The Electronegativity of Groups from Thermochemical Data

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RECENTLY Constantinides[2] published values for group electronegativities derived from thermochemical data using Pauling's postulate of the geometric mean. These values he reports seem somewhat low, especially for the methyl (1·57) and hydroxyl (3·24) groups. Since the Pauling electronegativity values for carbon and oxygen were based on calculations involving the methyl and hydroxyl groups, the data seem even more irregular.

Recently we had occasion to investigate the assignment of group electronegativities, and in the course of our studies evaluated a number of group electronegativities by various methods.[3] Among our unpublished values are values for groups mentioned by Constantinides, as well as a number missing from his set. These are listed in Table I. Calculations use the thermochemical data from the indicated references. They are based on the postulate of the arithmetic mean, following

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[2] E. Constantinides, *Proc. Chem. Soc.*, 1964, 290.
[3] D. H. McDaniel and A. Yingst, *J. Amer. Chem. Soc.*, 1964, **86**, 1334.

Huggins' suggestion[4] in assigning a value of 2·20 for the electronegativity of hydrogen. The values assigned in Table I are more in agreement with the values of electronegativities assigned by Pauling and by Huggins.

TABLE I

Electronegativities

Group	Value
OH	3·53
NH_2	3·17
CF_3	3·10
CH_3	2·64
C_2H_5	2·71
n-C_3H_7	2·66
i-C_3H_7	2·60
n-C_4H_9	2·69
t-C_4H_9	2·68

The values for the alkyl groups do not vary in a significant way, we feel, and it would probably be suitable to use the average value, 2·65, for all members of the alkyl sequence. The values for the other groups agree well with published values obtained by other authors by various methods.

There are limitations to thermochemical estimation of group electronegativities, however, that should be considered. Most important of these is the bond order of the bonds involved in the electronegativity calculations. For instance, the carbon–carbon bond in cyanogen probably has considerable double-bond character which shows up in the covalent contribution term, and has the effect of reducing the electronegativity value for that group when calculated from thermochemical data. Similarly there may be considerable double-bond character in the central bond of biphenyl, for, using Szwarc's data,[5] an electronegativity value for the phenyl group is obtained which is unrealistically low.

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[5] M. Szwarc, *Nature*, 1948, **161**, 980.