

Proton Affinity of Halogenoamines. A Theoretical Study

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A general order of decreasing proton affinity energies in the gas phase for the halogenoamines $\text{NH}_n\text{Hal}_{3-n}$ (Hal = F, Cl, Br, I) has been established by AM1 calculations.

The reactivity of halogen-derivatives of ammonia with respect to electrophilic reagents is connected with their basicity or their proton affinity (PA) in the gas phase.^{1,2} In addition, protonation not only of the nitrogen atom but also of the halogen atom may take place for halogenoamines, in contrast to alkylamines.³ However, it is difficult to determine the PA's of halogenoamines experimentally due to the low stability of protonated halogenoamines,⁴ so this energy has been determined only for NF_3 .^{5,6} The value of the PA for fluoroamines has been estimated on the grounds of IR spectral data of their HF-complexes.⁷ The PA's of halogenoamines may be determined on the grounds of quantum-chemical calculation data, but previous *ab initio* calculations of the PA's for NH_2F and NH_2Cl have been carried out in different basis sets.^{8,9} These available data are insufficient for the quantitative estimation of PA's and for the determination of the site of protonation for different halogenoamines.

We have calculated the values of PA energies of halogenoamines of general formula $\text{NH}_n\text{Hal}_{3-n}$ by semiempirical methods MNDO and AM1 (Hal = F, Cl, Br, I) and by an *ab initio* method at the SCF/4-31G level (Hal = F). The calculations were carried out with a fully optimized initial geometry of the molecules and their protonated forms using AMPAC and MICROMOL¹⁰ programs. Comparison of the geometry obtained with the experimental and calculated data on the structures of fluoro- and chloro-amines^{11,12} (the molecular geometry of bromo- and iodo-amines has not been investigated before) shows that MNDO and AM1 describe the halogenoamine structures satisfactorily.

The PA data obtained by the semiempirical methods were calculated using the experimental value of the enthalpy of proton formation $H_f(\text{H}^+)$ 1531.2 kJ mol⁻¹ with eqn. (1), where $\Delta_f H(\text{M})$ and $\Delta_f H(\text{MH}^+)$ are the enthalpies of formation of the initial and protonated molecules, respectively.

$$\text{PA} = \Delta_f H(\text{H}^+) + \Delta_f H(\text{M}) - \Delta_f H(\text{MH}^+) \quad (1)$$

Table 1 shows the results of the calculations and references on determining PA data. The PA's decrease consecutively in the order I > Br > Cl > F when the number of halogen atoms in the halogenoamines is the same in accordance with the MNDO and AM1 calculations, and also for the transition from

mono- to tri-halogenoamines in accordance with the results of Allenstein and Goubeau.⁴ However, the absolute value of the PA energies obtained by the MNDO and AM1 methods differ greatly. Compared with AM1, MNDO underestimates the PA energy for both the nitrogen and halogen atoms by 35–155 kJ mol⁻¹, the deviations not being systematic.

From the point of view of frontier molecular orbital (FMO) theory the protonation proceeds on an atom with the maximum contribution to the HOMO as a result of interaction between a nucleophilic HOMO and an unoccupied proton orbital.¹⁵ Our calculations confirm this conclusion: the lone-pair of the nitrogen atom makes the maximum contribution to the HOMO in every halogenoamine, and the PA values of this atom are greater than those of the halogens except in NH_2F and NF_3 . In these molecules the maximum contribution to the HOMO is made by the nitrogen atom but the PA of fluorine is higher than that of nitrogen according to our calculations. This is at variance with the experimental data as the IR spectra of fluoroamine–HF complexes and the UV spectra of NF_3 show that protonation of a nitrogen atom is favourable for these molecules.^{7,16}

At the same time *ab initio* calculations using the SCF/4-31G basis set are in accord with the experimental data and FMO theory shows that protonation of the nitrogen atom is favourable for fluoroamines, although the PA of nitrogen is higher than that of fluorine in NF_3 by only 21 kJ mol⁻¹ (see Table 1). It is necessary to note that values of the PA energies of nitrogen and fluorine obtained on this basis for NH_2F are close to those obtained using the wider basis set MP4//6-31G**.⁸ However, the calculations at the SCF/4-31G level underestimate the PA of nitrogen in NF_3 in comparison with the experimental and calculated data by 100 kJ mol⁻¹.

