

HAICl₄ in the gas phase is stronger than HTaF₆

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Ab initio MO calculations at the {MP2(fc)/6-311++G(d,p)/3-21G(*)+ZPVE[3-21G(*)]} and {MP2(fc)/D95++G(d,p)/3-21G(*)+ZPVE[3-21G(*)]} levels of sophistication and also an analogous DFT/DNP study reveal that HAICl₄ has a gas phase deprotonation energy of *ca.* 264 kcal mol⁻¹ (1 cal = 4.184 J) being lower than the value predicted for HTaF₆ (269 kcal mol⁻¹).

Superacids are a very intriguing tool in applied experimental¹⁻⁶ and theoretical⁷⁻⁹ chemistry. It was previously shown⁷ by applying the density functional theory (DFT) to calculating deprotonation energies (DEs) that in the gas phase HSbF₆ (HF·SbF₅) is the strongest acid known (DE = 258 kcal mol⁻¹), in full agreement with various investigations of the corresponding Hammett acidity function in condensed media.⁴ Further, HTaF₆ (HF·TaF₅) has been predicted to be clearly weaker⁷ possessing a DE of 269 kcal mol⁻¹.

On the other hand, the place of Friedel–Crafts acid of the HX·AlX₃ (X = Cl, Br) type in the acidity scale is unknown thus far. Moreover, there was a controversy more than 10 years ago^{4,10,11} concerning the relative strengths of HAIBr₄ (HBr·AlBr₃). Farcasiu *et al.*¹⁰ argued that the latter should exhibit an acidity comparable to HSbF₆ since it is capable of protonating benzene at 0 °C. Kramer proposed the same ranking based on his selectivity parameter.¹¹ However, it was claimed⁴ that HAIBr₄ is very unlikely comparable to HSbF₆ as it is incapable of protonating weak bases or ionising precursors. Although the order of acidic strength might change in solution¹² it is of principal significance to determine the DEs of HAICl₄ and HAIBr₄. Here, quantum chemical calculations on HAICl₄, AlCl₄⁻, AlCl₃, HCl and Cl⁻ are presented, which have been used to determine the energies of the following processes. (i) The DE of the superacid, HAICl₄ → H⁺ + AlCl₄⁻ (1); (ii) the decomposition energy of the superacid, HAICl₄ → HCl + AlCl₃ (2); (iii) the decomposition energy of the conjugated base, AlCl₄⁻ → AlCl₃ + Cl⁻ (3) and (iv) the DE of hydrogen chloride, HCl → H⁺ + Cl⁻ (4).

The last process is considered to obtain information of the performance of the methods used.

In order to obtain reliable results we used a suggestion of Koppel *et al.*¹³ that MP2(fc)/6-311++G(d,p) perform rather

well already at 3-21G [or 3-21G(*) in the cases of molecules containing second row elements] fully optimised geometries. Very recently we reported⁸ on the gas phase DEs of some superacids (HClO₄, FSO₃H, ClSO₃H) applying the 6-31+G(d) basis set for calculating structures. Nevertheless, we are of the opinion now that the smaller valence basis sets also attain this objective, providing deviations from experiment of <3 kcal mol mol⁻¹;¹³ at this point evidence is given of the reliability of the level of sophistication mentioned above for calculating DEs of HPF₆ (HF·PF₅).⁹

The geometries for two conformations of HAICl₄, *cis* and *trans*, the conjugated base AlCl₄⁻ and also for the Lewis acid AlCl₃ have been fully optimised (Table 1) by using the 3-21G(*) basis set followed by vibrational analyses at the same level. All stationary points were found to be minima. Then the energies were improved by carrying out MP2(fc)/6-311++G(d,p) calculations. Since for calculating the DE the energy of the low lying conformation of HAICl₄ had to be used depending on the level of investigation, the corresponding values of either *cis* or *trans* geometry have been employed. Nevertheless, both conformations are almost equal in stability and, therefore, DE is practically unaffected by the energy chosen for the acid.

