3.4 kcal, with **11** having the larger barrier. The earlier calculation predicted zero difference;[3b] our calculations predict **11** to have the larger barrier by 2.2 kcal. Similarly, the barriers of **12** and **13** differ experimentally by 1.3 kcal, with **12** having the larger barrier. The modified CF_3 parameters predict **12** to have the larger barrier, also with a difference of 2.2 kcal. Compounds **8** and **14** provide a similar pair, but our prediction of a difference of 2.2 kcal, with the larger barrier associated with **14**, disagrees with the experimental result that the barrier of **8** is the larger of the two by 0.8 kcal. While the predictions seem in many cases to be rather good, there are sufficient disagreements with experiment to indicate that the approach must be used cautiously.[3] The barrier results are actually not strongly dependent on the values chosen for the parameters whereas the ground-state predictions are. A set of calculations in which CF_3 was assigned an element effect equal to that of Cl gave reasonable barrier values also, although in this case there was a tendency to substantially underestimate the barriers in cases where the molecules contained several CF_3 groups. In this case also, the ground-state predictions for the fluorides are of course in agreement with experiment but, because of the equality of CF_3 and Cl effects, the ground states for chlorides were indeterminate. In view of the uncertainty surrounding the ground states of chlorophosphoranes, this state of affairs may be appropriate. It would seem that some effort to revise the parameters in order to lift the gross dependency on electronegativity might be useful particularly in the development of more reliable prediction of the correct ground states, but we suspect that the "correct" CF_3 parameters would not on the whole give a better set of barrier values than either the simple equation of CF_3 to F or the electronegativity-interpolated values given herein.

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Registry No. $F_4PN(CH_3)_2$, 51922-00-0; $F_4PN(H)CH_3$, 33099-40-0; $F_4PN(CH_3)CH_2C_6H_5$, 84926-50-1; $F(CF_3)_3PN(CH_3)_2$, 51874-41-0; $F(CF_3)_3PN(H)CH_3$, 84895-93-2; $F(CF_3)_3PN(CH_3)CH_2C_6H_5$, 84895-94-3; $Cl(CF_3)_3PN(CH_3)_2$, 51874-40-9; $CH_3(CF_3)_3PN(H)CH_3$, 84926-51-2; $(CF_3)_3P[N(CH_3)_2]_2$, 51874-38-5; $F(CH_3)(CF_3)_2PN(CH_3)_2$, 51888-43-8; $F(CH_3)(CF_3)_2PN(H)CH_3$, 84926-52-3; $F_3(CF_3)PN(CH_3)_2$, 84926-53-4; $(DF_3)_3PF_2$, 79549-41-0; $CH_3(CH_2C_6H_5)NH$, 103-67-3; PF_5, 7647-19-0; $CH_3(CF_3)_2PF_2$, 51874-46-5; $(CH_3)_3SiN(H)CH_3$, 16513-17-0; $CH_3(CF_3)_3PF$, 56396-13-5; CF_3PF_4, 79549-39-6; $(CH_3)_3SiN(CH_3)_2$, 7083-91-2; CH_3NH_2, 74-89-5; $PF_5{\cdot}NH(CH_3)CH_2C_6H_5$, 84895-95-4.

Supplementary Material Available: A matrix for $(CF_3)_3P$ systems with two axial and one equatorial CF_3 groups (1 page). Ordering information is given on any current masthead page.

Notes

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Symmetry of the Intermediate in the Hydroxylamine–Nitrous Acid Reaction[1]

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The reaction between hydroxylamine and nitrous acid leads to the products nitrous oxide and water (eq 1). A tracer

