the high acidity effect may be related to deprotonation of the O-nitrosation product $^+H_3NONO$, essential to its rearrangement to form ONNHOH.

We must remark that we have observed production of N_2O at much higher pH than has been previously reported, i.e. at pH 7, 8, and 9. According to current views, N_2O_3 appears to be the nitrosation agent of choice in NO_2^- solutions of low acidity,[16] but from recently reported thermodynamic information we calculate that the concentration of this species would lie in the extremely low range 10^{-8}–10^{-10} M in these experiments.[17] The isotopic composition of the N_2O produced at high pH clearly establishes the NH_2OH–HNO_2 interaction to be its origin and indicates that contributions from NH_2OH disproportionation are negligible, even though the N_2O product of the latter reaction has been observed at pH as low as 6.[18]

Acknowledgment. We are grateful to Dr. M. J. Akhtar for assistance with the mass spectrometry and to Drs. M. N. Hughes and G. Stedman for helpful discussions.

Registry No. HNO_2, 7782-77-6; $HONH_2$, 7803-49-8.

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Relative Energies of Deltahedral Clusters: Comments on the Use of the Bireciprocal Length–Energy Relationship $U = d^{-2} - d^{-1}$

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Received September 16, 1982

Fuller and Kepert[1] recently outlined an interesting new approach to the structures and rearrangements of *closo*-boranes $B_nH_n^{2-}$, in which each boron atom is considered to bond directly to all other boron atoms. They used a bireciprocal relationship, $U = d^{-x} - d^{-y}$, to link energy U to internuclear distance d and showed that the known structures of the anions $B_8H_8^{2-}$ and $B_9H_9^{2-}$ corresponded to potential energy minima when $x = 2$ and $y = 1$, though the precise values of x and y did not appear to be critical—a good fit for $B_8H_8^{2-}$ could also be obtained for $x = 1.5$ and $y = 1.25$. They computed the relative energies of various alternative possible polyhedral structures for these anions and showed them to exceed the energies of the known structures. They also showed that the relative energies of various alternative structures for the anion $B_{12}H_{12}^{2-}$ exceeded that of icosahedral $B_{12}H_{12}^{2-}$.

Their results show that their type of approach may have considerable value for exploring the relative energies of different hypothetical structures for specific compounds and for considering the energetics of rearrangements. However, some features that appear to have been overlooked make their approach inappropriate for some of the other applications advocated. We feel it may be helpful to users of the bireciprocal approach to draw attention to these features, which may be summarized as follows:

(1) The potential energies of *closo*-borane anions $B_nH_n^{2-}$ calculated by the approach, if used uncritically, can give a quite misleading impression of the way that the total skeletal bond energy of these anions varies with n.

Table I. Skeletal Energies (ΣU) of *closo*-Borane Anions $B_nH_n^{2-}$ Calculated from Measured Interatomic Distances (d) by Using the Fuller–Kepert Equation[1] $U = d^{-2} - d^{-1}$

	$-\Sigma U^a$	$(2n + 2)/n^b$	$-[\Sigma U]/n^c$	$-[\Sigma U]/(n + 1)^d$	$\% \Sigma U_{int}/\Sigma U^e$
$B_6H_6^{2-}$	3.6930	2.33	0.6155	0.5276	19.0
$B_8H_8^{2-}$	6.7530	2.25	0.8440	0.7503	34.7
$B_9H_9^{2-}$	8.6217	2.22	0.9580	0.8622	40.3
$B_{10}H_{10}^{2-}$	10.7650	2.20	1.0765	0.9786	45.4
$B_{12}H_{12}^{2-}$	15.4950	2.17	1.2910	1.1919	53.4

[a] Total skeletal energy, i.e., the sum of the $n(n - 1)/2$ pairwise interactions for which $U = d^{-2} - d^{-1}$. [b] Average number of skeletal electrons per boron atom. [c] Average skeletal energy per boron atom. [d] Average skeletal energy per skeletal electron pair. [e] Percentage of the total skeletal energy that arises from the internal (cross-polyhedron) pairwise interactions.

