

preference is based on the repulsive interactions which develop in the transition states. An important one of these involves the site of attack, where a hydrogen is driven upwards toward either another hydrogen or a methyl group at C-6. It seems reasonable to assume that the H-CH₃ repulsion generated during attack at C-1 would be the more serious one, and that consequently attack at C-2 would predominate.

The steric effect in the product-forming step is ascribed to a transition-state free-energy difference alone, since the ground states are either the same or effectively the same (a common nonclassical ion D, or if the opponents of such species insist, a pair of rapidly equilibrating classical ions). Whatever its detailed nature, a kind of specific destabilization similar to that in the transition state leading to the 6-endo-methyl-2-exo product must also be present in the solvolysis of a corresponding 6-endo-methyl-2-exo substrate. The present results provide experimental evidence that transition-state steric effects account for part of the observed² retardation in the 6,6-dimethyl case.

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Polyhedral Borane Free Radicals¹

Sir:

When the reaction of CuCl₂ with K₂B₁₀H₁₀ in organic solvents was first reported,² the paramagnetic species was presumed to be a copper(II)-cage complex. We wish to present evidence that in this and other hitherto unreported reactions, oxidation of polyhedral boranes produces true free radicals.

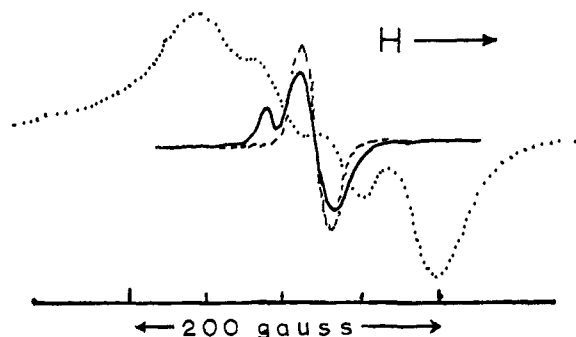


Figure 1. The esr spectra of radicals derived from B₁₀H₁₀⁻² (solid line) and B₂₀H₁₇OH⁻⁴ (dashed line), both in isopropyl ether, compared with that of anhydrous CuCl₂ in tetrahydrofuran (dotted line); all concentrations ca. 10⁻³ M.

Anhydrous CuCl₂ oxidizes B₁₀H₁₀⁻², B₂₀H₁₇OH⁻⁴,³ partially halogenated, and other cage-substituted systems to free radicals in over 30 organic solvents con-

(1) Research sponsored by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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taining oxygen or nitrogen. Of these, alkyl ethers give the most stable and purest (free of starting materials) solutions of the radical. Solutions in ethyl acetate or tetrahydrofuran, for example, are invariably contaminated with CuCl₂. In a typical preparation anhydrous ether is added to a finely ground mixture of K₂B₁₀H₁₀ and anhydrous CuCl₂; the mixture is stirred until it is dark violet-blue and filtered. In addition to the radical, such solutions contain traces of CuCl and varying amounts of HCl and radical decomposition products. A purple to wine-red color is a sign of extensive decomposition. Alkali, amines, and reducing agents such as I⁻ and BH₄⁻ rapidly destroy the radical. When FeCl₃ is used, ketones, alcohols, esters, and nitriles have been found to work best, even though in such solvents the radical seldom lasts more than a few minutes at room temperature.

