## Bond Energies in Compounds of Nitrogen, Oxygen, and Fluorine

*Sir:*

It is well known that the N–N, O–O, and F–F bond energies in the molecules $N_2H_4$, $H_2O_2$, and $F_2$ are abnormally low. However, it does not appear to have been emphasized that these weak bonds are but three members of a family of weak single bonds of the type N–X, O–X, and F–X, where X is a very electronegative atom.[1] We describe here a method for comparing thermochemical bond energies which shows that bonds of this type are weak and that this weakness increases with increasing electronegativity of the atom X.

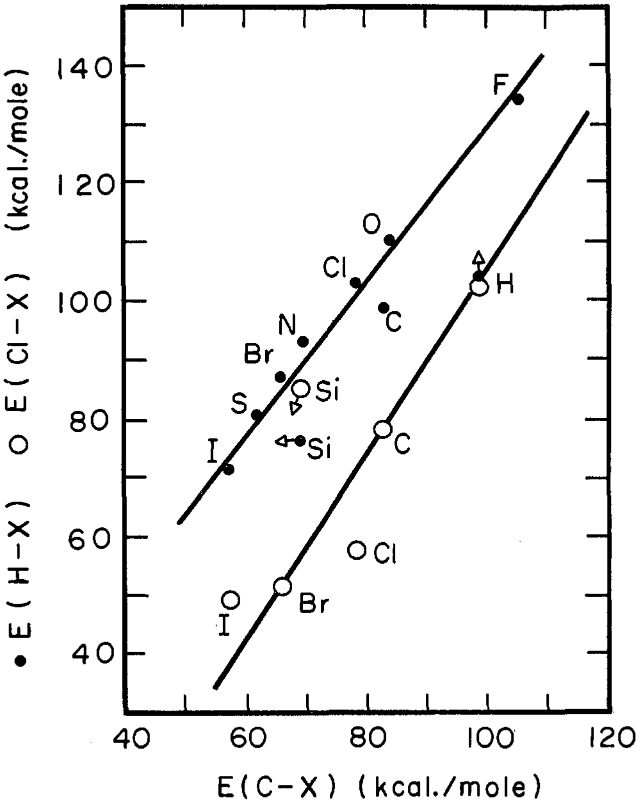

Fig. 1.—H–X and Cl–X bond energies *vs.* C–X bond energies.

If we exclude bonds between electronegative atoms and fluorine, oxygen, and nitrogen, it is usually found that, if $E$(L–A) > $E$(L–B), then $E$(M–A) > $E$(M–B). (Here $E$ refers to the bond energy[3]—a quantity not necessarily equal to the bond dissociation energy.) Consequently, a plot of L–X bond energies against the corresponding M–X bond energies yields a fairly smooth curve, in some cases a straight line. We show two plots of this type in Fig. 1, in which both H–X and Cl–X bond energies are plotted against C–X bond energies. We believe the points for X = Si fall off the curves because of the tendency for silicon to form double bonds to electronegative elements and because of hyperconjugation in the case of the Si–$CH_3$

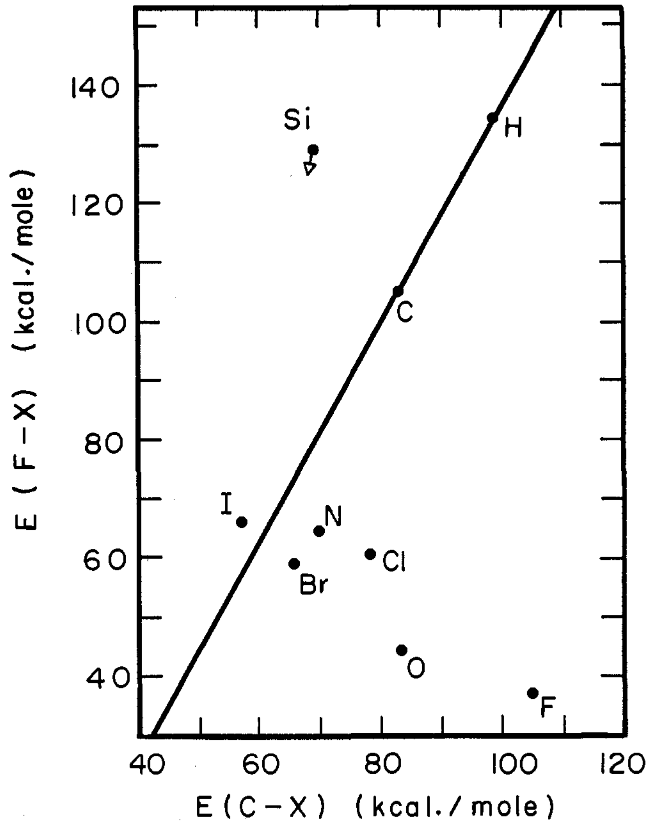

Fig. 2.—F–X bond energies *vs.* C–X bond energies.

