J. Am. Chem. Soc. 1994, 116, 1067-1071

An ab Initio Study Resulting in a Greater Understanding of the HSAB Principle

Pratim K. Chattaraj* and Paul v. R. Schleyer

Contribution from the Department of Chemistry, Indian Institute of Technology, Kharagpur, 721302, India, and Institut für Organische Chemie I, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Germany

Received August 5, 1993. Revised Manuscript Received October 21, 1993⊗

Abstract: The quantitative applicability of the hard–soft acid–base (HSAB) principle has been tested. Complexes of HF and Ag^+ with several bases (HF, HCl, HBr, H_2O, H_2S, H_2Se, NH_3, PH_3, and AsH_3) have been studied at the HF, MP2, and QCISD(T) levels with 6-311+G** basis sets. Ab initio pseudopotential calculations have been performed for the molecules containing heavier elements, viz., Br, Se, As, and Ag^+. For the hard acid HF, the HSAB principle has been found to be valid even at the HF level. Correlation is important for soft–soft interactions. The maximum hardness principle has been found to be valid for reactions of HF. Reactions of hard acids like H^+, Li^+, and Na^+ have also been studied at the MP2/6-311+G** level. Out of 45 reactions studied, there are only five reactions which are not in conformity with the HSAB principle.

Introduction

Pearson's[1-3] hard–soft acid–base (HSAB) principle states that "hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases for both their thermodynamic and kinetic properties". Although there have been several attempts[4-6] to provide formal proofs of this principle, a thorough ab initio quantitative study of it is still awaited. In the present paper we try to obtain the reaction energies for several bases reacting with a typical hard acid (HF, H^+, Li^+, Na^+) or with a soft acid (Ag^+) and to see how well the HSAB principle works. Using the present calculation as a template it can be checked as to the how HSAB principle reflects these theoretical results. The bases considered here are HX(X = F, Cl, Br), H_2Y (Y = O, S, Se), and H_3Z (Z = N, P, As). The order of preference for a hard acid to bind with these bases, according to HSAB principle,[3,7] is as follows: $F \gg Cl > Br$, $O \gg S > Se$, and $N \gg P > As$. For a soft acid the order of preference is the following: $F \ll Cl < Br$; $O \ll S < Se$ and $N \ll P > As$. It may be noted that this order[3,7] of base affinity of a Lewis acid has been observed in the aqueous medium. The present study provides results for gas-phase reactions. The lack of such results has given rise to a lot of controversy in the past.[8] The effect of solvation of ions[8,9] should be taken into consideration in order to have a proper understanding of a generalized acid–base reaction vis-a-vis HSAB principle. The data for soft–soft interactions are very scanty. The results obtained for the soft cation Ag^+ would provide the much awaited numerical test of the HSAB principle in case of soft–soft interactions. As revealed by the ΔH°_{298} values, for the process $Ag^+(g) + X^-(g) = AgX(g)$, the affinity of Ag^+ for the halide ions in the gas phase follows the trend $F^- > Cl^- > Br^- > I^-$. In the present study we have considered the reaction of $Ag^+(g)$ with HX(g), $H_2Y(g)$, and $H_3Z(g)$. Some of the hard–hard interactions studied here have been studied earlier with different levels of computation, in the context of hydrogen bonding[10,11] and proton, Li, and Na affinities.[12]

Pearson[13] also proposed the "maximum hardness principle"[14] (MHP) which states that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". Since these two principles are related,[6] we would also like to understand the implications of the MHP in the present context. For this purpose, we compute the hardness values for different species as[15]

$$\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2 \tag{1}$$

where ϵ_{LUMO} and ϵ_{HOMO} are the lowest unoccupied molecular orbital and the highest occupied molecular orbital energies, respectively. It may be noted that these energy values (especially ϵ_{LUMO}) are highly basis set dependent and they hardly carry any meaning for MP2 or QCISD(T) calculations. Accordingly, the values are calculated only at the HF level and only for complexes of HF.

Note that it is, however, possible to calculate η at the correlated level using the following formula

$$\eta = (I - A)/2 \tag{2}$$

where I and A are the ionization potential and the electron affinity, respectively. Due to the computational labor associated with I and A calculations we refrain from using this definition of η. Recently, Chattaraj and co-workers[16] have shown that these two definitions provide identical qualitative trends at the SCF level although the numerical values differ owing to the well-known limitations of Koopmans' theorem. An alternative definition[17]

---

* Author for correspondence.

⊗ Abstract published in *Advance ACS Abstracts*, December 1, 1993.

(1) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(2) Pearson, R. G. *J. Chem. Educ.* **1965**, *581*, 643.