$$H_2NOH + ONOH \rightarrow N_2O + H_2O \qquad (1)$$

investigation reported by Bothner-By and Friedman,[2] in which ^{15}N-labeled nitrite was caused to react with hydroxylamine of natural isotopic abundance, established that the N_2O product emerges from an N–N bound precursor and that HNO is therefore not an intermediate. It was further reported that the isomers $^{14}N^{15}NO$ and $^{15}N^{14}NO$ are produced in equal amounts at low acidity but that $^{14}N^{15}NO$ predominates over $^{15}N^{14}NO$ in 2:1 ratio when the reaction is carried out in 0.1 M HCl. (The pH at "low acidity" is not specified in ref 2, but from reactant concentrations given it was clearly below 7 and may have been as low as 3.) It was concluded that reaction occurs via a symmetric intermediate (hyponitrous acid) at low acidity but that a competing pathway involving an unsymmetric intermediate (perhaps *N*-nitrosohydroxylamine) becomes important in acid solution. The experiments were carried out in $H_2{}^{18}O$, and the incorporation of solvent oxygen in N_2O product (mainly in the form $^{14}N^{15}N^{18}O$) appeared to be substantially greater in the acid solution case, an observation considered to strengthen the asymmetric intermediate hypothesis.

The production of equal amounts of $^{14}N^{15}NO$ and $^{15}N^{14}NO$ at low acidity was confirmed by Clusius and Effenberger.[3] Kinetic and mechanistic studies of the HNO_2–NH_2OH reaction have been reported by Doering and Gehlen[4] and in a series of papers by Stedman et al.[5–7] The latter have demonstrated the existence of three pathways, one acid catalyzed, one anion catalyzed, and one (at low acidity) second order in HNO_2. Oxygen-18 solvent studies reported in ref 5 appeared to corroborate the appearance of an asymmetric intermediate in acid solution: with the assumption of isotopic equilibrium between HNO_2 and solvent, the ratio of ^{18}O atom excess in product N_2O to that in solvent H_2O should be very nearly 0.5 if equimolar quantities of the two isomers are present. This ratio was observed to rise from 0.50 (low acidity) to 0.60 (pH 4 to 5 M $HClO_4$),[5] in rough agreement with the value 0.66 reported for acid solution in ref 2. In a more extensive series reported in ref 7, however, the appearance of intermediate asymmetry was observed only at very high acidity (4.2–4.9 M H_2SO_4 and $HClO_4$). More recently, in the course of a study of the oxidation of hydroxylamine by nitric acid, Pembridge and Stedman[8] observed that the nitrogen from $^{15}NH_2OH$ becomes equally distributed between the two nitrogens of N_2O produced by its reaction with the HNO_2 product of the main reaction, at HNO_3 concentrations up to ca. 5 M.

(1) Research supported by National Science Foundation, Grant No. 78-24176.
(2) Bothner-By, A.; Friedman, L. *J. Chem. Phys.* **1952**, *20*, 459.
(3) Clusius, K.; Effenberger, E. *Helv. Chim. Acta* **1955**, *38*, 1834.
(4) Doering, C.; Gehlen, H. *Z. Anorg. Allg. Chem.* **1961**, *312*, 32.
(5) Hughes, M. N.; Stedman, G. *J. Chem. Soc.* **1963**, 2824.
(6) Morgan, T. D. B.; Stedman, G.; Hughes, M. N. *J. Chem. Soc. B* **1968**, 344.
(7) Hussain, M. A.; Stedman, G.; Hughes, M. N. *J. Chem. Soc. B* **1968**, 597.
(8) Pembridge, J. R.; Stedman, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1657.

Table I. Mass Spectra of Product N_2O at Various Acidities[a]

	expt no.											
m/e	1 5 M $HClO_4$	2 3.5 M $HClO_4$	3 2 M $HClO_4$	4 1 M $HClO_4$	5 0.1 M $HClO_4$	6 0.1 M HCl	7[b] 0.1 M HCl	8[c] pH 5	9[d] pH 7	10[d] pH 7	11[d] pH 8	12[d] pH 9
46	0.000	0.000	0.001	0.001	0.001	0.003	0.001	0.001	0.001	0.000	0.000	0.000
45	0.315	0.335	0.320	0.317	0.329	0.320	0.320	0.315	0.316	0.319	0.323	0.306
44	0.684	0.665	0.679	0.681	0.670	0.677	0.679	0.684	0.682	0.681	0.677	0.694
31	0.163	0.157	0.163	0.157	0.154	0.156	0.154	0.151	0.153	0.152	0.148	0.148
30	0.837	0.843	0.837	0.843	0.846	0.844	0.846	0.849	0.847	0.848	0.852	0.852

[a] Values at *m/e* 44–45 reported as fraction of total N_2O^+ and at *m/e* 30–31 as fraction of total NO^+. [Total nitrite] = 0.010 M in all experiments; [total hydroxylamine] = 0.10 M in all but expt 7. [b] [Total hydroxylamine] = 0.021 M. [c] Acetate buffer. [d] Phosphate buffer.