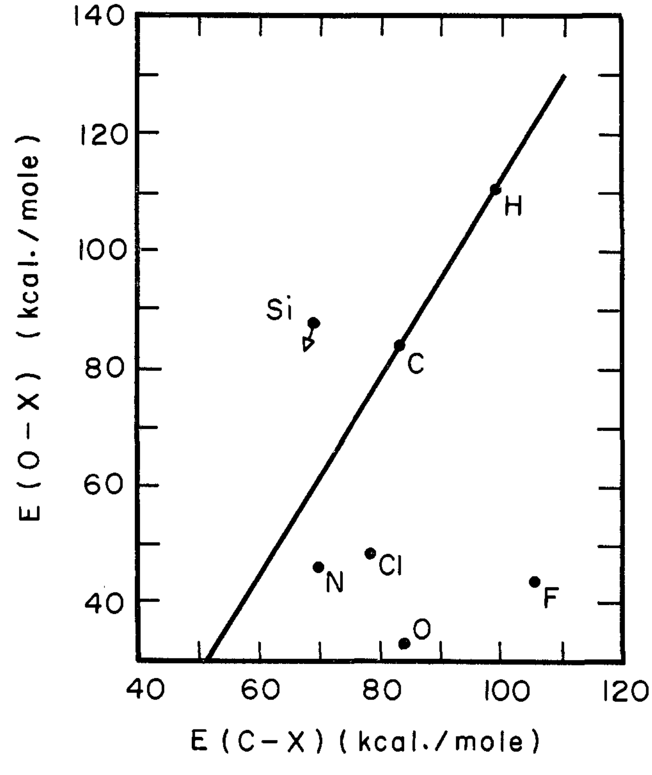

Fig. 3.—O–X bond energies *vs.* C–X bond energies.

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(1) Schomaker and Stevenson[2] have in effect shown that this is true by showing that the lengths of bonds of this type may be calculated by using abnormally long covalent radii for N, O, and F and by subtracting a term proportional to the difference in electronegativity of the bonded atoms.

(2) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

(3) For a table of bond energies and methods of calculation see L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 83–87.

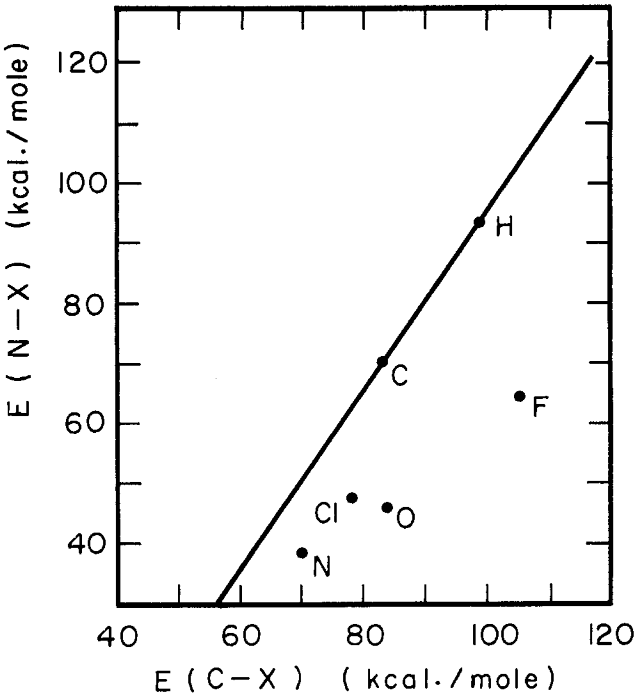

Fig. 4.—N–X bond energies *vs.* C–X bond energies.

bond. The H–H bond is weak because of poor overlap of the 1s-orbitals.[4]

When F–X, O–X, and N–X bond energies are plotted against C–X bond energies (Fig. 2–4), the points corresponding to very electronegative X atoms fall below the expected curve. In accordance with our contention that bond weakening increases with increasing electronegativity of the X atom, the points for X = F show the greatest discrepancies, the points for X = O show the next greatest discrepancies, and the points for X = Cl and N show relatively small discrepancies.

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(4) In molecular $H_2$ the 1s-orbitals of the atoms cannot overlap strongly because of the spherical symmetry of the orbitals and the proton–proton repulsion. However, when a hydrogen atom forms a bond to an atom which offers a highly directional bonding orbital (*e.g.*, $sp^3$), the hydrogen atom can "immerse itself" in the other atom's bonding orbital, and thus very strong orbital overlap can be achieved.