(3) (a) Pearson, R. G. In *Theoretical Models of Chemical Bonding*, Part 2, Maksic, Z. B., Ed.; Springer–Verlag: Berlin, 1990; pp 45–76. (b) Chattaraj, P. K.; Parr, R. G. In *Chemical Hardness*; Sen, K. D., Mingos, D. M. P., Ed.; Springer-Verlag: Berlin, 1993, Vol. 80, pp 11–25. (c) Chattaraj, P. K. *J. Ind. Chem. Soc.* **1992**, *69*, 173.

(4) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(5) Nalewajski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944.

(6) Chattaraj, P. K.; Lee, H.; Parr, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1855.

(7) Huheey, J. E. *Inorganic Chemistry: Principles of Structures and Reactivity*, 3rd ed.; Harper and Row: New York, 1983.

(8) Datta, D.; Singh, S. N. *J. Chem. Soc., Dalton Trans.* **1991**, 1541.

(9) Williams, R. J. P.; Hale, J. D. *Struct. Bonding (Berlin)* **1966**, *1*, 249.

(10) Scheiner, S. In *Theoretical Models of Chemical Bonding, Part 4*; Maksic, Z. B., Ed.; Springer–Verlag: Berlin, 1991; pp 171–227.

(11) Hinchcliffe, A. *J. Mol. Struct. (THEOCHEM)* **1984**, *106*, 361.

(12) Smith, S. F.; Chandrasekhar, J.; Jorgensen, W. L. *J. Phys. Chem.* **1982**, *86*, 3308.

(13) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.

(14) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854. See, also: (a) Parr, R. G.; Gázquez, J. L. *J. Phys. Chem.* **1993**, *97*, 3939. (b) Pearson, R. G.; Palke, W. E. *J. Phys. Chem.* **1992**, *96*, 3283.

(15) Pearson, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *89*, 1827.

(16) (a) Chattaraj, P. K.; Nath, S.; Sannigrahi, A. B. *Chem. Phys. Lett.* **1993**, *212*, 223. (b) Nath, S.; Sannigrahi, A. B.; Chattaraj, P. K., communicated.

(17) Orsky, A. R.; Whitehead, M. A. *Can. J. Chem.* **1987**, *65*, 1970.

0002-7863/94/1516-1067$04.50/0

Table 1. Total Energies (–au), Zero Point Vibrational Energies (kcal/mol), and Hardness Values (ev) of Different Bases at Different Levels of Theory

	/6-311+G**//MP2(FU)/6-311+G**								
species, PG	HF/6-311+G**// HF/6-311+G**	ZPE (NIMAG)	η	MP2(FU)	MP2	MP3	MP4	QCISD	QCISD(T)
HF, $C_{\infty v}$	100.05326	6.42(0)	10.48	100.29783	100.27879	100.27682	100.28613	100.28129	100.28523
HCl, $C_{\infty v}$	460.09533	4.50(0)	7.76	460.29421	460.24470	460.25976	460.26361	460.26116	460.26421
HBr, $C_{\infty v}$	13.72520	3.98(0)	7.16	13.84775	13.84775	13.86087	13.86350	13.86181	13.86402
H_2O, C_{2v}	76.05330	14.46(0)	8.95	76.29372	76.27472	76.27736	76.28703	76.28155	76.28662
H_2S, C_{2v}	398.70210	10.09(0)	6.23	398.96826	398.84751	398.86646	398.87204	398.86932	398.87317
H_2Se, C_{2v}	10.29660	8.86(0)	5.92	10.42542	10.42542	10.44355	10.44822	10.44624	10.44941
NH_3, C_{3v}	56.21467	22.90(0)	7.13	56.43444	56.41531	56.42621	56.43431	56.42940	56.43460
PH_3, C_{3v}	342.47799	16.09(0)	6.05	342.73743	342.61301	342.63543	342.64209	342.64016	342.64387
AsH_3, C_{3v}	7.76795	14.60(0)	6.03	7.89287	7.89287	7.91488	7.92102	7.91959	7.92288
Ag^+, K_h	145.84841			145.95095	146.18688	146.17176	146.18556	146.17646	146.18276

Table 2. Total Energies (–au), Zero Point Vibrational Energies (kcal/mol), and Hardness Values[a] (ev) of Binary Complexes of HF and Ag^+ at Different Levels of Theory