Table II. Interatomic Distances That Correspond to Potential Energy Minima for the *closo*-Borane Anions $B_nH_n^{2-}$ from the Fuller–Kepert Equation[1] $U = d^{-2} - d^{-1}$

	d_{calcd}/Å	d_{obsd}/Å	ref
$B_6H_6^{2-}$	1.91	1.69	2
$B_8H_8^{2-}$	*a*	1.58, 1.72, 1.76, 1.93	3, 4
$B_9H_9^{2-}$	*a*	1.69, 1.85, 1.93	5
$B_{10}H_{10}^{2-}$	1.69, 1.74, 1.90	1.68, 1.80, 1.82	6, 7
$B_{12}H_{12}^{2-}$	1.67	1.78	8

[a] The observed interatomic distances for $B_8H_8^{2-}$ and $B_9H_9^{2-}$ were used for calibration of the Fuller–Kepert equation.

(2) If used to estimate interatomic distances in borane anions $B_nH_n^{2-}$ other than those ($B_8H_8^{2-}$, $B_9H_9^{2-}$) used as reference systems, it seriously *over*estimates the bond lengths of smaller borane anions and *under*estimates the bond lengths of larger borane anions.

(3) In apportioning energy between the surface (polyhedron edge) and internal (cross-polyhedron) bonding of anions $B_nH_n^{2-}$, it progressively overestimates the significance of the latter as n increases.

(4) It overestimates the total energy of the bonding interactions of the more highly coordinated boron atoms in clusters (e.g., $B_8H_8^{2-}$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$) containing more than one type of boron atom, apparently indicating that these boron atoms are located at centers of higher electron density than the less highly coordinated boron atoms.

These points are illustrated by the data in Tables I–IV. Tables I and II list the energies and interatomic distances computed for the borane anions $B_nH_n^{2-}$ (n = 6, 8, 9, 10, and 12) by using the Fuller–Kepert equation, together with the interatomic distances determined by X-ray crystallographic studies.[2-8] In these anions, the n boron atoms are held together by $(n + 1)$ skeletal electron pairs. The number of electrons available per boron atom, $(2n + 2)/n$, accordingly decreases as n increases, ranging from a value of 2.33 for $B_6H_6^{2-}$ to 2.17 for $B_{12}H_{12}^{2-}$ (Table I). Various studies[9-15] have shown that

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Table III. Number of Two-Center Interactions between the Vertices of *n*-Vertex Deltahedra

no. of polyhedron vertices	n	4	5	6	7	8	9	10	11	12
no. of two-center interactions	$n(n-1)/2$	6	10	15	21	28	36	45	55	66
no. of polyhedron edges	$3(n-2)$	6	9	12	15	18	21	24	27	30
no. of internal interactions	$(n-3)(n-4)/2$	0	1	3	6	10	15	21	28	36

Table IV. Energies of Skeletal Atoms Calculated by Using the Relationship $U = d^{-2} - d^{-1}$ [a]

	$-U(B_4)$	$-U(B_5)$	$-U(B_{av})$
$B_6H_6^{2-}$	0.6155		0.6155
$B_8H_8^{2-}$	0.7114	0.9720	0.8420
$B_9H_9^{2-}$	0.9357	0.9679	0.9578
$B_{10}H_{10}^{2-}$	1.0498	1.0832	1.0765
$B_{12}H_{12}^{2-}$		1.2913	1.2913

[a] Atoms classified according to their skeletal coordination numbers (shown in subscript).

