)} + \frac{\Delta q(n - \Delta q)}{r_{AB}}. \quad (6)$$

At the first order of approximation, $\Delta q = (\chi_A - \chi_B)/2(\eta_A + \eta_B)$. Hence,

$$\Delta E_{CT}^{corr} = -\frac{1(\chi_A - \chi_B)^2}{4(\eta_A + \eta_B)} + \frac{n(\chi_A - \chi_B)}{2r_{AB}(\eta_A + \eta_B)} - \frac{(\chi_A - \chi_B)^2}{4(\eta_A + \eta_B)^2 r_{AB}} \quad (7)$$

For comparison, the corrected ΔE_{CT} values are also reported in table 2. It is clear that the additional electrostatic effect substantially reduces the magnitude of charge-transfer stabilization energy. The ΔE_{CT}^{corr} values predict the following order of charge transfer stabilization in the present series of polarization complexes:

$$\begin{aligned} (\text{B}:\text{Ne})^{+3} > (\text{B}:\text{He})^{+3} > (\text{Be}:\text{Ne})^{+2} > (\text{Be}:\text{He})^{+2} > \\ (\text{Li}:\text{Ne})^{+1} > (\text{Li}:\text{He})^{+1}. \end{aligned}$$

This ordering is nearly the same as predicted by the uncorrected ΔE_{CT}^0 values except that $\Delta E_{CT}^0(\text{Be-Ne})^{+2}$ is predicted to be 1 eV higher than $\Delta E_{CT}^0(\text{B-Ne})^{+3}$. Since the additional electrostatic effects make a substantial contribution to ΔE_{CT}^{corr} , one wonders whether the same effects would substantially alter the actual magnitude of charge transfer. In the following section we investigate this aspect.

6. Influence of additional electrostatic factors on $B \rightarrow A^{+n}$ charge transfer

In the $A^{+n}:\text{B}$ interacting system, let Δq be the flow of electrons from B to A^{+n} separated by a distance R . The charge distribution in the complex following the transfer of Δq electrons from $B \rightarrow A^{+n}$ then becomes $A^{+(n-\Delta q)}:\text{B}^{+\Delta q}$ leading to the creation of an extra electrostatic repulsion energy E^{es} , where

$$E^{es} = \frac{(n - \Delta q)\Delta q}{R}.$$

The total interaction energy of the ΔE_T in the $A^{+n}:\text{B}$ complex can then be written as follows:

$$\begin{aligned} \Delta E_T &= \Delta E_{CT}^0 - (n - \Delta q)\Delta q/R \\ &= E_A + (n - \Delta q) + E_B(+\Delta q) - (n - \Delta q)\Delta q/R \\ &\approx E_{A^{+n}}^0 + \chi_A(+n)\Delta q + \eta_A(+n)\Delta q^2 + E_B^0 - \chi_B\Delta q + \eta_B\Delta q^2 \\ &\quad - \frac{n\Delta q}{R} + \frac{\Delta q^2}{R}. \end{aligned}$$

Minimising ΔE_T with respect to Δq , we get

$$\begin{aligned} (\chi_{A^{+n}} - \chi_B) + 2\Delta q(\eta_{A^{+n}} + \eta_B + 1/R) - \eta R &= 0, \\ \Delta q' &= \frac{(\chi_B - \chi_{A^{+n}})}{2(\eta_{A^{+n}} + \eta_B + 1/R)} + \frac{n}{2R(\eta_{A^{+n}} + \eta_B + 1/R)}, \quad (\chi_{A^{+n}} \gg \chi_B) \\ &= \Delta q^0 + \Delta q^{es}, \end{aligned}$$

where Δq^0 is the flow of electron density from $B \rightarrow A^{+n}$ driven purely by electronegativity difference between the donor and the acceptor and Δq^{es} represents a small correction term (opposite in sign, relative to Δq^0) representing the effects of the additional electrostatic effect (repulsive). Table 2 displays Δq^0 and Δq^t ($\Delta q^t =$ net transfer of electrons) values at the equilibrium internuclear separation between the donor and the acceptor. It is clear from the entries in table 2 that Δq^{es} is rather small. From (8) we can easily see that if $n = 0$, we have

$$\Delta q^t = \Delta q^0 = (\chi_B - \chi_{A^{+n}})/(\eta_{A^{+n}} + \eta_B + 1/R).$$

This is in conformity with the result obtained by Balbas *et al* (1983) for the neutral donor and acceptor.

7. Net stabilization energies (a semiempirical estimate)

In the cation–inert gas systems, the charge transfer component of the interaction energy is seen to be quite high and varies systematically as the cation or the inert gas atom is changed. However, the net stabilization energy undoubtedly has contributions from other types of interactions as well. At the STO-3G level of calculations, computed interaction potentials or the minimum well depth (ϵ_m) are not expected to be very realistic. We have therefore, adopted a semiempirical procedure to obtain some idea of the variation of binding energy among the polarization complexes studied by us.

