CNH_3^{2+},[12a,d] but it also seems to constitute a general stabilization principle for many other dications.[12b,c]

The dication $\mathbf{1}^{2+}$ exists also in a well. Both charge separation to generate H^+ and $HBNH_2^+$ as well as isomerization to $\mathbf{2}^{2+}$ would require an activation energy of 17.5 kcal/mol. But nevertheless, $\mathbf{1}^{2+}$ cannot be generated by vertical electron removal from $\mathbf{1}^{\bullet+}$. According to the ab initio calculations, vertical ionization of $\mathbf{1}^{\bullet+}$ leads to a species located 22.7 kcal/mol *above* the dissociation/isomerization transition states of $NH_2BH_2^{2+}$. In contrast, vertical removal of an electron from $NH_3BH^{\bullet+}$ ($\mathbf{2}^{\bullet+}$) generates a dication with an energy of 29.7 kcal/mol above the ground state H_2NBH^{2+} but still well *below* the transition state energies for further reactions of NH_3BH^{2+}. This is further evidence that electron impact ionization of **1** leads to the ground state of $\mathbf{1}^{\bullet+}$ *and* (presumably via the first excited state of $\mathbf{1}^{\bullet+}$) to excited $\mathbf{2}^{\bullet+}$; the latter, upon charge stripping, serves as actual precursor to generate the new donor–acceptor complex H_3NBH^{2+} ($\mathbf{2}^{2+}$). This interpretation is substantiated by a comparison of the Q_{min} value (15.2 eV) with the theoretically predicted ionization energy (15.8 eV), as the difference of 0.6 eV is in excellent agreement with the 0.7 eV calculated for the energy difference between the ground and first excited state of $\mathbf{1}^{\bullet+}$.[3b]

Acknowledgment. The financial support of our work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Fonds National Suisse pour la Recherche Scientifique is gratefully acknowledged. We are indebted to the Computer Centre of TU Berlin for providing computer time.

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Fractional Bonds: Relations among Their Lengths, Strengths, and Stretching Force Constants

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Received June 25, 1986

Abstract: A simple modification of the Morse equation is shown to yield several relationships among bond lengths, energies, and stretching force constants that have been established empirically over the years. The adjustable parameters can be assigned to yield reasonable agreement with experimental observations. The Morse equation can also be adapted to deal with the energy variation along reaction paths involving changes in more than one bond length. The relationships derived provide a rationale for the strong dependence of reaction rate on small changes in ground-state structure that has been observed for several systems.

The study of chemical bonds in terms of dissociation energies D, equilibrium interatomic distances r_e, and stretching force constants k has led over the years to a number of empirical relationships involving the notion of fractional bonds. Thus the Pauling bond order (or fractional bond number)[1] n is defined in terms of the difference between an interatomic distance r, a standard "single bond" distance r_0, and an empirical constant c

$$r = r_o - c \ln n \qquad (1)$$

In the remarkably successful bond-energy–bond-order (BEBO) method developed by Johnston and Parr[2] expressions of the type

$$D(n) = D_0 n^p \qquad (2)$$

are used where p is a number close to unity (0.8–1.1 for various types of bond). Stretching force constants for a wide variety of diatomics, including covalent, polar, and van der Waals molecules, have been found[3] to correlate with bond distance according to

$$r = a - b \ln k \qquad (3)$$

We point out here that these three relationships may all be derived in a simple and intuitive way by what we have called the CNPE method.[4]

The Modified Morse Equation. The Morse equation

$$V(r - r_0) = D_0\{1 - \exp[-B(r - r_0)]\}^2\} - D_0 = D_0\{\exp[-2B(r - r_0)] - 2 \exp[-B(r - r_0)]\} \qquad (4)$$

is known to provide a good approximation to the potential energy of many classes of chemical bonds. For fractional bonds we merely multiply the attractive term by the bond number[5] or, more generally, by some power of it,[6] leaving the repulsive terms unaltered, to obtain

$$V(r - r_0) = D_0\{\exp[-2B(r - r_0)] - 2n^q \exp[-B(r - r_0)]\} \qquad (5)$$

With the modified Morse eq 5 the quantities describing the properties of fractional bonds become

$$r_e(n) = r_0 - qB^{-1} \ln n \qquad (6)$$

$$D(n) = D_0 n^{2q} \qquad (7)$$

$$k(n) = 2B^2 D_0 n^{2q} \qquad (8)$$

Equation 6 is evidently the same as the Pauling eq 1 with $qB^{-1} = c$; eq 7 has the same form as the empirical relationship (2). Moreover, combining (6) and (8) leads to

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[1] Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542.

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[4] Complete Neglect of Practically Everything. We modestly disclaim any priority for the invention or development of this method, the origins of which seem to be shrouded in obscurity.

[5] Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, New York, 1979; p 347.