Comparison of the results of the *ab initio* and semiempirical calculations shows that the MNDO method underestimates the PA energy of nitrogen by 120–155 kJ mol⁻¹ whereas the results of the AM1 calculations correspond well with the *ab initio* methods. In addition, both MNDO and AM1 underestimate the PA of fluorine in fluoroamines.

Thus, the protonation of nitrogen is favourable in ammonia halogen-derivatives. The results obtained in this work allow us to establish a general order of decreasing PA energy in the gas

Table 1 Proton affinities of halogenoamines and charge on acidic proton after protonation

Molecule	Charge on proton (AM1)	Proton affinity/kJ mol ⁻¹						References
		MNDO		AM1		SCF/4-31G		
		Hal	N	Hal	N	Hal	N	
NH_3	0.274	—	820.9	—	875.9	—	924.7	859.3 (± 2) ^a
NH_2F	0.304	603.8	674.8	719.4	771.8	631.1	796.8	611.3 (F), 781.2 (N) ^b
NH_2Cl	0.295	542.5	729.8	638.8	794.7	—	—	856.9 ^c
NH_2Br	0.287	535.7	758.2	661.6	812.4	—	—	
NH_2I	0.276	565.1	789.2	637.4	834.8	—	—	
NHF_2	0.343	566.2	527.6	695.0	658.4	564.0	660.8	682.0 (± 21) ^d
NHCl_2	0.313	524.2	652.7	627.6	724.3	—	—	
NHB_2	0.295	525.2	709.7	652.4	767.1	—	—	
NHI_2	0.277	554.5	763.9	627.1	806.1	—	—	
NF_3	0.400	586.1	374.1	667.9	528.8	506.4	527.5	617.2 (± 21) ^e
NCl_3	0.327	517.0	585.5	627.3	661.5	—	—	
NBr_3	0.299	523.6	669.9	654.1	734.2	—	—	
NI_3	0.276	542.9	727.7	479.8	775.1	—	—	

^a Ref. 14. ^b Ref. 8. ^c Ref. 9. ^d Ref. 7. ^e Ref. 6. ^f Error limit for our calculations of proton affinities is ± 1 kJ mol⁻¹.

phase for the investigated halogenoamines (based on AM1 calculation data): $\text{NH}_3 > \text{NH}_2\text{I} > \text{NH}_2\text{Br} \sim \text{NH}_2 > \text{NH}_2\text{Cl} > \text{NI}_3 \sim \text{NH}_2\text{F} > \text{NHBr}_2 > \text{NBr}_3 > \text{NHCl}_2 > \text{NHF}_2 \sim \text{NCl}_3 > \text{NF}_3$.

It is known that the PA energy of a base correlates with Taft's σ -constants,¹⁷ the electronegativity of the substituents at nitrogen,¹⁸ the ionization potential of molecules,¹⁹ or on the charge on the acidic proton after protonation of the base.²⁰ A linear dependence was observed of the calculated PA's on the sum of the Pauling electronegativities of the substituents at nitrogen (coefficient of correlation $r = 0.98$) [eqn. (2)] or on the charge on the proton after protonation ($r = 0.97$, see Table 1) [eqn. (3)].

$$\text{PA} = -55.78\text{EN} + 1199.18 \quad (2)$$

(EN = sum of electronegativity of substituents at nitrogen.)

$$\text{PA} = -2344.75Q + 1460.43 \quad (3)$$

(Q = charge on proton after protonation of nitrogen.)

The dependence of the PA values on the electronegativities of the substituents may be used for the estimation of the PA values of nitrogen in the mixed halogenoamines.

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