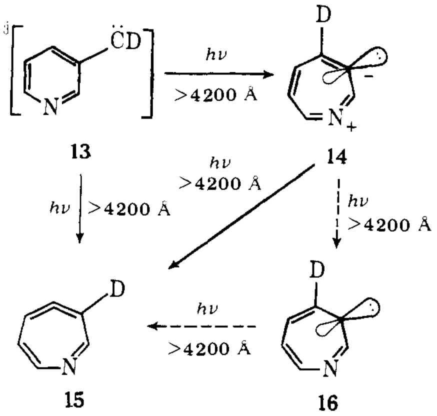
regiochemically opposite sense might be expected to give a different allene (**9**). The 1935-cm^{-1} band in the infrared spectrum shows that the new product is not the allene **9**, and the other ring-expanded structures (**10** and **11**) must be considered. The planar carbene (**10**, singlet or triplet) has no functionality which could account for the 1935-cm^{-1} band. The zwitterionic heterocumulene (**11**), however, should show a band in this region. The model zwitterionic heterocumulene (**12**) shows an intense band at 1930 cm^{-1} in an argon matrix.[7] Calculations by Salem[8] suggest that the C=N=C system in $HC^-{=}N^+{=}CH_2$ should be bent with an equilibrium angle of ~157° (the potential well is very broad). The relationship of **9, 10,** and **11** is of considerable interest. These structures are topological isomers and can be interconverted by a series of single-bond rotations. The barriers to rotation are probably small, and at room temperature **9, 10,** and **11** may be interconverting rapidly. The barriers are sufficiently large, however, to make **7** and **11** unique compounds at 10 K. It is not clear whether the nature of the compound formed is determined by the nuclear configuration at the point of entry to the energy surface in our experiments or by subtle electronic factors in the molecule. The zwitterionic heterocumulene (**11**) occupies the position assigned to the postulated allene (**9**) in our published scheme for the interconversion of the isomeric pyridylmethylenes and phenylnitrene.[3]

$$\mathrm{Ph\bar{C}{=}\overset{+}{N}{=}CH_2}$$

12

Irradiation (>4200 Å) of the zwitterionic heterocumulene (**11**) gives the allene **7** rapidly. This is the reason that only **7** is observed in the irradiation (>3640 Å) of 3-diazomethylpyridine. Irradiation (>4200 Å) of **7** slowly gives **8**. This amazing rearrangement may involve **11** (dashed arrows, Scheme I), but we have not been able to find evidence for the conversion of **11** into **8**. Irradiation (>4200 Å) of 3-pyridyldeuteriomethylene (**13**) gives a larger steady-state concentration of deuterated zwitterionic heterocumulene (**14**). The increase in the steady-state concentration of **14** is due to an increase in its rate of formation relative to the rate of its destruction. The change in stationary-state concentration of **14** when hydrogen is replaced by deuterium suggests that the conversion of **14** into **15** might involve a hydrogen shift. It is probable that the hydrogen shift would occur in the planar carbene (**16**) produced by irradiation of **14**. Tunneling has been shown by Ingold[9] to be the most important mechanism in an intramolecular hydrogen shift in a free radical at 28 K. It is an intriguing question whether tunneling is an important mechanism in hydrogen shifts of carbenes at low temperature. It is, however, possible that the change in stationary-state concentration of **14** could be due to secondary isotope effects in the conversion of **13** into **14**.



Acknowledgment. This research was supported by Grant CH75-10939 from the National Science Foundation and Grant GM-24427 from the General Medical Sciences Institute, U.S. Department of Health, Education, and Welfare.

