Quantitative gas-phase electrophilicities of the dihalogen molecules XY = F_2, Cl_2, Br_2, BrCl and ClF

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Intermolecular stretching force constants k_σ determined from the rotational spectra of complexes B···XY, where B is one of the Lewis bases CO, C_2H_2, C_2H_4, HCN, H_2S and NH_3 and XY is a dihalogen F_2, Cl_2, Br_2, BrCl and ClF, are used to establish a quantitative scale of gas-phase electrophilicities E_{XY} of the halogens.

The nature of the initial interaction of homo- or heteronuclear diatomic halogen molecules XY with simple Lewis bases B in chemically reactive mixtures of the two components is a matter of fundamental interest in chemistry.[1] It has recently proved possible to isolate pre-reactive complexes of the type B···XY in gaseous mixtures and then characterise them through their rotational spectra by using a fast-mixing nozzle[2] in combination with a Fourier-transform microwave spectrometer.[3,4] Thereby precise values of several properties of the isolated species B···XY become available, including its angular and radial geometry, the strength of binding (as measured by the intermolecular stretching force constant k_σ), and the extent of electric charge redistribution within XY on complex formation. The efficacy of the fast-mixing nozzle is such that even pre-reactive complexes formed by NH_3, CO, H_2S, C_2H_2 or C_2H_4 with F_2 or ClF can be detected,[5–11] despite the rapid and violent reactions that would attend mixing of the components under normal conditions. Consequently, trends in the properties of B···XY may be identified not only by variation of the Lewis bases over a wide range of types but also by examining complexes with halogens as reactive as fluorine and chlorine monofluoride.

Such an approach has already revealed[12] a remarkable parallelism between the angular geometries of B···XY and B···HX (X,Y = F, Cl or Br). Thus, the pair B···HX and B···XY are isostructural for a given B over the range of XY and HX. This parallelism establishes that some simple rules first proposed for predicting angular geometries of hydrogen-bonded species B···HX,[13,14] and based on simple electrostatic considerations, also apply to the halogen complexes B···XY. The question then arises: Does the parallelism extend to other properties?

Another property of B···HX complexes that was found to vary systematically with B and HX is k_σ, which is the restoring force per unit infinitesimal displacement of the hydrogen bond along its dissociation co-ordinate and, therefore, one measure of the strength of the interaction. In particular, it was discovered[15,16] that k_σ could be partitioned between B and HX to define a nucleophilicity N_B of the proton acceptor region of B and the electrophilicity E_{HX} of HX. The relationship between N_B, E_{HX} and k_σ was established to be[15]

$$k_\sigma = cN_BE_{HX} \qquad (1)$$

where c is constant. This empirical equation could be used to predict k_σ of a large number of B···HX from a few N_B and E_{HX} values. For the particular scales of nucleophilicities and electrophilicities chosen, the value $c = 0.25$ N m^{-1} was appropriate. The advantage of the N_B and E_{HX} thereby established is that they define the propensity of a molecule to interact with either an electrophile or a nucleophile, respectively, in the limit where one molecule probes the other with only minor perturbation, and in isolation in the gas phase. The empirical eqn. (1) has been rationalised on the basis of the electrostatic model of the hydrogen bond elsewhere.[15]

The purpose of this communication is to examine whether the k_σ values of B···XY complexes, where B is CO, C_2H_2, C_2H_4, HCN, H_2S or NH_3 and XY is F_2, Cl_2, Br_2, BrCl or ClF, obey eqn. (1) and, if so, to establish a scale of electrophilicities E_{XY} for halogens and interhalogens. Another aspect of interest is whether a common set of nucleophilicities N_B applies to both the B···HX and B···XY series.

Table 1 displays a matrix of k_σ values for the series of B···XY defined earlier.[5–11,17–32] All values were derived from centrifugal distortion constants D_J or Δ_J established from analyses of rotational spectra, the latter usually observed with the fast-mixing nozzle/FT microwave spectrometer combination. Relationships between k_σ and D_J or Δ_J valid in the quadratic approximation for rigid, unperturbed subunits B and HX or XY have been derived by Millen for complexes of various symmetries.[33]

To test the validity of eqn. (1) for the B···XY in Table 1, the following procedure was used. First, the electrophilicity of BrCl was arbitrarily assigned the value $E_{BrCl} = 9.0$. Then E_{BrCl} was used with the k_σ values of all but one member of the series B···BrCl and $c = 0.25$ N m^{-1} to generate the nucleophilicities N_B for the Lewis bases B = CO, C_2H_2, C_2H_4, HCN and H_2S. This approach was not used for N_{NH_3} because there is evidence (see later) that H_3N···BrCl (and H_3N···ClF) involve significant

Table 1 Values of the intermolecular stretching force constant k_σ/N m^{-1} for complexes B···XY[a]

B	XY F_2	 Cl_2	 Br_2	 BrCl	 ClF
CO	— (*1.3*)	3.70[b] (*3.6*)	5.13[c] (*5.2*)	6.27[d] (*6.3*)	7.02[e] (*6.9*)
C_2H_2	— (*2.0*)	5.61[f] (*5.4*)	— (*7.8*)	9.4[g] (*9.5*)	10.02[h] (*10.3*)
C_2H_4	— (*2.2*)	5.89[i] (*6.0*)	— (*8.7*)	10.5[j] (*10.6*)	10.98[k] (*11.5*)
HCN	2.61[l] (*2.3*)	6.6[m] (*6.2*)	— (*9.1*)	11.09[n] (*11.0*)	12.33[o] (*12.0*)
H_2S	2.36[p] (*2.6*)	6.3[q] (*6.9*)	— (*10.0*)	12.07[r] (*12.1*)	13.34[s] (*13.2*)
NH_3	4.7[t] (*4.7*)	12.71[u] (*12.6*)	18.5[v] (*18.3*)	26.7[w] (*22.3*)	34.3[x] (*24.3*)