[6] We could also multiply the repulsive term by some factor, leaving the attractive term unaltered, or we could multiply both attractive and repulsive terms by different factors, to obtain slightly different equations. However, in the spirit of the CNPE method,[4] it is only the general idea that matters.

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$$r_e(n) = r_0 + (\ln 2B^2D_0)/2B - [\ln k(n)]/2B \qquad (9)$$

which has the same form as eq 3. Another useful relationship we can derive from the modified Morse equation is

$$\mathrm{d}D(r_e)/\mathrm{d}r_e = -2BD_0n^{2q} \qquad (10a)$$

$$= -k(n)/B \qquad (10b)$$

The adjustable parameters in the modified Morse eq 5 can be chosen to reproduce quite a large range of experimental data, at least as far as order of magnitude agreement is concerned. With p (eq 2) ~ 1 ($q \sim 0.5$), $B \sim 2$ Å^{-1}, as found for many diatomic molecules, we obtain $k(n) \sim 8D_0n$. For C–C single bonds, $D_0 \sim 83$ kcal mol^{-1}, leading to $D(2) \sim 165$ kcal mol^{-1}, $D(3) \sim 250$ kcal mol^{-1}, $k(1) \sim 4.6$ mdyn Å^{-1}, $k(2) \sim 9.2$ mdyn Å^{-1}, $k(3) \sim 13.8$ mdyn Å^{-1}, all of the same order of magnitude as tabulated values.[7] With the same B and D_0 eq 9 yields $r_e(n) = 1.92–0.575 \log k(n)$ (r in Å, k in mdyn Å^{-1}, 1 mdyn Å = 144 kcal mol^{-1}), which compares well with Johnston's result[2b] for bonds between first-row atoms, $r_e(n) = 1.85 - 0.55 \log k(n)$.[8] Also, for $B = 2$ Å^{-1}, $q = 0.50$, the constant in Pauling's equation becomes 0.25 Å^{-1}, to be compared with values of 0.31 Å^{-1} for C–C bonds with $1 \leq n \leq 3$ and 0.26 Å^{-1} for fractional bonds with $n < 1$.[1] Thus, as far as orders of magnitude are concerned, eq 6–9 give a rather good account of themselves.

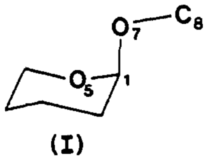
Applications

These equations are also useful for discussing chemical reaction paths derived for quite complex molecules from crystallographic data[10] together with other evidence. In this approach, the observed equilibrium structure of a given molecular fragment is to be regarded as a distortion of some standard structure with known or assumed bond distances. A change in one bond distance is usually coupled with changes in others. To estimate the energy required for a small displacement along the reaction coordinate we have to take into account the distance changes Δr_i for all bonds affected. In the harmonic approximation we thus need $2V = \sum k_i(\Delta r_i)^2$, and for a rough estimate we assume that each Δr_i is a linear function of some progress coordinate, arbitrarily chosen as Δr_1. Hence $2V = k_1(\Delta r_1)^2\sum(k_i/k_1)a_i^2 = k_1(A\Delta r_1)^2$. Adapting eq 4 to yield this expression for small Δr_1, we obtain

$$V(\Delta r_1) = D_0\{\exp[-2B'(\Delta r_1)]-2\exp[-B'(\Delta r_1)]\} \qquad (4')$$

with $B' = AB$. Since $A \geq 1$, B' will always be greater than B, but all equations involving B retain the same form in the primed versions.

By combining crystallographic and kinetic data for acetals and related molecules Kirby and Jones[11] have found a linear relationship between the extension of a C–O bond (relative to some standard bond length) in the ground state and the free energy of activation for heterolytic fission of the bond. For aryl tetrahydropyranyl acetals (I) and phosphate monoester anions



(I)

($\mathrm{ROPO_3}^{2-}$) the slope $\partial\Delta G^\ddagger/\partial r$ was about 250 kcal mol^{-1} Å^{-1}. A similar study[12] of the hydrolysis of $[\mathrm{Ni(en)}_n(\mathrm{H_2O})_{6-2n}]^{2+}$ and $[\mathrm{Ni(tach)}_m(\mathrm{H_2O})_{6-3m}]^{2+}$ complexes (en = ethylenediamine, n = 0, 1, 2, 3; tach = *cis,cis*-1,3,5-triaminocyclohexane, m = 0, 1. 2) leads to analogous linear relationships, $\partial\Delta G^\ddagger/\partial r \sim 60$ kcal mol^{-1} Å^{-1} for the rate-determining Ni–N bond rupture and $\partial\Delta G^\ddagger/\partial r \sim 40–50$ kcal mol^{-1} Å^{-1} for the water-exchange reaction. For these reactions it would appear that differences in the transition state are unimportant compared with differences in ground-state structure.