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Received August 28, 1978

Spin Trapping in Electrochemistry. 1. On the Electrooxidation of Organoborides

Sir:

In the course of identifying supporting electrolytes having inert anions of low nucleophilicity and high anodic discharge potentials for use in oxidative electrochemical characterization of substrates in nonaqueous, aprotic media,[1] we have examined the anodic electrochemistry of analogues of the widely used tetraalkylammonium tetrafluoroboride, R_4NBF_4. In contrast to BF_4^- which undergoes oxidation at >+3 V,[2] tetraphenylboride anion (BPh_4^-) is oxidized at a platinum electrode in acetonitrile (MeCN) at a potential of +0.92 V.[3] We have observed that the tetra-*n*-butylboride anion (BBu_4^-), however, is more easily oxidized than BPh_4^- and exhibits a well-defined, monoelectronic oxidation wave at $E_{p(a)} = +0.35$ V.[5] Exhaustive electrooxidation of BBu_4^- in MeCN indicates a charge release of 1 faraday/mol and this *n* value is invariant over the concentration range of 80 μM to 10 mM. That the corresponding electrooxidation of BPh_4^- affords concentration dependent *n* values ranging from $n \simeq 2$ at low (80 μM) BPh_4^- concentrations to $n \simeq 1$ at high (10 mM) BPh_4^- concentrations[4,6] has led us to examine the mechanisms of electrooxidation of these two organoborides. The expectation that free-radical intermediates might be formed in both cases (Ph· in BPh_4^- oxidation and *n*-Bu· in BBu_4^- oxidation) suggested the use of spin trapping[7] as a technique with which these highly reactive species could be detected.

Bard has demonstrated the utility of α-phenyl-*N*-*tert*-butyl nitrone (PBN) as a spin trap in direct electroreductions[8] and in photoassisted oxidations.[9] The "potential window" of PBN and that of the corresponding nitroxides[10] make PBN well suited to the oxidative examination of these organoborides.

Controlled potential electrolysis (CPE)[11] of rigorously deoxygenated millimolar solutions of $TBABBu_4$ in MeCN containing 0.10 M TBAP and 0.10 M PBN afforded very persistent spin adducts whose ESR spectra are typified by that shown in Figure 1A. Identical spectra were obtained from the in situ electrolysis[12] of rigorously deoxygenated $TBABBu_4$/PBN solutions. CPE without deoxygenation of the $TBABBu_4$/PBN solution prior to electrolysis gave a mixture of two nitroxide spin adducts, one of which was spectrally identical with that obtained under oxygen-free electrolysis conditions (Figure 1B). CPE of oxygen-saturated solutions of $TBABBu_4$/PBN afforded the spectrum of a single nitroxide

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Table I. ESR Hyperfine Splitting Constants of Spin Adducts

radical source and expl condn[a]	trap[b]	a_N	$a_\beta{}^H$	radical assignment
external CPE of TBABBu$_4$ (rigorous deoxygenation)[c]	PBN	14.88 (±0.02)[d]	3.06 (±0.02)[d]	*n*-Bu·
in situ CPE of TBABBu$_4$ (rigorous deoxygenation)[c]	PBN	14.88 (±0.02)	3.05 (±0.02)	*n*-Bu·
external CPE of TBABBu$_4$ (no deoxygenation)[c]	PBN	14.88	3.05	*n*-Bu· (68%)[e]
		13.80	2.27	*n*-BuO· (32%)[e]
external CPE of TBABBu$_4$ (oxygen saturated)[c]	PBN	13.80 (±0.02)	2.27 (±0.02)	*n*-BuO·
in situ photolysis of *n*-Bu$_3$PbOAc (rigorous deoxygenation)[f]	PBN	14.89 (±0.02)	3.05 (±0.02)	*n*-Bu·
in situ CPE or TBABBu$_4$ (rigorous deoxygenation)[c]	NtB	15.44 (±0.03)	10.30 (±0.03)[g]	*n*-Bu·
reaction of 1-brompentane with KO$_2$ in MeCN containing 0.025 M dicyclohexyl-18-crown-6[h]	PBN[i]	13.83 (±0.01)	2.27 (±0.01)	*n*-pentyloxy

[a] At room temperature in MeCN containing 0.10 M TBAP unless otherwise noted. [b] 0.10 M unless otherwise noted. [c] At the Pt electrode poised at +0.40 V vs. SCE. [d] Hyperfine splitting constants are given in gauss; parenthesis contain one standard deviation. [e] Composition assigned from simulation. [f] Reference 16. [g] γ-H hfsc, 0.54 (±0.01) (2 H). [h] Reference 17a. [i] 0.05 M.

