and chloro-substituted cage ions and decreases the intensity of the 18,000-cm^{-1} band in proportion to the amount of boron extracted, proof that the radical retains a closed cage structure. Double integration of the esr spectra of several radical solutions containing iron(III) acetylacetonate as internal standard showed that the $B_{10}H_{10}^{-2}$-derived radical had *one* unpaired electron per cage. The observed properties and the fact that $B_{12}H_{12}^{-2}$, $B_{10}Cl_{10}^{-2}$, $B_{10}Br_{10}^{-2}$, and other hard-to-oxidize derivatives fail to generate radicals under comparable conditions are difficult to reconcile with an iron–cage or copper–cage complex as the paramagnetic species, but point at a metastable intermediate in the oxidation of polyhedral boranes.

When salts of $B_{10}H_{10}^{-2}$ are titrated with $CuCl_2$ in tetrahydrofuran or ethyl acetate, one observes a sharp rise in equivalent conductance, which abruptly levels off after the appearance of color; the initial rise was found to be due to HCl. Except where side reactions occur, neither hydrogen gas nor $B_{20}H_{18}^{-2}$ are important by-products. A possible "gross" reaction sequence is shown below.

$$2CuCl_2(s) + K_2B_{10}H_{10}(s) \xrightarrow{\text{ether}} 2KCl(s) + CuCl(s) + HCl + CuB_{10}H_9$$

$$CuCl_2(s) + CuB_{10}H_9 \longrightarrow 2CuCl(s) + (B_{10}H_9)\cdot$$

The extraction of cage-substituted salts, the destruction of radicals by reducing agents, and preferential solvation by solvents with nonbonding electron pairs are all consistent with a species having a vacant bonding orbital. It is harder to explain the apparently indispensable role of HCl in the absence of which no radical is ever formed nor able to survive; any attempt to remove it physically or chemically results in immediate decomposition. Spin–orbit coupling in a radical–HCl complex might explain the unusual *g* values.[2] Whether an ion such as $B_{10}H_9^-$ would pair with a proton or a Cu(I) ion is not certain, but the latter is known to form covalent salts[2,5] with $B_{10}H_{10}^{-2}$ and might be the preferred partner. That iron(III) and copper(II) chlorides act similarly in organic solvents but differently in water, where the former produces $B_{20}H_{18}^{-2}$ readily[2] but the latter does not, is not surprising since in weakly coordinating solvents the Cu(II)–Cu(I) and Fe(III)–Fe(II) couples have comparable reduction potentials.[6] In aqueous solutions coordination with polyvalent cations would promote the coupling of $B_{10}H_9^-$ with the $B_{10}H_{10}^{-2}$ present in large excess to form $B_{20}H_{19}^{-3}$, which indeed is an intermediate[3,7] in the oxidation of $B_{10}H_{10}^{-2}$ to $B_{20}H_{18}^{-2}$.

The radical formation and decomposition mechanism, the nature of the decomposition products, and the results of work with other clovoboranes and other transition metals will be presented at a later date.[8]

Acknowledgment. We thank Professor Paul R. Shafer for assistance in the determination of the esr spectra, Professor W. T. Doyle for the use of his spectrometer, and W. P. Townsend for the flame-photometric copper determinations.

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The Absence of a Barrier in the Theoretical Potential Energy Surface for the Reaction of Hydride with Hydrogen Fluoride

Sir:

We have carried out *ab initio* calculations of the potential energy surface for the reaction of hydrogen fluoride with hydride ion and report two unexpected results. First, no barrier separating reactants from products is found; and second, a rather broad flat minimum along the reaction coordinate suggests the possible existence of a stable intermediate, the H_2F^- molecule ion.

Proton-transfer reactions are frequently discussed in terms of a three-step mechanism:[1] $AH + B \rightleftarrows AH \cdots B \rightleftarrows A \cdots HB \rightleftarrows A + HB$. It is thought that any one of the steps can be rate determining, depending upon the actual system investigated.

A great deal of interest in these reactions has evolved in recent years, both from a theoretical and experimental standpoint. The reactions are among the fastest bimolecular reactions known in solution, and special techniques have only recently been developed for the measurement of rates. On the theoretical side, emphasis has been placed on the calculation of the frequency of tunneling of the proton through a potential barrier separating reactants from products.[2-4] Much attention has been devoted to the effect of the shape of the potential barrier in such calculations, and it, therefore, seemed of interest to compute a potential energy surface for a system sufficiently simple that high accuracy could be attained in the computations.