	/6-311+G**//MP2(FU)/6-311+G**								
species, PG	HF/6-311+G**// HF/6-311+G**	ZPE (NIMAG)	η	MP2(FU)	MP2	MP3	MP4	QCISD	QCISD(T)
FH···FH, C_s	200.11338	14.45(0)	9.86	200.60327	200.56510	200.56109	200.57975	200.56989	200.57798
FH···ClH, C_s	560.15141	12.01(0)	7.89	560.59695	560.52831	560.54127	560.55457	560.54700	560.55425
FH···BrH, C_s	113.78093	11.44(0)	7.27	114.14969	114.13062	114.14151	114.15371	114.14688	114.15331
FH···OH_2, C_s	176.12000	23.31(0)	9.16	176.60705	176.56890	176.56906	176.58836	176.57755	176.58700
FH···SH_2, C_s	498.76123	18.46(0)	6.44	499.27469	499.13483	499.15137	499.16665	499.15856	499.16679
FH···SeH_2, C_s	110.35513	17.05(0)	6.10	110.73130	110.71223	110.72787	110.74229	110.73496	110.74250
FH···NH_3, C_{3v}	156.28540	32.45(0)	7.54	156.75363	156.71535	156.72324	156.74138	156.73079	156.74060
FH···PH_3, C_{3v}	442.53745	24.38(0)	6.30	443.04437	442.90086	442.92084	442.93725	442.92984	442.93796
FH···AsH_3, C_{3v}	107.82569	22.68(0)	6.21	108.19676	108.17769	108.19714	108.21293	108.20618	108.21374
$[Ag\cdots FH]^+$, C_s	245.92482	6.76(0)		246.27382	246.49245	246.47474	246.49828	246.48408	246.49449
$[Ag\cdots ClH]^+$, C_s	605.96051	5.19(0)		606.27173	606.46158	606.45923	606.47919	606.46635	606.47693
$[Ag\cdots BrH]^+$, C_s	159.59350	4.69(0)		159.82852	160.06890	160.06401	160.08366	160.07137	160.08124
$[Ag\cdots OH_2]^+$, C_{2v}	221.94111	15.98(0)		222.29036	222.51093	222.49615	222.52164	222.50614	222.51807
$[Ag\cdots SH_2]^+$, C_s	544.58452	11.68(0)		544.96753	545.08870	545.08810	545.11180	545.09768	545.10975
$[Ag\cdots SeH_2]^+$, C_s	156.18171	10.37(0)		156.42763	156.67004	156.66839	156.69164	156.67830	156.68973
$[Ag\cdots NH_3]^+$, C_{3v}	202.11672	25.28(0)		202.45232	202.67544	202.66657	202.69269	202.67681	202.68967
$[Ag\cdots PH_3]^+$, C_{3v}	488.37273	17.83(0)		488.75006	488.86972	488.87028	488.89622	488.88174	488.89369
$[Ag\cdots AsH_3]^+$, C_{3v}	153.63525	14.66(0)		153.87798	154.11971	154.12303	154.14745	154.13417	154.14616

[a] Only for HF complexes.

Table 3. Reaction Energies (–kcal/mol) for Reactions of HF and Ag^+ with Various Bases at Different Levels of Theory

	/6-311+G**//MP2(FU)/6-311+G**							
reactions	HF/6-311+G**// HF/6-311+G**	ZPE[a]-corrected values	MP2(FU)	ZPE[a]-corrected values	MP4SDTQ	ZPE[a]-corrected values	QCISD(T)	ZPE[a]-corrected values
HF + HF = FH···FH	4.30	2.87	4.77	3.34	4.70	3.27	4.72	3.29
HF + HCl = FH···ClH	1.77	0.80	3.08	2.11	3.03	2.06	3.02	2.05
HF + HBr = FH···BrH	1.55	0.62	2.58	1.65	2.56	1.63	2.55	1.62
HF + H_2O = FH···OH_2	8.43	6.27	9.73	7.57	9.54	7.38	9.51	7.35
HF + H_2S = FH···SH_2	3.68	1.94	5.40	3.66	5.32	3.58	5.26	3.52
HF + H_2Se = FH···SeH_2	3.31	1.73	5.05	3.47	4.98	3.40	4.93	3.35
HF + NH_3 = FH···NH_3	10.96	8.17	13.40	10.61	13.14	10.35	13.03	10.24
HF + PH_3 = FH···PH_3	3.89	2.23	5.72	4.06	5.67	4.01	5.56	3.90
HF + AsH_3 = FH···AsH_3	2.81	1.33	3.80	2.32	3.63	2.15	3.53	2.05
Ag^+ + HF = $[Ag\cdots FH]^+$	14.53	14.23	15.71	15.41	16.68	16.38	16.63	16.33
Ag^+ + HCl = $[Ag\cdots ClH]^+$	10.52	9.91	16.67	16.06	18.84	18.23	18.80	18.19
Ag^+ + HBr = $[Ag\cdots BrH]^+$	12.48	11.85	18.71	18.08	21.71	21.08	21.62	20.99
Ag^+ + H_2O = $[Ag\cdots OH_2]^+$	24.72	23.37	28.67	27.32	30.78	29.43	30.55	29.20
Ag^+ + H_2S = $[Ag\cdots SH_2]^+$	21.34	19.92	30.32	28.90	34.01	32.59	33.77	32.35
Ag^+ + H_2Se = $[Ag\cdots SeH_2]^+$	23.03	21.69	32.16	30.82	36.31	34.97	36.12	34.78
Ag^+ + NH_3 = $[Ag\cdots NH_3]^+$	33.66	31.54	42.00	39.88	45.69	43.57	45.37	43.25
Ag^+ + PH_3 = $[Ag\cdots PH_3]^+$	29.07	27.52	38.70	37.15	43.03	41.48	42.08	40.53
Ag^+ + AsH_3 = $[Ag\cdots AsH_3]^+$	11.85	11.80	21.43	21.38	25.64	25.59	25.42	25.37