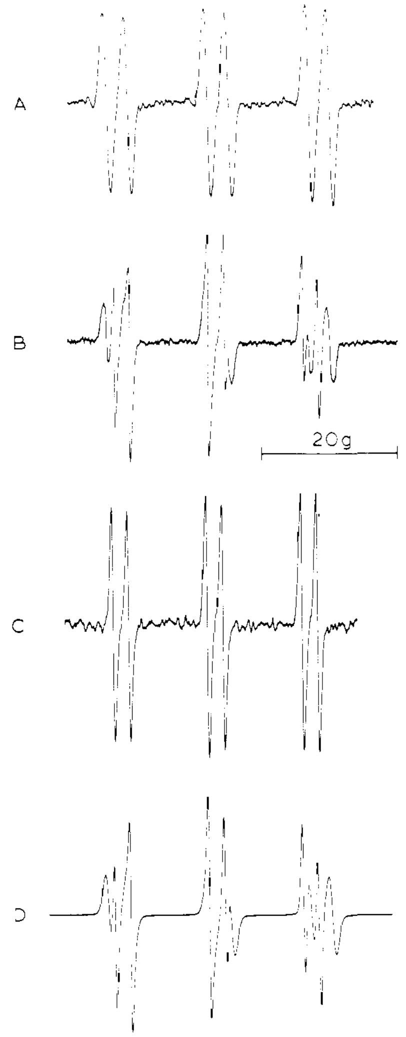

Figure 1. ESR spectra of PBN spin adducts formed upon electrooxidation of TBABBu$_4$ in MeCN/TBAP under various conditions: (A) rigorous exclusion of oxygen during electrolysis; (B) no exclusion of oxygen during electrolysis; (C) saturation with oxygen during electrolysis; (D) computer simulation of a mixture of 68% A and 32% C (cf. spectrum B).

spin adduct (Figure 1C) identical with the second component of the mixture spectrum shown in Figure 1B. Computer simulation of a mixture of 68% 1A and 32% 1C using the parameters in Table I produced the spectrum shown in Figure 1D.

Assignment of the spectrum shown in Figure 1A to the *n*-Bu· adduct of PBN was made on the basis of in situ photolysis of tri-*n*-butylplumbyl acetate (*n*-Bu$_3$PbOAc) in MeCN containing 0.10 M TBAP and 0.10 M PBN.[16] Support for this assignment was provided by the detection of R-CH$_2$-CH$_2$· radicals in the in situ electrolysis of TBABBu$_4$ in oxygen-free MeCN containing 0.10 M TBAP and 0.10 M nitroso-*tert*-butane (NtB)[13] (see Table I). The spectrum shown in Figure 1C is assigned to the *n*-BuO· adduct on the basis of the following: firstly, *n*-BuO· radicals are expected to be formed from the reaction of *n*-Bu· radicals with O$_2$ via *n*-BuOO·.[17] Secondly, the narrow line widths observed (0.52 *g*) are consistent with the absence of unresolved γ-H hyperfine splitting (hfs) arising from the trapped radical.[7,16] Thirdly, the slightly higher relative *g* value noted for this spin adduct (2.0062 vis-á-vis 2.0059 for the Bu· spin adduct) is consistent with the trapping of oxygen-centered radicals.[7] Lastly, the hfs parameters are in very good agreement with those reported for the PBN spin adduct of *n*-pentyloxy radical[17a] (see Table I). These findings suggest that electrooxidation of alkylborides[18] may be a convenient way of producing alkyl, alkyloxy, and alkylperoxy radicals under controlled conditions.