the bonding power of these electrons probably increases, though not systematically, from $B_6H_6^{2-}$ to $B_{12}H_{12}^{2-}$, probably enough to compensate for the slight decrease in electron density as n increases. However, the figures in Table I, whether expressed as the skeletal energy per boron atom, $[\sum U]/n$, or as the skeletal energy per skeletal electron pair, $[\sum U]/(n+1)$, suggest a totally unrealistic twofold increase from $B_6H_6^{2-}$ to $B_{12}H_{12}^{2-}$. Moreover, the data correspond effectively to linear relationships between $[\sum U]/(n+1)$ and n:

$$[\Sigma U]/n = 0.133n - 0.060$$

(correlation coefficient 0.99985)

$$[\Sigma U]/(n+1) = 0.111n - 0.137$$

(correlation coefficient 0.9991)

In both respects—the magnitude of the increase in $\sum U$ from $B_6H_6^{2-}$ to $B_{12}H_{12}^{2-}$ and the implication that all these closo anions $B_nH_n^{2-}$ use their skeletal electron pairs with precisely the same efficiency—the Fuller–Kepert approach is at variance with experimental[9,12] and other theoretical[10,11,13-15] studies on these systems, by predicting the stability sequence $B_6H_6^{2-} \ll B_8H_8^{2-} < B_9H_9^{2-} < B_{10}H_{10}^{2-} \ll B_{12}H_{12}^{2-}$. Other studies suggest that the species $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$ differ but slightly in the efficiency with which they use their skeletal electron pairs, though they do so more effectively than $B_8H_8^{2-}$ and $B_9H_9^{2-}$.[9,12]

The failure of the Fuller–Kepert approach to afford accurate interatomic distances for *closo*-borane anions $B_nH_n^{2-}$ other than those ($B_8H_8^{2-}$ and $B_9H_9^{2-}$) used for calibration purposes is illustrated by the interatomic distances d given in Table II. For example, for the octahedral anion $B_6H_6^{2-}$, the approach predicts an energy minimum at $d = 1.91$ Å, whereas an X-ray crystallographic study[2] on the tetramethylammonium salt afforded a value of $d = 1.69 \pm 0.01$ Å. For this borane, smaller than those used for calibration purposes, and with fewer cross-polyhedron bonding terms (see Table III—of the total of $n(n-1)/2$ two-center interactions in these n-vertex polyhedra, $(n-3)(n-4)/2$ are cross-polyhedra) the Fuller–Kepert approach thus seriously *over*estimates the polyhedron edge length. For the higher borane anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, by contrast, the approach *under*estimates the polyhedron edge lengths, as the data in Table II show. This change from over- to underestimation of the interatomic distances may arise in part from the failure of the approach to allow for the variation in electron density as the cluster size increases. A far greater source of error, however, is considered to be the emphasis placed on internal (cross-polyhedron) bonding interactions. The proportion of the total energy assigned to these is given in the final column of Table I. This shows the internal interactions to increase in significance with the size of the polyhedron, from 19% of the total energy in the case of $B_6H_6^{2-}$ to 53% in the case of $B_{12}H_{12}^{2-}$, as the number of these interactions (Table III) increases from 25% of the total number of pairwise interactions for $B_6H_6^{2-}$ to 54.5% of the total for $B_{12}H_{12}^{2-}$.

These figures show how closely the energy assigned to the cross-polyhedron interactions reflects their number. This is because the Fuller–Kepert equation $U = d^{-2} - d^{-1}$ corresponds to a minimum energy of -0.2500 F–K energy unit at $d = 2.0$ Å, with little variation in U as d varies over the range of interatomic distances found in *closo*-borane anions. Typical F–K energies for atom pairs at specific interatomic distances (Å, in parentheses) are as follows: −0.2422 (1.7); −0.2469 (1.8); −0.2493 (1.9); −0.2500 (2.0); −0.2400 (2.5); −0.2222 (3.0). Similar energies are thus assigned to cross-polyhedron as to polyhedron-edge interactions, even though these differ very markedly in length. For this reason, the total energies $\sum U$ assigned to these clusters are roughly proportional to the number of skeletal pairwise interactions, $n(n-1)/2$. The effectively linear relationship between $[\sum U]/n$ and n or $(n+1)$ noted above is therefore readily understood, since $\sum U$ itself varies with $n(n-1)$.