The reaction chosen for study is calculated to be exothermic by about 27 kcal/mole in the gas phase. The total energies (zero point and relativistic energy excluded) of the reactants, $HF + H^-$, and products, $H_2 + F^-$, in their ground states are -100.985 and -101.029 au, respectively.[5] The corresponding Hartree–Fock energies are -100.550 and -100.592 au.[5,6]

The calculations were carried out in the Hartree–Fock approximation using Gaussian basis functions. Many preliminary calculations using Harrison's[7] basis set B were carried out to survey the potential energy surface. These indicated that the lowest energy configuration is

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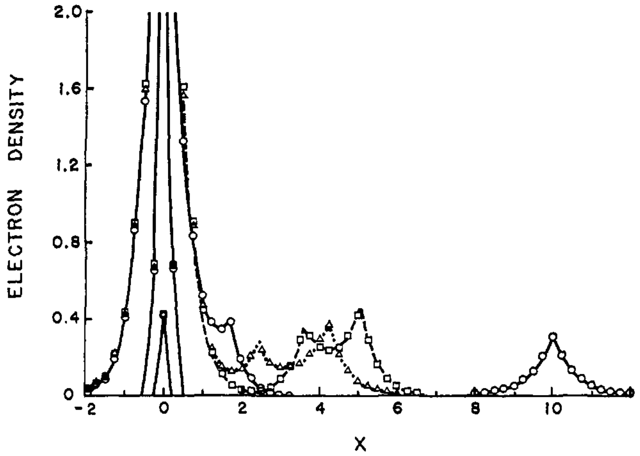

Figure 1. Electron density along the internuclear axis for three different linear configurations of FHH^-: circles refer to HF and H^- at infinite separations; triangles refer to r(HF) = 2.40 and r(HH) = 1.8 au; squares refer to r(HF) = 3.60 and r(HH) = 1.45 au. The density about F is shown with three different scales, differing by a factor of 10.

linear with fluorine in a terminal position, showed no barrier, indicated an intermediate complex stable by 55 kcal/mole, and served to define clearly the reaction coordinate. Further calculations were then carried out with an extended basis set of ten s-type and six of each p-type bases on fluorine, and five s-type and two of each p-type bases on each of the hydrogens. These calculations were limited to points along the minimum energy path found in the preliminary investigation, except for occasional checks to be sure that the minimum path was being reproduced. Exponential parameters were kept constant for all calculations. It is doubtful, however, that significantly different results could be obtained by reoptimization at each point since we are within 0.03 au of the estimated Hartree–Fock limits at both ends of the reaction coordinate. The results of the calculations are shown in Table I.

Table I. Potential Energies for the Linear H_2F^- System[a]

d_{FH}	d_{H-H}	Energy
1.74	∞	−100.517
1.85	3.00	−100.569
1.95	2.35	−100.574
1.80[b]	2.20[b]	−100.567[b]
2.20[b]	2.10[b]	−100.574[b]
2.20	1.90	−100.575
2.40	1.80	−100.577
2.70	1.60	−100.582
2.70[b]	1.40[b]	−100.577[b]
3.00[b]	1.80[b]	−100.577[b]
3.10	1.50	−100.585
3.60	1.45	−100.586
∞	1.40	−100.574

[a] Internuclear distances and energies are in atomic units. [b] These points are off the reaction coordinate.

Again no barrier is observed. A stable intermediate is still indicated, but the energy difference between intermediate and separated products is now only 8 kcal/mole. The bond lengths are also drastically different from that found with the smaller basis set.

Long-range attraction between H_2 and F^- is to be expected, but the attraction persists to smaller separations than are typically found[8] experimentally and theoretically for ion–molecule interactions. For example, H_2 and H^- are calculated[9] to be strongly repulsive in the range of our broad minimum. The flat curve we observe is the result of several opposing effects as is indicated by the electron-charge shifts. In Figure 1 the low electron density at the central hydrogen nucleus at about the middle of the reaction coordinate is particularly noticeable.

The energy difference between the highest occupied and the lowest unoccupied orbitals remains nearly constant from point to point along the reaction coordinate. Thus, it appears unlikely that configuration interaction calculations would drastically alter the present results.

It is possible that the basis set used gives better results for the intermediate than for reactants or products. As mentioned above, however, we are within 0.03 au of the Hartree–Fock limit at both ends of the reaction coordinate. It does not, therefore, appear likely that significant changes in the shape of the curve would result from this source.

An accurate *ab initio* calculation of electron correlation energy has never been carried out for a system of this complexity. An estimate of correlation energies based on method I of Sinanoglu's recent paper[10] indicates that these effects may stabilize the intermediate relative to the products by approximately 6 kcal. Thus, consideration of correlation effects may actually cause a larger dip in the reaction coordinate than that shown by the Hartree–Fock calculation. In view of the extreme approximations involved, however, it is possible that the effect may actually be in the opposite direction. In any case we do not expect any change large enough to introduce a barrier along the coordinate.

Acknowledgments. We express our gratitude to the Computer Center of the State University of New York at Buffalo for the donation of computer time, and to Dr. R. E. Stanton for many helpful discussions and suggestions.

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Received December 14, 1965

A New Isomer of $C_2B_3H_5$, C,3-Dimethyl-1,2-dicarbaclovopentaborane(5)

Sir:

Although three isomers having a trigonal bipyramidal structure are theoretically possible for the carborane $C_2B_3H_5$, only the 1,5 isomer, in which the carbons occupy the apical positions, has been prepared.[1] We now report the isolation of a dimethyl derivative (I) of a second isomer, 1,2-dicarbaclovopentaborane(5), from the reaction of acetylene and diborane in an electric discharge.

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