In pronounced contrast to the BBu$_4^-$ case, CPE of TBABPh$_4$ in MeCN containing 0.10 M TBAP and 0.10 M PBN failed to produce any detectable PBN spin adducts. This was true both for in situ electrolyses and for those carried out external to the cavity (cf. ref 11) at potentials ranging from +0.5 to +2.2 V.[19] That biphenyl is a major product of the electrooxidation of BPh$_4^-$ [4] suggests the existence of phenyl radical intermediates, especially in view of our observations of the BBu$_4^-$ system. Various experiments designed to check possible causes for this negative result were performed. Thus the rate of formation of the Ph· spin adduct in the room-temperature thermal decomposition of phenylazotriphenylmethane (PAT)[20] in MeCN containing 0.10 M TBAP and 0.10 M PBN was unaltered by electrolysis of the solution using a platinum electrode poised at +1.0 V. Also, the rate was unaltered by the presence of 0.10 M TBABPh$_4$. These observations indicate that (1) the Ph· spin adduct is electroinactive at potentials sufficiently anodic to discharge BPh$_4^-$; (2) Ph· radicals are not oxidized to phenyl carbonium ions at these potentials; and (3) BPh$_4^-$ is not a better trap for Ph· than PBN. It seems reasonable to conclude that free Ph· radicals are never produced in this system. Since biphenyl is an isolated product,[4] an intramolecular coupling of two phenyl groups in neutral ·BPh$_4$ suggests itself.[21]

Acknowledgment. This work was supported in part by grants from the National Research Council of Canada and NATO (Grant No. 1578). The assistance of E. R. Davis is gratefully acknowledged.

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(3) Peak anodic potential, $E_{p(a)}$, for a 1.0 mM solution of the tetra-*n*-butylammonium (TBA) salt in 0.10 M tetra-*n*-butylammonium perchlorate (TBAP). Geske[4] has noted a concentration dependence of the anodic discharge potential of $NaBPh_4$ in MeCN containing $LiClO_4$.

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(6) In MeCN containing 0.10 M TBAP, we have noted extreme *n* values of 1.90 (±0.06) for 80 μM $TBABPh_4$ and 1.06 (±0.04) for 10 mM $TBABPh_4$; cf. ref 4.

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(10) In MeCN at a platinum electrode, PBN is oxidized and reduced at +1.5 V and −2.4 V, respectively, while the phenyl adduct of PBN is estimated to be electroinactive between +0.7 V and −2.0 V.[8]

(11) The potential of the platinum working electrode in a conventional three-electrode, three-compartment cell was controlled at +0.35 V. Following electrolysis, samples were withdrawn, introduced into flat cells, and deoxygenated again and their ESR spectra were recorded on a Varian E-104 spectrometer.

(12) CPE in the ESR cavity were carried out using a Varian E-256 electrolytic sample cell.

(13) In MeCN/TBAP, NtB is electroinactive between +1.82 and −1.77 V.[14] Spin adducts of NtB provide direct structural information regarding the radical from which the adduct is derived.[15]

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(19) Note that $E_{p(a)}$ for $TBABPh_4$ is +0.92 V in this medium. At potentials >1.4 V, PBN also undergoes electrooxidation. No radical species were detected by either CPE technique (in situ or external) at $TBABPh_4$ concentrations corresponding to coulometric values of $n \simeq 1$ (10 mM) and $n \simeq 2$ (80 μM).

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Received February 20, 1979

Photosynthesis of Polyatomic Organic Molecules from Carbon Dioxide and Water by the Photocatalytic Action of Visible-Light-Illuminated Platinized Chlorophyll *a* Dihydrate Polycrystals

Sir:

Sunlight is converted by green plants into the driving force for photosynthesis according to the reaction stoichiometry[1]

$$CO_2 + 2H_2O \xrightarrow[\text{Chl } a]{\text{visible light}} CH_2O + H_2O + O_2 \tag{1}$$

in which water cleavage by the chlorophyll is accompanied by the reduction of carbon dioxide. That water is the source of O_2 evolution in eq 1 was suggested around 1930.[2-5] Experimental support for this suggestion was provided by several workers.[6-8] Recent work in this laboratory demonstrated the Chl *a* water splitting reaction[9,10]

$$2H_2O \xrightarrow[\text{Chl } a]{\text{visible light}} 2H_2 + O_2 \tag{2}$$

using platinized, polycrystalline Chl *a* electrodes. In this communication we report evidence for the photoreduction of CO_2 by H_2O to formic acid by platinized $(\text{Chl } a\cdot 2H_2O)_n$. The reduction is shown to be photocatalyzed by the chlorophyll and may additionally produce formaldehyde.

