A Quantitative Approach to the Pseudo-π Nature of Cyclopropane

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A quantitative measure of limiting gas-phase nucleophilicity is proposed for ethyne, ethene, and the pseudo-π donor cyclopropane and allows the conclusion that cyclopropane is the best nucleophile of the three.

There is a long-standing recognition among chemists that cyclopropane behaves in several ways like an unsaturated hydrocarbon, that is cyclopropane can be assigned a pseudo-π character. The question then arises: can this pseudo-π property be measured and compared quantitatively with the π-donor ability of ethyne and ethene, for example?

We have recently developed[1] numerical scales of limiting, gas-phase nucleophilicities N and electrophilicities E of molecules which are based on the strength of the hydrogen bond in dimers B · · · HX, as measured by the intermolecular stretching force constant k_σ. The scales have been based so far on dimers B · · · HX in which angular geometry can be predicted[2] if the HX molecule is assumed to lie along the axis of a nonbonding electron pair on the acceptor atom in B (*i.e.* on *n*-type hydrogen bonds). We now extend the scale of nucleophilicities to include the series B = ethyne, ethene, and cyclopropane (see Figure 1 for geometries) and show that the pseudo π-bonded system is more nucleophilic than the π-systems.

$$k_\sigma = cEN \qquad (1)$$

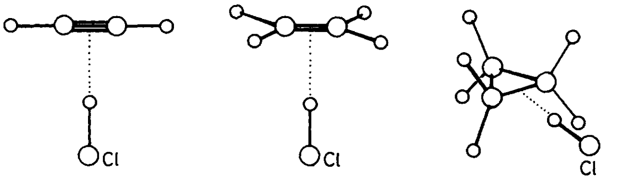

Figure 1. Observed angular geometries of B · · · HCl where B = ethyne, ethene, and cyclopropane.

The electrophilicity E of the H end of HX and the nucleophilicity N of the acceptor region of B are related to k_σ empirically according to equation (1), where $c = 0.25\ \mathrm{N m^{-1}}$ and E and N are numbers.[1] By use of this equation, we have been able to reproduce the k_σ for a large number of dimers using only a small number of E and N values. This empirical relationship can be rationalized on the basis of the electrostatic model of the hydrogen bond. It has been shown that the major contribution to equilibrium dissociation energies (D_e) is electrostatic and that, moreover, this contribution is controlled mainly by the local interaction between the net charges

Table 1. Observed and calculated force constants $k_\sigma/\mathrm{Nm^{-1}}$ for π- and pseudo-π hydrogen-bonded complexes.[a]

	Ethyne	Ethene	Cyclopropane
HCl	6.4 (6.4)[b]	5.9 (5.9)[c]	8.0 (8.0)[d]
HCN	5.2 (5.4)[e]	4.5 (5.0)[f]	6.3 (6.8)[g]

[a] Figures in parentheses are calculated using equation (1). See text for discussion. [b] A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Chem. Phys.*, 1981, **75**, 625. [c] P. D. Aldrich, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.*, 1981, **75**, 2126. [d] A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Am. Chem. Soc.*, 1982, **104**, 1486. [e] P. D. Aldrich, S. G. Kukolich, and E. J. Campbell, *J. Chem. Phys.*, 1983, **78**, 3521. [f] S. G. Kukolich, W. G. Read, and P. D. Aldrich, *J. Chem. Phys.*, 1983, **78**, 3552. [g] S. G. Kukolich, *J. Chem. Phys.*, 1983, **78**, 4832.

Table 2. Nucleophilicities *N*(B) of a series of *n*-acceptors and π-acceptors B.

n-Type	N_2	CO	PH_3	H_2S	HCN	H_2O	NH_3
	2.2	3.4	4.4	4.8	7.3	10.0	11.5
π-Type	C_2H_2	C_2H_4	∇[a]				
	5.1	4.7	6.4				

[a] ∇ = cyclopropane.

on the acceptor atom and the active proton.[3,4] Since it now appears that, from the limited number of accurate D_e values known,[5—8] D_e is almost proportional to k_σ, the basis of the empirical relationship (1) is evident.

We are now in a position to determine nucleophilicities *N* for B = ethene, ethyne, and cyclopropane from the values of k_σ recorded in Table 1 for B · · · HX, where X = Cl and CN. The k_σ in Table 1, like those referred to above, have been determined from centrifugal distortion constants[9] obtained by analyses of rotational spectra of B · · · HX. We first take E = 5.0 and 4.25 for X = Cl and CN obtained by use of equation (1) for several series of *n*-type dimers.[1] Then, *N*(B) are available from k_σ for B · · · HCl in Table 1 as follows: *N*(ethyne) = 5.1, *N*(ethene) = 4.7 and *N*(cyclopropane) = 6.4. Finally, as a check on the validity of these π-type *N* values, we calculate k_σ for all three species B · · · HCN in Table 1 and compare them with observed values. The agreement is satisfactory.

A result of immediate chemical interest is available from the π-type *N*(B) values. While, as might be expected, ethyne is a slightly stronger nucleophile than ethene, we find the surprising result that cyclopropane is appreciably stronger than both. Indeed, we note, from the series of both *n*-type and π-type *N*(B) values collected in Table 2, that the order of the limiting gas-phase nucleophilicities of B is

$$N_2 < CO < PH_3 \sim C_2H_4 \sim C_2H_2 < H_2S \sim \nabla < HCN < H_2O.$$

The above arguments cannot be extended to the π-type series B · · · HF at the moment because the only value of k_σ presently available is that for B = cyclopropane.[10] Further work on the rotational spectra of B · · · HF where B = ethyne and ethene is necessary in order to determine k_σ.

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