As the literature now stands, it seems unlikely that the hypothesis of intermediate asymmetry in this reaction, proposed on the basis of a single acid solution experiment,[2] can be correct. However, the report continues to be cited, and the assumption persists.[9] Experimentally, the situation does not appear to be entirely resolved since the $H_2{}^{18}O$ method employed in ref 7 is neither as sensitive nor as direct as an ^{15}N method, and only a single acid solution experiment in the absence of HNO_3 has been reported in ref 8. It is for these reasons that we have carried out the ^{15}N tracer study reported here.

Experiments were carried out in Y-shaped reaction vessels, employing standard vacuum-line techniques. A weighed quantity of labeled $NaNO_2$ (32.25% ^{15}N; Stohler) was placed in one leg of the vessel in 5.0 ml of aqueous solution, and a weighed quantity of $NH_2OH{\cdot}HCl$, plus any required acid or buffer solution, was placed in the other leg, also in a total volume of 5.0 mL. Both solutions were degassed on the vacuum line by successive freeze–pump–thaw cycles. The reaction was then initiated by rotation of the vessel; after sufficient time was allowed for reaction (ranging from a few minutes in strong acid to 48 h at pH 7–9), the aqueous phase was frozen at 194 K and the product gas collected at 77 K. The collected gas was isotopically analyzed in an AEI MS-30 mass spectrometer.[10] Since any NO produced by the HNO_2 disproportionation reaction concurrently with the HNO_2–NH_2OH reaction could lead to erroneous results, gas chromatographic analyses[11] were carried out on the products collected under several of the experimental conditions employed. No significant amount of NO was observed, a result undoubtedly assisted by our employment of an excess of hydroxylamine. Additional assurance that no self-decomposition NO product was present was obtained by comparison of the mass ratio (30 + 31)/(44 + 45 + 46) in NH_2OH–HNO_2 reaction products with that of pure, normal-abundance N_2O under similar mass spectrometer conditions.

Results of 12 experiments, ranging from 5 M $HClO_4$ to pH 9, are summarized in Table I. As expected, occurrence of doubly labeled N_2O at *m/e* 46 is negligible. The mean value of the fraction of N_2O at *m/e* 45 is 0.320, within one standard deviation of the value 0.3225 expected for N_2O containing one N atom from each reactant molecule. For NO^+ arising from electron impact on N_2O containing equal amounts of $^{14}N^{15}NO$ and $^{15}N^{14}NO$ the expected ratio 31/(30 + 31) would be 0.1612 in these experiments; the mean of the observed values is 0.155, with a standard deviation of 0.005. As discussed in ref 2, the electron-impact rearrangement reported in the case of $^{15}N^{14}NO$[12] would be expected to undergo an effective self-cancellation in the case of an equimolar mixture of isomers. However, it is also pointed out in ref 2 that the ratio 31/(30 + 31) must be expected to reflect something less than the concentration of $^{14}N^{15}NO$ in mass spectrometry performed on a mixture containing $^{14}N^{14}NO$ in addition to the ^{15}N isomers because of the greater probability of $^{14}N^{14}N$ bond rupture in comparison with that of the $^{14}N^{15}N$ bond.[13] We conclude that the observed mean value 0.155 for this ratio is reasonable for N_2O containing equimolar amounts of $^{14}N^{15}O$ and $^{15}N^{14}NO$. Additional weight is given this conclusion by the fact that there is no discernible trend in the ratio over the enormous acidity range 5–10^{-9}M H^+. Since the acid solution experiment of ref 2 was carried out in 0.1 M HCl, a comparison of HCl with $HClO_4$ was carried out at that concentration (experiments 5 and 6); there is no evidence of asymmetry in either case. Experiments 6 and 7 show that a change of reaction mole ratio from 10:1 to 2:1 has no effect on the reaction product in 0.1 M HCl. (The starting ratio specified in ref 2 is 1:1), but under the conditions described, a substantial loss of HNO_2 due to self-decomposition would have occurred prior to reaction initiation.)