$$2CO_2 + 2H_2O \xrightarrow[\text{Chl } a]{\text{visible light}} 2H_2CO_2 + O_2 \tag{3}$$

A Pt foil was platinized by passing a 30-mA current for 10 min through a 7×10^{-2} M chloroplatinic acid solution containing 6×10^{-4} M lead acetate. Chl *a* was prepared in the usual manner from fresh spinach leaves by chromatographic methods and suspended in *n*-pentane as polycrystalline chlorophyll *a* dihydrate.[11] The Pt black electrode was plated with Chl *a* by suspending the electrode in an aluminum trough filled with 10^{-4} M Chl *a* and subjecting it to a 1000 V cm^{-2} potential under the illumination of a 200-W tungsten lamp. The Chl *a* plated electrode, still under illumination, was platinized again for 15 s at 30 mA in the chloroplatinic acid solution. The platinized $(\text{Chl } a\cdot 2H_2O)_n$ sample was immersed in warm water (40-60 °C) for 2 h and then allowed to equilibrate in the water at room temperature overnight. The electrode was then placed in a cell, fitted with Kel-F valves, containing a mixture of $H_2{}^{16}O$, $D_2{}^{16}O$, and/or $H_2{}^{18}O$. The sample cell containing doubly distilled ^{18}O- and/or D-enriched water was deaerated by purging with Ar gas for 20 min. The water was then saturated with CO_2. Research grade CO_2, purchased from Matheson, was further purified by passing the gas over a red-hot platinum coil to eliminate organic impurities and then through a Pyrex U-tube containing BTS Cu-Mn pellets for oxygen removal.[12] Following CO_2 saturation the cell was closed, and the sample was illuminated with a 1000-W xenon arc lamp. Corning CS 3-69 and water filters were used to eliminate short wavelength (λ <520 nm) and IR photons, respectively. After 30 min of illumination, the gaseous mixture above the aqueous solution was analyzed using a Consolidated Electrodynamics Model 21-110-B mass spectrometer. During the entire procedure the Pt/Chl *a* electrode was not allowed to dry in extended exposure to air.

The effect of CO_2 on the product distribution of the Pt/Chl *a* light reaction is illustrated by the mass spectral results in Figure 1. It is evident that the hydrogen evolution obtained in the absence of CO_2 (Figure 1A) is suppressed in the presence of CO_2 (Figures 1B and 1C). The appearance of $^{16}O^{18}O^+$ (mass 34) and $^{18}O_2{}^+$ (mass 36) lines in the $H_2{}^{18}O$-labeled solution ($^{16}O/^{18}O = 1.82$) establishes that O_2 is liberated from water as the oxidation product.[9,10] The mass 34/36 ratio is 3.2, in agreement with the random scrambling $^{16}O^{18}O/^{18}O_2$ ratio of 3.6 based on the known $^{18}O/^{16}O$ content in the water. (See also ref 9.) There is no evidence for the formation of H_2O_2 on account of the lack of intensity increases at masses 35 ($DH^{16}O_2{}^+$), 37 ($DH^{16}O^{18}O_2{}^+$), 38 ($D_2{}^{16}O^{18}O^+$, $H_2{}^{18}O_2{}^+$), 39 ($HD^{18}O_2{}^+$), or 40 ($D_2{}^{18}O_2{}^+$).

From a comparison of Figures 1B and 1C it is apparent that thermal radiation from the xenon arc lamp produces little effect on the product distribution. Previous work has shown[10] that Pt in water produces H_2 but no O_2 upon heating, and that the concurrent production of H_2 and O_2 occurs only when both light and Chl *a* are present. The observation of O_2 in the presence CO_2 upon illumination in Figures 1B and 1C thus suggests a photochemical pathway involving the chlorophyll. The effects in Figures 1B and 1C are not observed using visible light and a Chl *a* free Pt sample under otherwise identical conditions.