[a] Values in italics in parentheses are calculated from the N_B and E_{XY} of Table 2 used in eqn. (1). [b] Ref. 18. [c] Ref. 24. [d] Ref. 26. [e] Ref. 7. [f] Ref. 19. [g] Ref. 27. [h] Ref. 10. [i] Ref. 20. [j] Ref. 28. [k] Ref. 11. [l] Ref. 17. [m] Ref. 21. [n] Ref. 29. [o] Ref. 32. [p] Ref. 6. [q] Ref. 22. [r] Ref. 30. [s] Ref. 8. [t] Ref. 5. [u] Ref. 23. [v] Ref. 25. [w] Ref. 31. [x] Ref. 9.

charge transfer in addition to a simple electrostatic interaction.

Next, the N_B values so generated and recorded in Table 2 were used to establish E_{XY} for XY = F_2, Cl_2, Br_2 and ClF. For example, the appropriate N_B and k_σ pair was substituted into eqn. (1) to give one E_{ClF} value for each member of the series B···ClF. The mean value was then taken. Values of E_{F_2}, E_{Cl_2}, E_{Br_2} and E_{ClF} obtained in this way are included in Table 2 with the set of nucleophilicities N_{CO}, $N_{C_2H_2}$, $N_{C_2H_4}$, N_{HCN}, N_{H_2S} and N_{NH_3}. For the series B···Cl_2, B = NH_3 was not used to give a value of E_{Cl_2}, but instead the mean value of E_{Cl_2} from the remaining members was combined with k_σ of $H_3N\cdots Cl_2$ to define N_{NH_3}. This approach was preferred because N_{NH_3} could not be satisfactorily obtained from $H_3N\cdots BrCl$, for reasons alluded to earlier. Likewise, $H_3N\cdots ClF$ was not used in the evaluation of E_{ClF}.

As a check on the procedure, the N_B and E_{XY} of Table 2 were employed in eqn. (1) to generate k_σ for all complexes implied in Table 1. The predicted k_σ, shown in Table 1 in parentheses, are in good agreement with the experimental values when available, except for $H_3N\cdots BrCl$ and $H_3N\cdots ClF$, whose large k_σ are seriously underestimated. These disagreements can be understood when the electric charge redistribution in the XY subunit, as estimated from the halogen nuclear quadrupole coupling constants, is considered for each member of the series B···Cl_2,[34] B···BrCl[35] and B···ClF.[12] Only a few hundredths of an electronic charge is transferred from X to Y in most complexes except $H_3N\cdots BrCl$ and $H_3N\cdots ClF$ and, in particular, it was shown to be necessary to assume a significant contribution of the ionic structure $[H_3NCl]^+\cdots F^-$ in a valence bond description of the latter complex.[9] Presumably a similar assumption is appropriate to the strongly bound $H_3N\cdots BrCl$[31] but all other B···XY can be understood on the basis of the simple electrostatic model without invoking such charge transfer.[12,34,35]

Some interesting conclusions about B···XY interactions are available by reference to Tables 1 and 2. First, the fact that eqn. (1) applies to the two series of complexes B···HX and B···XY (with exceptions noted) suggests that the intermolecular binding is of a common type in both. For B···HX, the hydrogen bond interaction is well established to be of the simple electrostatic type $\mathrm{B}\cdot\cdot{}^{\delta+}\mathrm{H{-}X}^{\delta-}$, where $^{\delta+}\mathrm{H}$ interacts with a nucleophilic region of B.[13,14,36] Presumably, this is also the case for the halogen complexes, with interactions of the type $\mathrm{B}\cdot\cdot{}^{\delta+}\mathrm{X}\overset{\delta-}{\underset{\delta-}{-}}\mathrm{X}^{\delta+}$ or $\mathrm{B}\cdot\cdot{}^{\delta+}\mathrm{X{-}Y}^{\delta-}$. It is noteworthy that the order of the electric quadrupole moments of the homonuclear dihalogens is $F_2 < Cl_2 < Br_2$, while BrCl and ClF have electric dipole moments of similar magnitude.[37] This order of electric moments is consistent with the order $F_2 < Cl_2 < Br_2 <$ BrCl < ClF established here for the electrophilicities E_{XY} of the halogens (see Table 2).

The second conclusion is that, with one exception, the nucleophilicity N_B obtained for each B from the experimental k_σ of Table 1 and eqn. (1) is similar to that established from the B···HX series. The exception is HCN. The N_B and E_{HX} from the B···HX series are included in Table 2 for convenience. Evidently, HCN is a better nucleophile with respect to the hydrogen halides than to dihalogen molecules.

Table 2 Nucleophilicities N_B and electrophilicities E_{XY} of a series of Lewis bases B and dihalogen molecules XY

Nucleophilicities N_B

B	CO	C_2H_2	C_2H_4	HCN	H_2S	NH_3
This work[a]	2.8	4.2	4.7	4.9	5.4	9.9
Refs. 15 and 16[b]	3.4	5.1	4.7	7.3	4.8	11.5

Electrophilicities E_{XY}[c] or E_{HX}[d]

XY	F_2	Cl_2	Br_2	BrCl	ClF	HBr	HCl	HF
E_{XY} or E_{HX}	1.9	5.1	7.4	9.0	9.8	4.2	5.0	10.0

[a] Estimated by using the k_σ from Table 1 with eqn. (1) in the manner described in the text. [b] Estimated from the k_σ of a series of B···HX complexes and eqn. (1) (see refs. 15 and 16). [c] This work. [d] Ref. 15.

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Notes and references

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