The Fuller–Kepert approach thus places great emphasis on the cross-polyhedron interactions, particularly those in the larger polyhedra. By contrast, MO treatments of these clusters[3-9,11-14,16,17] have shown that, of the $(n+1)$ skeletal bonding MO's, only one, of A symmetry, involves exclusive cross-cage bonding interactions between inwardly pointing AO's. The remaining n skeletal bonding MO's involve nearest-neighbor (polyhedral edge) bonding interactions of the AO's orientated tangential to the pseudospherical surface of the polyhedron (these AO's are actually orientated so as to concentrate electron density just *outside* the polyhedra, over the polyhedral edges and faces). Although some of these polyhedron surface orbitals are stabilized a little by contributions from suitable symmetry combinations of inwardly pointing orbitals, these contributions generate only very weak net cross-polyhedron bonding, as the relevant Mulliken overlap populations or bond indices indicate.[11]

A crude estimate of how evenly the skeletal electrons are distributed within the $B_nH_n^{2-}$ polyhedron can be made by using the Fuller–Kepert approach as follows. The strength of attachment of any one skeletal atom to the remainder is assessed by summing the $(n-1)$ pairwise interactions involving that atom and dividing by 2. A clear correlation emerges with the skeletal coordination number—the number of polyhedral edges radiating from the atom in question (Table IV). The more highly coordinated boron atoms in $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{10}H_{10}^{2-}$ are calculated to be held significantly more strongly than the less highly coordinated boron atoms, the disparity being such as to suggest that more bonding electrons are available to the former, a charge distribution opposite to that indicated by other approaches.[11-15]

To summarize: we suggest that these various features of the Fuller–Kepert approach, as applied to n-vertex closo clusters, make it unsuitable for certain of the applications advocated for it and indeed cast doubt on its value for assessing

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which polyhedron is likely to be the most stable for a particular value of n. The equation $U = d^{-2} - d^{-1}$, corresponding to a shallow potential energy minimum at $d = 2.0$ Å, in our opinion grossly overemphasizes the significance of the longer range interactions and is not directly transferable to smaller or larger polyhedra than those used for calibration purposes. A more satisfactory variation of the approach would, we suggest, be one that focused attention on the dominant bonding interactions, i.e. those between nearest neighbors, by use of a more realistic bond length–bond energy relationship, according much lesser significance to the internal cross-polyhedral interactions. Ideally, it would also make some allowance for the way the skeletal electron density of *closo*-borane-type clusters varies with the cluster size. We have elsewhere outlined an approach[15] by which the known structures of the borane anions $B_nH_n^{2-}$ (n = 6, 8, 9, 10, or 12) can be used as guides to the strength of their skeletal bonding and are extending this approach to allow its use for structural predictions.

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Kinetics and Mechanism of the Copper(II)-Catalyzed Oxidation of Lactic Acid with Chloramine T (CAT) in Alkaline Solutions

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Received April 20, 1982

N-Chloro-*p*-toluenesulfonamide, better known as chloramine T or CAT, has long been used as an analytical reagent. There are excellent reviews covering its oxidizing action, by Ozerassi,[1] Filler,[2] Mathur and Narang,[3] Mukherji,[4] and Campbell and Johnson.[5] There are a number of publications on the mechanistic aspects of the redox reactions in acidic media in which one of the species, RNHCl (R = $CH_3C_6H_4SO_2$), HOCl, or H_2OCl^+, has been considered reactive. A recent report[6] describes the oxidation of iodide studied by a fast-mixing technique. Osmium(VIII)-catalyzed oxidations[7-11] have received greater attention in alkaline medium with an operation of the Os(VIII)/Os(VI) cycle and/or complex formation of Os(VIII) with the reducing substance. Since copper(II) is known to form[12,13] copper(III) if oxidized and stabilized by suitable ligands in alkaline solutions, we thought the mechanistic study involving copper(II) as a catalyst in oxidations with CAT might enable us to know more of the chemistry of copper(III). α-hydroxy acids seemed to us a suitable family of reducing substances for the study, and a beginning was made with lactic acid (LA). There is one report[14] on copper(II) catalysis in the oxidation of arginine hydrochloride with CAT in alkaline solutions, and the catalysis has been ascribed to the complexation of Cu(II) and the reducing substance.