[a] Scaled by 0.89; ZPE values are calculated at the HF/6-311+G** level.

of η has been found to provide better hardness ordering as well as acceptable trends in diatomic bond energy values of several hard and soft acids and bases.

Hardness can also be calculated within the density functional theory (DFT)[18] which often provides results comparable to that of traditional ab initio calculations. It may be noted that Kohn–Sham orbitals are different from canonical MOs, and the calculation of η in terms of HOMO–LUMO gap is not straightforward. However, other definitions may be suitable for hardness calculation within DFT. For example, Kostyk and Whitehead[19] have calculated η using the Orsky–Whitehead[17] definition using

---

(18) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

Table 4. Geometrical Parameters[a] of Binary Complexes of HF and Ag^+ Calculated at the MP2/6-311+G** Level

species, PG	F–H	H(Ag)–X	X–H′	<F–H–X	<H(Ag)–X–H′	<H′–X–H′
FH···FH, C_s	0.921	1.870	0.919	171.37	124.56	
FH···ClH, C_s	0.920	2.412	1.275	174.73	101.43	
FH···BrH, C_s	0.920	2.554	1.418	175.45	92.90	
FH···OH_2, C_s	0.931	1.731	0.960	177.81	117.89	104.68
FH···SH_2, C_s	0.925	2.313	1.333	178.85	104.55	92.67
FH···SeH_2, C_s	0.926	2.434	1.469	179.38	95.14	91.60
FH···NH_3, C_{3v}	0.948	1.701	1.015	180.00	111.95	106.89
FH···PH_3, C_{3v}	0.926	2.377	1.405	179.98	121.03	95.82
FH···AsH_3, C_{3v}	0.924	2.501	1.512	180.00	122.29	94.13
$[Ag\cdots FH]^+$, C_s		2.403	0.925		179.21	
$[Ag\cdots ClH]^+$, C_s		2.597	1.283		103.67	
$[Ag\cdots BrH]^+$, C_s		2.679	1.426		97.54	
$[Ag\cdots OH_2]^+$, C_{2v}		2.275	0.963		127.15	105.71
$[Ag\cdots SH_2]^+$, C_s		2.524	1.339		100.04	93.91
$[Ag\cdots SeH_2]^+$, C_s		2.630	1.474		95.48	92.15
$[Ag\cdots NH_3]^+$, C_{3v}		2.242	1.018		112.70	106.05
$[Ag\cdots PH_3]^+$, C_{3v}		2.468	1.395		116.27	101.90
$[Ag\cdots AsH_3]^+$, C_{3v}		2.820	1.540		57.03	93.19

[a] Distances in Å and angles in deg; X = F, Cl, Br, O, S, Se, N, P, As; for $[Ag–AsH_3]^+$: Ag–H′ = 2.366, <H′–Ag–As = 33.10, and <H′–Ag–H′ = 56.45; H′ is H bound to X.

DFT. An ab initio DFT has been used[20] recently to calculate η as the first derivative of chemical potential with respect to the number of electrons at constant external potential. A dynamical variant of MHP has been provided recently by Chattaraj and Nath[21] within a quantum fluid density functional framework. In this calculation hardness has been calculated as a time-dependent density functional.