Details on current *ab initio* MO theory and common standard procedures are given elsewhere.¹⁴ Furthermore, single point energy calculations have been also performed with Dunning's split valence basis set D95.¹⁵ All *ab initio* MO calculations were performed using Hyperchem software¹⁶ and run on a Pentium PC.

All *ab initio* DFT computations were performed with the DMol program¹⁷ on an Indigo-2 workstation. The Becke 1988 exchange functional¹⁸ was used in combination with the Lee–Yang–Parr correlation (LYP).¹⁹ All electrons were taken into account and the DNP (double numeric augmented by polarization functions at both hydrogen and non-hydrogen atoms) basis set was used together with a high number of mesh points that is almost to the saturation point of the mesh grid. Completely optimised geometries as well as the corresponding energies have been calculated with this basis which is¹⁷ comparable to 6-31G(d,p) followed by vibrational analyses. All stationary points were found to be minima. It has been shown⁷ that DNP reproduces the DE of strong acids and superacids quite well.

Table 1 Calculated total energies ($-E_h$) and ZPVEs (kcal mol⁻¹)

Compound	Point group	ZPVE 3-21G(*)	ZPVE	6-31+ G(d) ^a	6-31+ G(d,p)	D95++ G(d,p)	6-311++ G(d,p)	MP2/6-31+ G(d,p)	MP2/D95++ G(d,p)	MP2/6-311++ G(d,p)	B-LYP/DNP	
			B-LYP/DNP									
HAICl ₄ , <i>cis</i>	C _s	8.78	7.78	2071.08345	2080.64470	2080.65075	2080.62684	2080.77494	2081.28968	2081.66018	2081.72054 (2081.72000) ^b	2084.14452
HAICl ₄ , <i>trans</i>	C _s	8.84	7.64	2071.08350	2080.64438	2080.65085	2080.63852	2080.77496	2081.28998	2081.67213	2081.72075 (2081.71482) ^b	2084.14448
AlCl ₄ ⁻	T _d	3.91	3.37	2070.67394	2080.23457	2080.23455	2080.22098	2080.35608	2080.86515	2081.23394	2081.29120 (2081.29098) ^b	2083.71675
AlCl ₃	D _{3h}	3.19	2.87	1613.09168	1620.57802	1620.57802	1620.55913	1620.67310	1621.05833	1621.36398	1621.40989	1623.31904
HCl	D _{∞v}	4.56	3.94	457.98139	460.06100	460.06734	460.06191	460.09621	460.21834	460.28323	460.29680	460.82018
Cl ⁻	¹ S ₀	0.00	0.00	457.44410	459.53964	459.53964	459.53440	459.56562	459.68144	459.74856	459.75418	460.28427

^a Fully optimised geometries. ^b Energies at 6-31+G(d) geometries.

Table 2 Processes considered in this investigation^a (kcal mol⁻¹)

Reaction	3-21G ^{(*)b}	6-31+ G(d) ^b	6-31+ G(d,p)	D95++ G(d,p)	6-311++ G(d,p)	MP2/6-31+ G(d,p)	MP2/D95++ G(d,p)	MP2/6-311++ G(d,p)	B-LYP/ DNP
(1) HAICl ₄ → H ⁺ + AlCl ₄ ⁻	252.6	253.0	256.8	257.6	258.5	262.1	263.1	265.0 (264.8) ^c	264.1
(2) HAICl ₄ → HCl + AlCl ₃	5.61	2.63	2.45	10.00	2.59	7.40	14.69	7.87	2.37
(3) AlCl ₄ ⁻ → AlCl ₃ + Cl ⁻	86.0	72.7	72.7	79.3	73.0	78.0	75.6	79.1	70.7
(4) HCl → H ⁺ + Cl ⁻	333.0 ^d	323.0	327.0	326.9	328.8	332.8	331.4	333.5	332.3

^a The ZPVE corrections are scaled by 0.9 for the 3-21G^(*) calculations and they are unscaled when the DFT values were used. ^b Fully optimised geometries. ^c The DE when the 6-31+G(d) geometry is used. ^d Experimental values (enthalpies at 298 K) are²⁶ 333.4 ± 0.3 and 333.7 ± 2.2 kcal mol⁻¹.