Table I. Variation of OH^- and Cu(II) in the Oxidation of Lactic Acid with CAT and the Values of k_0 ([LA] = 0.05 M, [CAT] = 4.0 × 10^{-3} M, I = 0.5 M, 45 °C)

10^5 × [Cu(II)]/M	$10^5k_0/s^{-1}$ 0.1 M [OH^-]	0.2 M [OH^-]	0.3 M [OH^-]	0.4 M [OH^-]	0.5 M [OH^-]
1.0	3.2	3.7	4.0	4.6	5.0
2.0					5.5
3.0	3.7	4.2	4.8	5.5	6.0
4.0					6.6
5.0	4.1	4.9	5.3	6.4	7.0
6.0					8.0
7.0	4.4	5.3	6.3	7.3	
9.0	4.5	5.7	6.9	8.4	
10.0		6.35	7.4	8.8	10.0

Table II. First-Order Rate Constants of the Cu(II)-Catalyzed Reaction between CAT and Lactic Acid in the Presence of PTS ([CAT] = 2.5 × 10^{-3} M, [LA] = 5.0 × 10^{-2} M, [OH^-] = 0.5 M, 45 °C)

10^3 × [PTS]/M	$10^5k_0/s^{-1}$ 1.0 × 10^{-5} M [Cu(II)]	3.0 × 10^{-5} M [Cu(II)]	5.0 × 10^{-5} M [Cu(II)]	7.0 × 10^{-5} M [Cu(II)]
1.0	3.2	4.4	5.4	
3.0		3.7	4.15	5.0
5.0	2.7	3.5	3.7	4.5
7.0	2.6	3.15	3.45	4.0
9.0	2.5	3.0	3.15	3.7

Experimental Section

Chloramine T of E. Merck quality was used as received, and its solution was prepared in doubly distilled water and stored in black-coated bottles to prevent its photochemical decomposition.[15] It was standardized iodometrically.[16] Solutions of lactic acid (Koch Light), sodium hydroxide (BDH AnalaR), and copper(II) sulfate (BDH AnalaR) were also prepared in doubly distilled water and standardized by the known methods. Other chemicals employed were either of BDH AnalaR or E. Merck quality. All glass vessels were of Corning make.

CAT and other constituents in required quantities were separately temperature equilibrated in a thermostat at 45 ± 0.1 °C unless mentioned otherwise. The reaction was initiated by adding a known volume of CAT to the other bottle. Aliquots of 5 or 10 mL were analyzed iodometrically after intervals of 10 or 15 min and acidification of the mixture. A blank for copper(II) was deducted from the volume of thiosulfate required for titration. The data were initially treated for initial rates[17] to make a plot of rate vs. [CAT] and to know the order in this respect. This was unity, and hence subsequently pseudo-first-order plots were made in all cases by plotting log [CAT] vs. time. The duplicate measurements were reproducible to ±10%. In most cases the extent of the reaction studied was 50–60%.

Spectrophotometric measurements were made on a Toshniwal spectrophotometer with a 1-cm cell to characterize the various species existing in the system and to detect the complex formation between copper(II) and CAT, copper(II) and lactic acid, and copper(II) and *p*-toluenesulfonamide, which is one of the products.

Results

Stoichiometry and Products. Reaction mixtures containing excess CAT along with 0.5 M NaOH and 5 × 10^{-5} M Cu(II) were left for more than 100 h at 80 °C for the completion of the reaction. One mole of lactic acid required 1.0 ± 0.1 mol of CAT for its oxidation to pyruvic acid, identified by sub-

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