Following the earlier work of Sondergaard and Mason (1975) we express the interaction potential (V_{AB}) between a closed-shell ion A^{+n} and a closed-shell atom B as a function of the internuclear separation r as a superposition of an exponential in r and the polarization potential as follows:

$$V_{AB}(r) = ae^{-r/\rho_{AB}} - n^2e^2\alpha_B/2r^4,$$

where α_B is the electric dipole polarizability of the inert-gas atom B, $\rho_{AB} = \frac{1}{2}(\rho_{AA} + \rho_{BB})$, ρ_{AA} and ρ_{BB} being the “range” parameters for ion–ion (A–A) and atom–atom (B–B) interactions, respectively. a is treated as the only adjustable parameter in the potential. The range parameter for the $B^{+3}:B^{+3}$ interaction was not available in the literature. However, since it is not expected to be very much different from that for the $Be^{+2}:Be^{+2}$ interaction, we have used $\rho_{B^{+3}} \approx \rho_{Be^{+2}}$ and adjusted the a parameter only. *The adjustment was done in each case by requiring the minimum of $V_{AB}(r)$ to coincide with the r_e predicted by STO-3G calculations.* If r_0 be the equilibrium internuclear separation predicted by minimal basis set SCF calculations, then according to our prescription the a parameter should be given by the following condition:

$$\begin{aligned} \left(\frac{\delta V}{\delta r}\right)_{r=r_0} &= 0, \\ \frac{a}{\rho}e^{(-r_0/\rho)} - \frac{2n^2e^2\alpha_B}{r_0^5} &= 0, \\ a &= 2n^2e^2\alpha_B\rho e^{(r_0/\rho)}/r_0^5. \end{aligned}$$

Table 3. The parameters of the effective potential $V(r)$ and the calculated well depth parameters.

| Ion (A^{+n}) | Atom (B) | Range parameter for the ion (ρ_{AA}) and atom (ρ_{BB}) | | Pre- exponential factor a in $V(r)$ | Predicted minimum well depth (ϵ_m) parameter (eV) |
|---------------------|-------------|-------------------------------------------------------------------------|-------------------------|------------------------------------------------|-----------------------------------------------------------------------|
| | | $\rho_{AA}(\text{\AA})$ | $\rho_{BB}(\text{\AA})$ | | |
| Li ⁺ | He | 0.1396 | 0.2295 | 1513.66 | -0.0625 (-3.50) ^a |
| Li ⁺ | Ne | 0.1396 | 0.2161 | 1358.07 | -0.2662 (-4.17) |
| Be ⁺² | He | 0.0995 | 0.2295 | 7047.64 | -0.4823 (-11.20) |
| Be ⁺² | Ne | 0.0995 | 0.2161 | 13569.60 | -1.2260 (-11.33) |
| B ⁺³ | He | 0.0995 | 0.2295 | 8738.68 | -1.6954 (-24.13) |
| B ⁺³ | Ne | 0.0995 | 0.2161 | 25129.66 | -3.1806 (-25.23) |

^a Net charge transfer stabilization energies (see table 2) are given for comparison.

ϵ_m values computed this way are reproduced in table 3 along with the range parameters and the optimum preexponential factor a used. It is worth noting that this semiempirical technique predicts the minimum well depth for the Li-He⁺ system in fairly close agreement with experimental or accurate *ab initio* theoretical data available in the literature. For the other systems no experimental or accurate *ab initio* theoretical data are available for comparison. The quality of results obtained for Li-He⁺ gives us some degree of confidence in the remaining results. This, however, assumes that the r_e^{SCF} values have been estimated fairly well at the STO-3G level. It would be interesting to compare these results with larger basis set SCF results.

The relative ordering of the computed minimum well depths (ϵ_m) at $r = r_e$ obtained by our semiempirical procedure is as follows:

- (i) $\epsilon_m(\text{Li-He})^+ < \epsilon_m(\text{Be-He})^{+2} < \epsilon_m(\text{B-He})^{+3}$,
- (ii) $\epsilon_m(\text{Li-Ne})^{+1} < \epsilon_m(\text{Be-Ne})^{+2} < \epsilon_m(\text{B-Ne})^{+3}$,
- (iii) $\epsilon_m(A^{+n}\text{-He}) < \epsilon_m(A^{+n}\text{-Ne})$: $A^{+n} = \text{Li}^+, \text{Be}^{+2}, \text{B}^{+3}$.

It may be noted that the predicted ordering based on ϵ_m values is not much different from what was predicted on the basis of ΔE_{CT} values alone. The ordering of the ϵ_m values appears to be quite consistent with the expectations based on intuitive chemical reasoning that the stabilization energy of the polarization complexes should increase systematically with (i) decrease in the cationic radius and increase in the positive charge on the acceptor ion; (ii) increase in the polarizability of the donor (inert gas) atoms. We may conclude therefore that the formation of cation-inert gas pairs is dominated by the polarization of the inert atom in the field of the cation. Thus, in hard-hard interactions which are supposed to be dominantly ionic, polarization forces may be called into play if there is a pronounced degree of asymmetry in the hardness of the acid relative to the base. This may affect the degree of charge transfer compared to what could be expected on the basis of electronegativity difference alone. Investigations employing much larger basis sets of expansion are underway and will be reported in due course of time.

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