Detailed information on the current state and performance of modern DFT theory is given in the user manual¹⁷ and in some recent comprehensive books and papers.²⁰

In order to turn out an incidental failure of the chosen procedure, the geometries have also been fully optimised employing the medium size 6-31+G(d) basis set. The gradients of the 6-311++G(d,p) energies (not given in the text) are smaller when the 3-21G^(*) geometries are used and the corresponding energies (Table 1) are lower. Thus, the 3-21G^(*) structures are closer to the 6-311++G(d,p) ones and they are applied throughout in this study. The DE values are practically unaffected by this difference in the geometries used. The values calculated (Table 2) are 265.0 kcal mol⁻¹ (3-21G^(*)) and 264.8 kcal mol⁻¹ (6-31+G(d)).

It is noteworthy that the results for DE from all MO calculations rigorously depend on the size of the basis sets applied (Table 2). It was found that the MP2(fc)/6-31+(d,p) level of investigation provides a good estimate for predicting the acidity of HAICl₄. On the other hand, it is remarkable that both remaining MP2 calculations provide almost identical values of DE (263.1 and 265.0 kcal mol⁻¹). Moreover, the DFT gives a value (264.1 kcal mol⁻¹) lying between the two latter ones. Thus, the mean DE of HAICl₄ amounts to ca. 264 kcal mol⁻¹. This is less than the corresponding value for HTaF₆ (269 kcal mol⁻¹)⁷ which was obtained applying the same DFT procedure as in the present work. The order of acidity is, therefore, HSbF₆ > HAICl₄ > HTaF₆ since there is a complete agreement between the experimental and DFT results of DEs on one hand⁷ and the same was found for the DFT and MP2(fc)/6-311++G(d,p) sets of values, on the other hand.⁸

Beside the acidity the decomposition of the acid toward HCl and AlCl₃ is of interest. The positive energies for reaction (2) collected in Table 2 reveal that generation of HAICl₄ is favoured, however, the values are small and indicate a weak van der Waals (vdW) interaction. Indeed, all attempts of Brown and Pearsall²¹ failed to detect any complexation of AlCl₃ with HCl even at temperatures as low as 150 K. Many years later, however, aggregates were found²² with a composition corresponding to 2HAICl₄·3Et₂O indicating the necessity of an auxiliary 'complexation generator'.

Finally, the stability of the anion AlCl₄⁻ towards chloride ion detachment has been investigated (Table 2). Previously it was found²³ that the MP2/6-31+G(d) energy required to dissociate AlCl₄⁻ in agreement with reaction (3) is 51.57 kcal mol⁻¹. The latter value is, however, erroneous. We calculated from the total energies reported²³ the correct one (77.6 kcal mol⁻¹). This result was confirmed by our calculations (Table 2).

Thus, AlCl₄⁻ is, for example, comparable in stability to the conjugated base PF₆⁻ for which a fluoride ion detachment of 85 ± 10 kcal mol⁻¹ was determined experimentally,²⁴ in complete agreement with quantum chemical calculations.^{9,25}

The following significant concluding remarks can be made. (a) HAICl₄ belongs to the strongest superacids since its gas phase acidity is between those of HSbF₆ and HTaF₆. (b) The acid itself exhibits a weakly bonded vdW complex between HCl and AlCl₃ which is rather unstable *in vacuo* even at low temperatures. (c) The conjugated base (AlCl₄⁻) is a stable

species with respect to chloride ion abstraction possessing a detachment energy which is comparable to those of usual ordinary chemical bonds.

All optimised geometries are available from the authors by request. Furthermore, they will be published in a subsequent paper.

Notes and References

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Received in Exeter, UK, 17th October 1997; 7/07493J