Computational Details

For various bases and their complexes with HF or Ag^+, computation comprises four steps, viz. (i) geometry optimization at the HF level, (ii) frequency calculation at the HF level, (iii) geometry optimization at the MP2 level, and (iv) QCISD(T) single point calculation at the MP2-optimized geometry. Unless otherwise specified the basis set used is 6-311+G**. For molecules containing heavier elements, Br, Se, As, and Ag^+ ab initio pseudopotential calculations have been performed. The basis set used for Br (7 ve-ecp-mwb, dz+p with diffuse exponents, s, 0.051, p, 0.038) has been taken from Kaupp et al.[22] who fitted it to the pseudopotential of Br calculated by Schwerdtfeger et al.[23] For Se (6 ve-ecp-mwb, dz + p with diffuse exponents, s, 0.043, p, 0.033) and As (5 ve-ecp-mwb, dz+p with diffuse exponents, s, 0.037, p, 0.029) they are from Küchle et al.[24] Both the basis set and the pseudopotential for Ag (19 ve-ecp-mwb, 8s7p6d/6s5p3d) have been taken from Andrae et al.[25] The basis set of Ag has been augmented by an additional f function with exponent 1.7 (obtained through a quadratic fit for the minimum energy) during QCISD(T) single point calculations. Hardness values for HF complexes have been calculated using eq 1 and orbital energy values from HF optimization. For H^+, Li^+, and Na^+ complexes, geometries are optimized at the MP2/6-311+G** level. All calculations have been carried out with the Gaussian 90 program.[26]

Table 5. Total Energies (–au) of Binary Complexes of H^+, Li^+, and Na^+ with Various Bases Calculated at the MP2/6-311+G** Level and Comparison to Other Literature Values

species, PG	MP2/6-311+G**// MP2/6-311+G**	Smith et al. values (6-31G*//3-21G)
$[FH_2]^+$, C_{2v}	100.49044	100.19553
$[ClH_2]^+$, C_{2v}	460.51823	460.26528
$[BrH_2]^+$, C_{2v}	14.07349	
$[OH_3]^+$, C_{3v}	76.56895	76.28603
$[SH_3]^+$, C_{3v}	399.25167	398.94042
$[SeH_3]^+$, C_{3v}	10.70518	
$[NH_4]^+$, T_d	56.77493	56.53056
$[PH_4]^+$, T_d	343.05265	342.76127
$[AsH_4]^+$, T_d	8.19166	
$[Li–FH]^+$, $C_{\infty v}$	107.58362	107.28209
$[Li–ClH]^+$, C_s	467.57102	467.31691
$[Li–BrH]^+$, C_s	21.12327	
$[Li–OH_2]^+$, C_{2v}	83.59939	83.30750
$[Li–SH_2]^+$, C_s	406.25635	405.93062
$[Li–SeH_2]^+$, C_s	17.71281	
$[Li–NH_3]^+$, C_{3v}	63.74827	63.48958
$[Li–PH_3]^+$, C_{3v}	350.02869	349.72438
$[Li–AsH_3]^+$, C_{3v}	15.17758	
$[Na–FH]^+$, $C_{\infty v}$	262.11901	261.69445
$[Na–ClH]^+$, C_s	622.10542	621.73274
$[Na–BrH]^+$, C_s	175.65843	
$[Na–OH_2]^+$, C_{2v}	238.12810	237.71402
$[Na–SH_2]^+$, C_s	560.78798	560.34586
$[Na–SeH_2]^+$, C_s	172.24483	
$[Na–NH_3]^+$, C_{3v}	218.27410	217.89347
$[Na–PH_3]^+$, C_{3v}	504.55987	504.13506
$[Na–AsH_3]^+$, C_{3v}	169.71002	
Li^+, K_h	7.24835	7.23554
Na^+, K_h	161.79415	161.65929

Results and Discussion

Total energies, zero point vibrational energies (ZPE), and hardness values of the acids (HF and Ag^+) and the bases and their complexes are presented in Tables 1 and 2, respectively. These tables also contain the respective numbers of imaginary frequency (NIMAG) obtained from the frequency calculations. The zero value for NIMAG of any given species assures that the molecular symmetry considered for the geometry optimization corresponds to the minimum energy structure. The hardness values are calculated at the HF level because in other calculations orbital energy values are not very meaningful quantities. It is quite gratifying to note that for the interaction with the hard acid, HF, the η values follow the same trend as that of expected stability of the products as suggested by the HSAB principle.[3,7] In this case it is nothing but the implication of the maximum hardness principle.[13,14] For a given group of species, the most favorable reaction according to the HSAB principle will give the most stable product with maximum hardness value. Thus, for HF interaction, the hardness order is the same as the order of

---

(19) Kostyk, R. J.; Whitehead, M. A. *J. Mol. Struct.* (*THEOCHEM*) **1991**, *230*, 83.

(20) Galván, M.; Pino, A. D.; Joannopoulos, J. D. *Phys. Rev. Lett.* **1993**, *70*, 21.

(21) (a) Chattaraj, P. K.; Nath, S. *Chem. Phys. Lett.*, in press. (b) Chattaraj, P. K.; Nath, S. *Proc. Indian Acad. Sci.* (*Chem.Sci.*), in press.

(22) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Am. Chem. Soc.* **1991**, *113*, 6012.