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## Boron Hydrides.[1] VII. The Metal Ion Catalyzed Hydrolysis of Sodium Borohydride in Heavy Water

*Sir:*

We wish to describe a hitherto unknown aspect of the hydrolysis of sodium borohydride. If the hydrolysis

$$BH_4^- + H_3O^+ + 2H_2O \longrightarrow H_3BO_3 + 4H_2 \qquad (1)$$

is performed in heavy water, analysis of the gas has been reported to vary greatly with the investigator[2,3] and a large solvent deuterium isotope effect was reported.[4]

We wish to report that the changes in isotopic composition are due to *metal ion catalyzed reactions* and that *micromolar* amounts of heavy metals will greatly change the composition of the gas. More important the reaction is an extremely useful technique to convert $D^+$ or $T^+$ in water into reductive $D^-$ or $T^-$ for isotopic synthesis, in some aspects almost as useful as the $D^+$ to $D^-$ and $T^+$ to $T^-$ exchange we reported previously.[1,5]

The data are presented in Table I for Co, Pd, and Pt. It is obvious that *micromolar* amounts of heavy metals can produce the strange results of ref. 2–4. One microgram of cobalt can reduce the amount of HD from 98 to 82%. The catalytic effect of the preformed cobalt catalyst finally levels off at 64% $D_2$. Platinum is the best catalyst both for hydrolysis[6] and the exchange. The last entry in the table demonstrates that even minute amounts of supported platinum can produce very high $D_2$ concentrations. The use of $D_2$ produced from this reaction or the hydrolysis–exchange of trimethylamine borane[1] in $D_2O$ has obvious and immediate synthetic utility to produce controlled amounts of $D_2$ gas for reductive deuterogenations. The controlled external generation of $D_2$ gas extends

$$NaBH_4 \xrightarrow[\text{excess } D_2O]{\substack{Pt/C \\ Na_2CO_3}} 4 \text{ moles of } D_2\uparrow \qquad (2)$$

the synthetic utility of the borohydride hydrogenator.[5,6]

The mechanism of the exchange is not clear. In other experiments the hydrolysis in deuterium oxide was allowed to proceed from 10 to 80% (as measured by the gas evolution) and the catalyst removed by ultrafiltration. The borohydride remaining was pure $BH_4^-$ (D less than 2%) as determined by reduction of benzophenone to produce pure benzhydrol, $(C_6H_5)_2CHOH$, which was analyzed for deuterium content.

Likewise the gas once formed does not exchange with the solvent in the presence of the catalyst and borohydride (see footnote of Table I). Experiments are in progress to modify the catalysis so that sodium borodeuteride could possibly be produced by a very convenient exchange technique.

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(1) Paper VI: R. E. Davis, A. E. Brown, R. Hopmann, and C. L. Kibby, *J. Am. Chem. Soc.*, **85**, 487 (1963).

(2) T. Freund, *J. Inorg. Nucl. Chem.*, **9**, 246 (1959). See the footnote on p. 249.

(3) W. L. Jolly and R. Mesmer, *J. Am. Chem. Soc.*, **83**, 4470 (1961). $NaBD_4$ in water gave 95.62% HD, 3.10% $H_2$, and 1.28% $D_2$. Hydrolysis of $NaBH_4$ in $D_2O$ at pD of 7 gave 83.30% HD, 7.94% $H_2$, and 17.78% $D_2$ during the last 40% of reaction.

(4) In an earlier paper we reported the solvent isotope effect of reaction 1 by two techniques to be 4.9 and 3.0 [*J. Am. Chem. Soc.*, **84**, 885 (1962)]. These high results have been traced to metal ion catalysis. Measurement of the solvent isotope effect in $D_2O$–$H_2O$ mixtures places $k_{H_3O^+}/k_{D_3O^+}$ at 1.3 using mass spectral analysis. This value agrees better with the value of 1.56 reported by Mesmer and Jolly [*Inorg. Chem.*, **1**, 608 (1962)] and is in the range to be expected for the solvent isotope effect of a general acid catalyzed reaction. It was our two original high values, reported without comment, that started the investigations reported in the present paper.

(5) Cyclohexene can be converted to 1,2-dideuteriocyclohexane using the easily controlled external generation of $D_2$ from $NaBH_4$–Pt/C–$D_2O$ using the techniques of Brown [*J. Am. Chem. Soc.*, **84**, 1493, 1494, 1495 (1962)].

(6) H. C. Brown and C. A. Brown, *ibid.*, **84**, 1493 (1962).