Jones and Kirby[11] concluded from their aryl tetrahydropyranyl results that "there must be a linear region of considerable extent in the reaction coordinate", but when they tried to fit their data to an unmodified Morse function they obtained a B value of about 14 Å^{-1}, several times larger than can be expected. From the primed version of eq 10 the slope should be $-2B'D_0$ for bonds with n close to unity. The structural data[13] indicate that extension of the fissionable $\mathrm{C_1–O_7}$ bond by $\sim$0.065 Å is accompanied by contraction of the $\mathrm{C_1–O_5}$ bond by $\sim$0.045 Å and of the $\mathrm{O_7–C_8}$ bond by $\sim$0.085 Å, leading to $A \sim 1.8$. With $B \sim 2$ Å^{-1}, $B' \sim 3.6$ Å^{-1}, and with Jones and Kirby's value of 39 kcal mol^{-1} for D_0(C–O),[11] the slope $2B'D_0$ is now estimated to be 280 kcal mol^{-1}, in good agreement with the observed value.

A similar interpretation applies to the data on the Ni complexes. Here D_0(Ni–N) $\sim$ 15 kcal mol^{-1} and D_0(Ni–O) $\sim$ 10 kcal mol^{-1}. Since rupture of a Ni–N or Ni–O bond is probably accompanied mainly by bond–angle adjustments and k (angle) $\ll$ k (bond), then $A \sim 1$; with $B \sim 2$ Å^{-1}, as before, we obtain from eq 10 k(Ni–N) $\sim$ 0.8 mdyn Å^{-1} and k (Ni–O) $\sim$ 0.6–0.7 mdyn Å^{-1}, within 20% of reported values.[14]

Other types of interatomic potential functions may be modified in a similar way. For example, the general inverse power potential may be modified to

$$V(r) = [D_0/(l - m)][m(r_0/r)^l - s^q l(r_0/r)^m] \qquad l > m \quad (11a)$$

or

$$V(r) = [D_0/(l - m)][s^{-q}m(r_0/r)^l - l(r_0/r)^m] \qquad (11b)$$

leading to a new equilibrium distance $r_e(s)$ such that $(r_e/r_0)^{m-1} = s^q$. Although these equations are symmetrical in m and l for $s = 1$, they are not for $s \neq 1$. The modified equations define bond valences s that are similar to Pauling's bond numbers n and have been much used in correlating experimental observations.[15] Relationships analogous to eq 7–10 can easily be derived from eq 11A or 11B. For (11B) the relationships are

$$V(s) = -D[r_0/r_e(s)]^m \qquad (12)$$

$$\mathrm{d}V(s)/\mathrm{d}r_e(s) = (mD_0/r_0)[r_0/r_e(s)]^{m+1} \qquad (13)$$

$$k(s) = [mlD_0/(r_0)^2][(r_0/r_e(s)]^{m+2} \qquad (14)$$

and for (11A) they have exactly the same form but with m and l interchanged. With r_0 = 1.54 Å, D_0 = 83 kcal mol^{-1}, $m \sim 3.6$, $l \sim 5.1$, and $g \sim 0.33$, the bond lengths, bond energies, and force constants of C–C bonds with s = 1, 2, 3 and reproduced reasonably well by these equations.[16]

Discussion

We do not imagine that this interpretation of bond numbers is the last word to be said on the subject, but it seems to provide

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[7] Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, Toronto and London, 1955; p 175.

[8] We would not have obtained quite such good agreement for N–N bonds with n = 1, 2, 3. The bond energy of the N–N single bond is anomalously low and is evidently not suitable to serve as a "standard" value; similarly for the O–O single bond. Explanations abound. These bonds also show anomalously low "bonding" electron densities compared with C–C bonds.[9]

[9] Dunitz, J. D.; Seiler, P. *J. Am. Chem. Soc.* **1983**, *105*, 7056.

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[14] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3nd ed.; Wiley: New York, 1978.

[15] For a review, see: Brown, I. D. In *Structure and Bonding in Crystals*; O'Keeffe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. 2, p 1.

[16] Note that in this example, the version with the repulsive term modified (eq 11B) seems to be more appropriate (see footnote 6).