Our results constitute definitive evidence that N_2O arises from a symmetric precursor species in the hydroxylamine–nitrous acid reaction over the entire acidity range pH 9 to 5 M $HClO_4$. The evidence of asymmetry reported for the reaction in dilute HCl,[2] and again at very high acidity,[7] appears to have been the result of experimental artifacts. As demonstrated by Stedman et al.[5-7] the following disparate mechanisms are involved: (1) N-nitrosation of NH_2OH by N_2O_3 (low acidity); (2) N-nitrosation of NH_2OH by NOX (anion catalysis); (3) O-nitrosation of NH_3OH^+ by NO^+ (acid catalysis). All three initial steps appear to be accompanied by displacement of a proton, in which cases 1 and 2 lead to ON–NHOH and case 3 leads to $^+H_3NONO$ as primary products. Observed yields of *trans*-hyponitrite coproduct have led to the supposition that ON–NHOH undergoes tautomerization to a mixture of *cis*- and *trans*-hyponitrous acids, the cis isomer then undergoing rapid decomposition to N_2O.[7] The postulate that the acid solution species $^+H_3NONO$ undergoes rapid rearrangement to form the same immediate N_2O precursor is supported by the results reported here.

Stedman et al. observed a sharp maximum in rate constant for the NH_3OH^+–HNO_2 reaction in the vicinity of 2 M H^+ in $HClO_4$ and H_2SO_4 solutions, an effect originally interpreted as due to a shift of rate-determining step.[6] Similar results for nitric acid solutions have recently been reported and mathematically described by Brown et al.[14] These authors treat the phenomenon as a kinetic effect rather than a fundamental change of mechanism, a view that is now supported by the total lack of change in isotopic pattern observed in our results over the acidity range of interest. Stedman[15] has postulated that

(9) See, e.g.: Garber, E. A. E.; Hollocher, T. C. *J. Biol. Chem.* **1982**, *257*, 4705.
(10) Stony Brook Mass Spectrometry Facility.
(11) Pearsall, K. A.; Bonner, F. T. *J. Chromatogr.* **1980**, *200*, 224.
(12) Friedman, L.; Bigeleisen, J. *J. Chem. Phys.* **1950**, *18*, 1325.
(13) Schaeffer, O. A. *J. Chem. Phys.* **1950**, *18*, 1501.
(14) Bennett, M. R.; Brown, G. M.; Maya, L.; Posey, F. A. *Inorg. Chem.* **1982**, *21*, 2461.
(15) Stedman, G., private communication.

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]

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

(16) Ridd, J. H. *Adv. Phys. Org. Chem.* **1978**, *16*, 1.
(17) Markovits, G. Y.; Schwartz, S. E.; Newman, L. *Inorg. Chem.* **1981**, *20*, 445.
(18) Bonner, F. T.; Dzelzkalns, L. S.; Bonnucci, J. A. *Inorg. Chem.* **1978**, *17*, 2487.

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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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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.

(1) D. J. Fuller and D. L. Kepert, *Inorg. Chem.*, **21**, 163 (1982).

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

(2) R. Schaeffer, Q. Johnson, and G. S. Smith, *Inorg. Chem.*, **4**, 917 (1965).
(3) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).
(4) L. J. Guggenberger, *Inorg. Chem.*, **8**, 2771 (1969).
(5) L. J. Guggenberger, *Inorg. Chem.*, **7**, 2260 (1968).
(6) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).
(7) J. T. Gill and S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975).
(8) J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960).
(9) E. L. Muetterties and W. H. Knoth "Polyhedral Boranes", Marcel Dekker, New York, 1968.
(10) K. Wade, *Inorg. Nucl. Chem. Lett.*, **8**, 823 (1972).
(11) D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc., Dalton Trans.*, 627 (1973).
(12) R. L. Middaugh, "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, 1975, Chapter 8.
(13) D. A. Dixon, D. A. Kleier, T. A. Halgren, J. H. Hall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **99**, 6226 (1977).

0020-1669/83/1322-1391$01.50/0