That B₁₀H₁₀⁻² and B₂₀H₁₇OH⁻⁴ yield such similar radicals is significant and suggests that in contrast with B₂₀H₁₈⁻², where electrons appear free to move between cages,⁴ systems joined through a B-B bond remain electronically isolated, which confines the spin to one cage. The visible spectrum of every radical so far investigated consists of a single band between 17,000 and 19,000 cm⁻¹ with a half-width of 3000 cm⁻¹. Since its molar extinction coefficient is about 3000 and the frequency depends on concentration and solvent polarity, it is undoubtedly a charge-transfer band. In ethereal solutions, which obey Beer's law, good correlation exists between boron content and absorbance at 18,000 cm⁻¹. No such correlation could be established for copper whose concentration, as determined by flame photometry, in isopropyl ether solutions of unit absorbance (1-cm path length) varied from 2 × 10⁻⁵ to 2 × 10⁻⁴ M. In general, solutions of radical derived from B₁₀H₁₀⁻² contained more copper than did those of radical produced from B₂₀H₁₇OH⁻⁴, which might account for the presence of the secondary low-field peak in the esr spectra of the former (Figure 1); though the nature of this peak is still under investigation, variations in its relative intensity and the larger *g* value favor the assignment of the peak to a soluble copper(II)-cage complex.

Table I. Physical Properties of Borane Radicals

Source	Medium	<i>g</i> value	$\Delta H/2$, gauss ^a	$\nu \times 10^3$, cm ⁻¹ ^b
K ₂ B ₁₀ H ₁₀ and CuCl ₂	Acetic acid	2.020	21.4	18.5
	Isopropyl ether	2.0202	22.0	18.0
	Tetrahydrofuran	2.0183 ^c	36.0 ^c	17.8
K ₂ B ₁₀ H ₁₀ and FeCl ₃	Methanol	17.5
	Acetonitrile	2.021	...	17.8
	Ethyl acetate	18.2
K ₄ B ₂₀ H ₁₇ OH and CuCl ₂	Isopropyl ether	2.0166	23.7	18.4

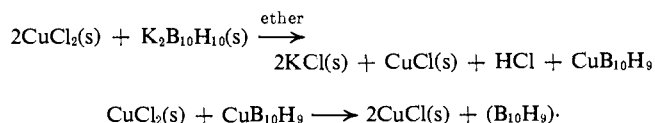
^a These are dimensions at room temperature. At 77.4°K the bands are twice as wide. ^b For absorbance <1 and 1-cm path length. ^c In this solvent the principal peak and the shoulder 25 gauss downfield (Figure 1) were not resolved.

Shaking ethereal solutions with hydrochloric acid solutions of (CH₃)₄NCl precipitates salts of hydroxy-

(4) A. Kaczmarczyk and G. B. Kolski, *ibid.*, **4**, 665 (1965).

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 B₁₀H₁₀⁻²-derived radical had *one* unpaired electron per cage. The observed properties and the fact that B₁₂H₁₂⁻², B₁₀Cl₁₀⁻², B₁₀Br₁₀⁻², 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 B₁₀H₁₀⁻² are titrated with CuCl₂ 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 B₂₀H₁₈⁻² are important by-products. A possible "gross" reaction sequence is shown below.



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 B₁₀H₉⁻ 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 B₁₀H₁₀⁻² 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 B₂₀H₁₈⁻² readily² 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 B₁₀H₉⁻ with the B₁₀H₁₀⁻² present in large excess to form B₂₀H₁₈⁻³, which indeed is an intermediate^{3,7} in the oxidation of B₁₀H₁₀⁻² to B₂₀H₁₈⁻².

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

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(6) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1825 (1957).

(7) M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *ibid.*, **87**, 1893 (1965).

(8) NOTE ADDED IN PROOF. Conclusive evidence that transition metal ions are not an integral part of the free radicals reported in this communication has just been obtained in this laboratory. Radicals with very similar optical and magnetic properties have now been made using KClO₃, KBrO₃, KIO₃, KIO₄, and Na₄XeO₆ in acetic acid as oxidizing agents.

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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 H₂F⁻ molecule ion.

Proton-transfer reactions are frequently discussed in terms of a three-step mechanism:¹ AH + B ⇌ AH...B ⇌ A...HB ⇌ 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, H₂ + 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's⁷ basis set B were carried out to survey the potential energy surface. These indicated that the lowest energy configuration is

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(7) M. C. Harrison, *J. Chem. Phys.*, **41**, 499 (1964).