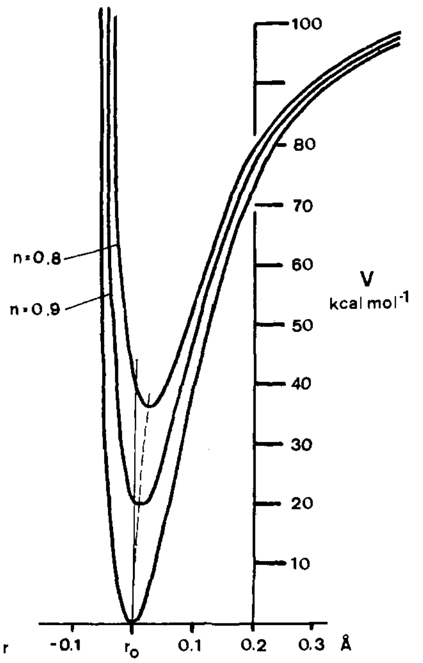

Figure 1. The modified Morse function $V(r - r_0) = D_0\{\exp[-2B(r - r_0)] - 2n^q \exp[-B(r - r_0)]\}$ (eq 5) with D_0 = 100 kcal mol^{-1}, B = 2 Å^{-1}, q = 1, n = 1 (outer curve), 0.9, 0.8. Note the sharp decrease in dissociation energy as the equilibrium distance increases (compare eq 10).

a unifying thread connecting changes in bond energy, bond distance, and stretching force constants.

The connection between bond distance and energy (eq 10) is particularly interesting and important, because it provides a rationale for the astonishingly sharp sensitivity of activation energy of bond-breaking processes to quite small changes in ground-state geometry[11,12] (Figure 1). With $\partial\Delta G^{\ddagger}/\partial r$ values of the order of 200–300 kcal mol^{-1} Å^{-1}, bond length differences of a few hundredths of an Å between corresponding bonds in related structures should have a profound influence on the rates of corresponding bond-breaking reactions.[17] This connection underlines the need for accurate bond length measurements in structural studies bearing on questions of chemical reactivity.[19] Since careful X-ray diffraction studies, especially at low temperatures, are perfectly capable of determining interatomic distances with a precision of the order of 0.001–0.002 Å, interesting results can be expected in this direction.

Another problem of interest is the dependence of ground-state structure on bond environment factors such as hydrogen bonding, donor–acceptor interactions, stereoelectronic effects, etc. and the consequences for reactions involving bond breaking. In particular, we envisage that binding of a substrate to the active site of an enzyme may be accompanied by small structural changes that could have dramatic effects on reaction rate.

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(17) Of course, the identification of $\partial\Delta G^{\ddagger}/\partial r$ with $\partial D(r_e)/\partial r_e$ is valid only insofar as $\partial\Delta S^{\ddagger}/\partial r$ is small. In the few cases where $\partial\Delta H^{\ddagger}/\partial r$ and $\partial\Delta G^{\ddagger}/\partial r$ values are available they are indeed not very different.[12,18]

(18) Müller, E.; Bürgi, H. B. *Helv. Chim. Acta*, in press.

(19) For example, the retardation of the rate of aquation of $[Cr(NH_2Me)_5Cl]^{2+}$ as compared with $[Cr(NH_3)_5Cl]2^+$ can be explained[20] in terms of the shorter Cr–Cl bond length found for the former, 2.299 (1) vs. 2.327 (1) Å for the latter. This interpretation runs counter to previous arguments that ascribed the difference in rate constant to a difference in reaction mechanism.

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On the Nature of the Low-Lying Electronic Levels of a Tetranuclear Copper(II) Complex

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Abstract: The magnetic susceptibility and the EPR spectra of tetrakis[aqua(3-(pyridin-2-yl)-5-(pyrazin-2-yl)-1,2,4-triazolato)copper(II)] tetranitrate dodecahydrate (I) were recorded in the temperature range 4.2–300 K. The magnetic data show that the four copper(II) ions are antiferromagnetically coupled. The temperature dependence of the magnetic susceptibility was fit with J' = 12.2 cm^{-1} (spin Hamiltonian in the form $\mathcal{H} = J'S_1 \cdot S_2$). The room-temperature EPR spectra are satisfactorily analyzed as due to an S = 2 species, with $g_{\parallel}$ = 2.03, $g_{\perp}$ = 2.16, and $|D|$ = 0.0379 cm^{-1}, while the spectra obtained at 4.2 K are typical of a triplet with $g_{\parallel}$ = 2.03, $g_{\perp}$ = 2.16, and $|D|$ = 0.0906 cm^{-1}. The spin-Hamiltonian parameters are interpreted within a model which relates them to the corresponding parameters of the individual ions and to the exchange and dipolar contributions.

The exchange interactions between paramagnetic centers have been actively investigated in the last few years.[2] As a conclusion of this research we can say that much is now understood of the details of the interaction in pairs, where the role of both the ground[3-11] and the excited[12-15] magnetic orbitals has been fully clarified, providing a set of rules which extends the original Goodenough–Kanamori rules[16,17] and allowing the rationalization

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(1) (a) I.S.S.E.C.C., C.N.R. (b) University of Florence. (c) State University Leiden.

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(5) Kahn, O. In ref 2, p 37.

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(7) Willett, R. D. In ref 2, p 389.

(8) Hodgson, D. J. In ref 2, p 497.

(9) Hendrickson, D. N. In ref 2, p 523.

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