(23) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J. Chem. Phys.* **1989**, *91*, 1762.

(24) Küchle, W.; Bergner, A.; Dolg, M.; Stoll, H.; Preuss, H., to be published.

(25) Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 124.

(26) Gaussian 90, Revision F; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian Inc.*; Pittsburgh, PA, 1990.

Table 6. Reaction Energies (–kcal/mol) for Reactions of H^+, Li^+, and Na^+ with Various Bases at the MP2/6-311+G** Level and Comparison to Available Literature and Experimental Data

reactions	MP2/ 6-311+G**// MP2/ 6-311+G**	ZPE[a]-corrected values	Smith et al. values 6-31G*// 3-21G	exptl values
$H^+ + HF = [FH_2]^+$	120.86	115.48	121.4	117
$H^+ + HCl = [ClH_2]^+$	140.57	135.22	129.1	128.6
$H^+ + HBr = [BrH_2]^+$	141.65			139
$H^+ + H_2O = [OH_3]^+$	172.70	165.05	173.3	166.5
$H^+ + H_2S = [SH_3]^+$	177.83	170.68	171.8	170.2
$H^+ + H_2Se = [SeH_3]^+$	175.54			171.3
$H^+ + NH_3 = [NH_4]^+$	213.65	204.28	218.4	204.0
$H^+ + PH_3 = [PH_4]^+$	197.79	190.49	197.0	188.6
$H^+ + AsH_3 = [AsH_4]^+$	187.48			
$Li^+ + HF = [Li{-}FH]^+$	23.49	23.28	27.9	
$Li^+ + HCl = [Li{-}ClH]^+$	17.86	16.93	13.7	
$Li^+ + HBr = [Li{-}BrH]^+$	17.05			
$Li^+ + H_2O = [Li{-}OH_2]^+$	35.97	34.17	39.0	34.0
$Li^+ + H_2S = [Li{-}SH_2]^+$	24.94	23.17	17.9	
$Li^+ + H_2Se = [Li{-}SeH_2]^+$	24.50			
$Li^+ + NH_3 = [Li{-}NH_3]^+$	41.09	38.43	44.9	39.1
$Li^+ + PH_3 = [Li{-}PH_3]^+$	26.92	25.01	26.0	
$Li^+ + AsH_3 = [Li{-}AsH_3]^+$	22.81			
$Na^+ + HF = [Na{-}FH]^+$	16.96	16.73	20.7	
$Na^+ + HCl = [Na{-}ClH]^+$	10.70	10.07	8.8	
$Na^+ + HBr = [Na{-}BrH]^+$	10.37			
$Na^+ + H_2O = [Na{-}OH_2]^+$	25.24	23.84	28.2	24.0
$Na^+ + H_2S = [Na{-}SH_2]^+$	16.04	14.66	12.5	
$Na^+ + H_2Se = [Na{-}SeH_2]^+$	15.85			
$Na^+ + NH_3 = [Na{-}NH_3]^+$	28.56	26.45	32.5	
$Na^+ + PH_3 = [Na{-}PH_3]^+$	17.75	16.26	17.8	
$Na^+ + AsH_3 = [Na{-}AsH_3]^+$	14.43			

[a] Scaled by 0.89, calculated at the 6-31+G* level and in two cases with different geometries, viz., $[Li{-}FH]^+(C_s)$ and $[Na{-}FH]^+(C_s)$.

preference (HSAB principle) of HF to react with different bases, viz., F ≫ Cl > Br, O ≫ S > Se, and N ≫ P > As.

Recently, Datta[27] has shown that an exchange reaction of the type AB + CD = AC + BD proceeds in a direction such that the hardest possible species is formed and the average hardness value of the products is more than that of reactants. It may be noted that neither of these conclusions seems to be valid in case of complexes of HF. It may be due to the fact that HF is exceptionally hard and Datta's calculation[27] was on the MNDO level as opposed to the present ab initio calculation. It has also been observed that in a reaction where anomeric effect is operative[28] and in a proton-transfer reaction[16] the driving force is the formation of the hardest possible species as product. The former calculation[28] was on the MNDO level, whereas the latter one[16] is on the ab initio SCF level. Chattaraj and co-workers have verified the validity of MHP in static[16] as well as dynamic[21] situations.

Table 3 comprises reaction energies for the reactions of both HF and Ag^+ with various bases at different levels of computation including their zero point energy (ZPE)-corrected values. The ZPE values are all calculated at the HF/6-311+G** level and have been scaled[29] by 0.89. Reaction energy values for the reactions of the hard acid, HF, with different bases reveal that for these reactions the HSAB principle works even at the HF level. Calculations at the correlated levels produce different energy values, but the trend remains the same. It is interesting to note that S, Se, P, and As can form reasonably strong hydrogen bonds.

The calculation of reaction energies of the reactions of the soft acid, Ag^+, at the HF level is not able to reproduce the proper energy order. It may be due to the fact that for soft–soft interaction covalent bonding predominates, whereas hard acids and bases prefer to have ionic bonding.[3,19] A numerical support to this statement has been provided[19] within DFT. Thus, it appears that the effect of correlation is important in case of soft–soft interaction which is quite understandable because Ag^+ is having a highly polarizable core and unless the in–out correlation is properly taken into account the results would not be very meaningful. At the MP2 level, the order has been found to be altered in most cases, e.g., F < Cl < Br and O < S < Se. For these bases, the reaction energies from the MP2 level or higher level single point calculations clearly show that Ag^+, like any other soft acid, follows the same order of preference as suggested by HSAB principle. Although the difference in reaction energies for the reactions producing $[Ag{-}NH_3]^+$ and $[Ag{-}PH_3]^+$ has been reduced considerably, as we go from the HF level to the MP4SDTQ level, Ag^+ still prefers to bind to NH_3 rather than to PH_3 which is against the HSAB principle. However, it may be noted that AsH_3 is less preferable to Ag^+ than PH_3 as predicted by the HSAB principle.[3,5,7]

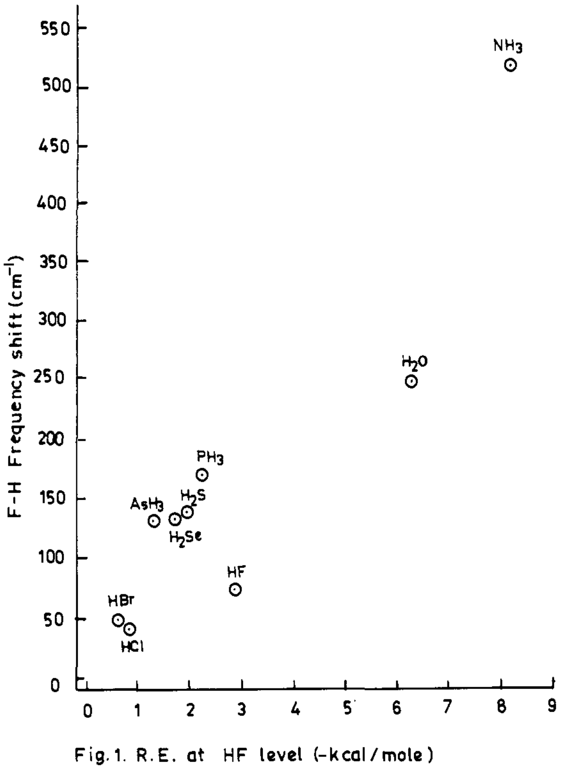

Figure 1. Dependence of F–H frequency shift (in cm^{-1}) in binary complexes of HF on the respective ZPE-corrected complexation energies (in kcal/mol) calculated at the HF/6-311+G** level.

Figures 1 and 2 depict the variation of shifts in frequency of F–H stretching absorption bands in HF when it forms hydrogen-bonded complexes with different bases, with the corresponding reaction energies (ZPE-corrected) calculated at the HF/6-311+G** and MP2/6-311+G** levels, respectively. An approximate linear correlation is discernible in these plots. Similar studies were carried out earlier[30,31] in the context of hydrogen bonding abilities of alkyl halides and chalcogenides where an apparent violation[31] of the Badger–Bauer rule[32] was observed. Our $\Delta\nu_{F-H}$ and reaction energy values, however, follow the same order but for the $\Delta\nu_{F-H}$ values for the bases FH and ClH, where the order has been reversed. As in earlier studies,[30,31] the present calculation also shows that oxygen and nitrogen bases are strong proton acceptors during hydrogen bonding compared to their halide counterparts.

---

(27) Datta, D. *Inorg. Chem.* **1992**, *31*, 2797.

(28) Hati, S.; Datta, D. *J. Org. Chem.* **1992**, *57*, 6056.

(29) (a) Pople, J. A.; Schlegel, B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, H.; Whiteside, R.; Hout, R. F., Jr.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 269. (b) DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333. (c) Komornicki, A.; Pauzat, F.; Ellinger, Y. *J. Chem. Phys.* **1983**, *87*, 3847.

(30) Schleyer, P. v. R.; West, R. *J. Am. Chem. Soc.* **1959**, *81*, 3164.

(31) West, R.; Powell, D. L.; Whatley, L. S.; Lee, M. K. T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1962**, *84*, 3221.

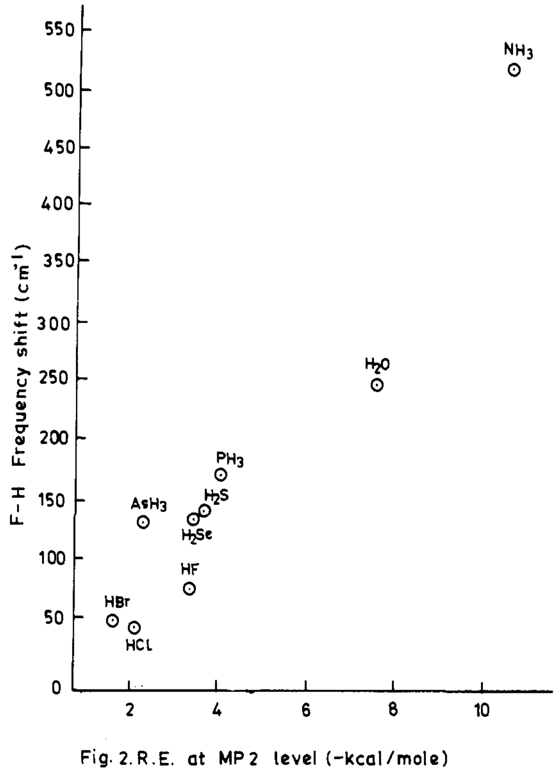

Figure 2. Dependence of F-H frequency shift (in cm^{-1}) in binary complexes of HF on the respective ZPE-corrected complexation energies (in kcal/mol) calculated at the MP2/6-311+G** level.

Various geometrical parameters calculated at the MP2/6-311+G** level for these complexes are reported in Table 4. As expected from HSAB principle, in most of the HF bonded complexes, the HF bond lengths decrease in the direction of their decreasing magnitude of complexation energies.

In $[Ag-AsH_3]^+$, three hydrogen atoms in AsH_3 come very close to Ag and form strong Ag-H bonds, and hence the respective geometrical parameters are also given at the bottom of Table 4.

Table 5 compares the total energies of several H^+, Li^+, and Na^+ bonded complexes calculated at the MP2/6-311+G** level with the corresponding ab initio MO calculation results of Smith et al.[12] at 6-31G*//3-21G level. Similar comparison for the corresponding reaction energies is made in Table 6. The ZPE-corrected values (except for the complexes containing heavier elements, viz., Br, Se, and As) and experimental values[33-35] wherever available are also listed in Table 6. The ZPE values are calculated at the HF/6-31+G* level and in two cases with different geometries, viz., C_s symmetry for $[Li-FH]^+$ and $[Na-FH]^+$. They are scaled[29] by 0.89, the ZPE-corrected values compare favorably with the available experimental values.[33-35] Both the hard acids, Li^+ and Na^+, prefer to bind to bases in the order governed by HSAB principle. However, for reactions with protons it is not always true. It behaves very erratically as far as the HSAB principle is concerned. It may be noted that the ionization potential and hence the hardness (eq 2) of proton cannot be defined properly.

In the present study we have noticed that the HSAB principle works in many cases. At the same time it fails to predict the proper order of preference for several reactions. Out of 45 reactions studied there are five exceptions. Perhaps the hard-soft factor should be properly supplemented by the strengths of acids and bases[36-38] in order that the HSAB principle can predict the correct directionality of all acid-base reactions.

Conclusions

Ab initio calculations have proved the validity of the HSAB principle in many reactions. However, there are several cases where the principle does not work. For interactions involving hard acids the Hartree-Fock level calculation is sufficient, whereas the effect of correlation has been found to be important for the reactions of soft acids. Maximum hardness principle can be viewed as the principle dictating the formation of the hardest possible species as the product in the reaction of a hard acid, with a given group of bases, which is the most favorable according to the HSAB principle.

Acknowledgment. We are grateful to the referees for constructive criticisms. P.K.C. would like to thank the Indian National Science Academy, the Deutsche Forschungsgemeinschaft, and CSIR, New Delhi for financial assistance. He is also thankful to Martin Kaupp for helpful discussions.

---

(32) Badger, R. M.; Bauer, S. H. *J. Chem. Phys.* **1937**, *5*, 839. Badger, R. M. *J. Chem. Phys.* **1940**, *8*, 288.

(33) Lias, S. C.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas-Phase Ion and Neutral Thermochemistry, J. Phys. Chem. Ref. Data*; 1988; Vol. 17, Suppl. 1.

(34) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.

(35) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466.

(36) Drago, R. S.; Kabler, R. A. *Inorg. Chem.* **1972**, *11*, 3144.

(37) Pearson, R. G. *Inorg. Chem.* **1972**, *11*, 3146.

(38) Drago, R. S. *Inorg. Chem.* **1973**, *12*, 2211.