Systematic Studies on Redox Behavior of Homonuclear Double-bond Compounds of Heavier Group 15 Elements

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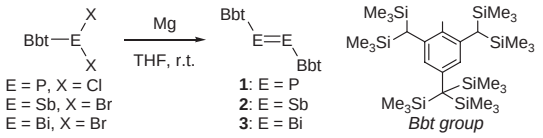
Electrochemical properties of BbtE=EBbt (E = P, Sb, Bi; Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)-methyl]phenyl) systems have been elucidated based on the measurement of cyclic voltammetry and DFT calculations.

The chemistry of double-bond compounds between heavier group 15 elements (dipnictenes) has long fascinated many chemists.[1] The previous reports on properties of kinetically stabilized diphosphenes have already revealed the intrinsic properties of P=P bonds.[1,2] It is generally accepted that the LUMO of a diphosphene is mainly P=P π^* molecular orbital, where the π^* orbital level is lower than that of N=N double bond due to the smaller overlap of p orbitals. In addition, the redox behavior of diphosphenes and diarsenes has also been examined to reveal that it is possible to generate the corresponding anion radical species by reduction.[3] These unique properties of diphosphenes and diarsenes are most likely interpreted in terms of their low-lying π^* orbital levels. It should be very interesting to perform systematic studies on the electrochemical properties of dipnictenes from the viewpoints of elemento-chemistry. We present here the systematic studies on redox properties of the kinetically stabilized BbtE=EBbt systems (E = P, Sb, and Bi),[4] using cyclic voltammetry. Although the experimental data are missing for the As-derivative, theoretical calculations helped us to understand their intrinsic properties systematically.

Kinetically stabilized diphosphene **1**, distibene **2**, and dibismuthene **3** can be easily prepared via reported procedures (Scheme 1).[4] In Figure 1 are shown the cyclic voltammograms for their reduction (a) and oxidation (b). One can see that **1**–**3** showed reversible one-electron redox couples in the reduction region, respectively. Of particular note is that distibene **2** showed the lowest $E_{1/2}$ as reduction potential among the three dipnictenes **1**–**3** here examined. The experimental results observed here suggest that a distibene system is most easily reduced among all dipnictenes. We performed DFT calculations on dipnictenes using model compounds having less bulky substituents such as H, Me, Ph, and Mes (mesityl) groups (Figure 2).[5] Redox behavior observed in cyclic voltammetry is not "vertical" but "adiabatic" electron-transitions, since there is enough time for geometry relaxation during redox process of cyclic voltammetry. Therefore, we calculated the adiabatic electron affinity (EA), which represents the difference between the total energies of the neutral and anionic species.[6]



Scheme 1.

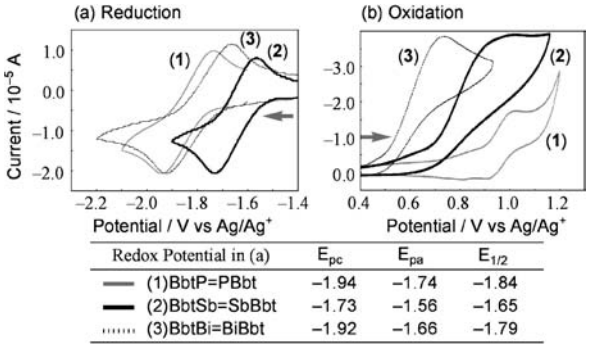


Figure 1. Cyclic voltammograms of BbtE=EBbt (E = P, Sb, Bi). (a) In THF with $Bu_4N^+PF_6^-$ (0.1 M) at rt with a scan rate of 50 mVs^{-1}. (b) In CH_2Cl_2 with $Bu_4N^+BF_4^-$ (0.1 M) at $-50\,^\circ$C with a scan rate of 50 mVs^{-1}.

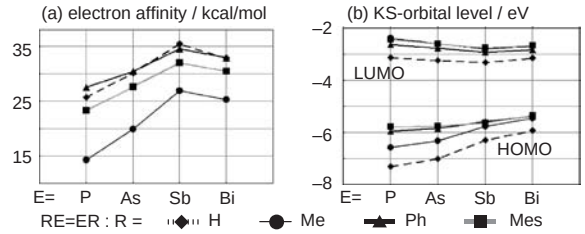


Figure 2. Calculations[7] of (a) electron affinity (b) KS-orbital level.

As a result, the EAs of RE=ER were found to increase on going from P through Sb but the EAs of dibismuthenes decreased as compared with those of distibenes (Figure 2a).[7] That is, the calculations indicate that the reduction of RSb=SbR systems is the most exothermic reaction among the cases of dipnictenes. This theoretical interpretation is consistent with the experimental results observed in cyclic voltammetry. It is useful to think of the tendencies of EA values in analogy to their LUMO levels, which mainly consist of π^* orbitals of E=E double bonds. The same tendency was found in the calculations of their Kohn–Sham (KS) LUMO levels,[7] that is, distibene systems have the lowest KS-LUMO levels in the calculations (Figure 2b), supporting the experimental results and calculations of their EAs. These results are contrary to the intuitive expectation that the π^* orbital level of an E=E double-bond will be lowered as the element row descends.

The unique tendency of π electron systems of heavier group 15 elements observed here is most likely interpreted in terms of

the "relativistic effect of the 6th row elements."[8] It may be expected that the sizes of the *ns* and *np* orbitals increase monotonously on going down the periodic table from N through Bi together with the increase of principal quantum number (n). However, the 6s orbital of Bi is known to shrink to nearly the same size of the *5s* orbital of Sb due to "relativistic effect,"[8] and a unique properties of heavier group 15 elements have been explained as the results of relativistic effects in many cases. One of the popular examples is the very low reactivity of the lone pair of organobismuth(III) compounds, which mainly consists of 6s orbitals. On the other hand, the shrinkage of 6s orbitals causes interesting phenomena. For example, the difference between the Bi=Bi bond lengths in ArBi=BiAr (Ar = bulky aryl substituent)[4,9] and the Sb=Sb bond lengths in ArSb=SbAr[4,9] is ca. 0.2 Å, which is undoubtedly smaller than those between the Sb=Sb bond lengths in ArSb=SbAr and the As=As bond lengths in ArAs=AsAr[9] (ca. 0.4 Å). This feature is most likely interpreted in terms of the shrinkage of 6s orbitals of Bi atom, which can make smaller anti-bonding interaction to each other, due to the relativistic effect. Calculated structural parameters for HE=EH systems (Figure 3) also supported such tendency for bond lengths.[4,10] Consequently, it can be concluded as follows. Stable π bonds should be constructed by favorable overlapping of p orbitals. Essential factors for favorable overlapping of p orbitals should be (1) shorter bond lengths and (2) larger p orbitals. In the case of P, As, and Sb, an order of the overlapping of p orbitals, which indicates strength of the π bond and the π–π^* energy gaps, is P=P > As=As > Sb=Sb, since the factor of (1) is much more effective than (2). On the other hand, the bond length of a Bi=Bi bond is longer than that of an Sb=Sb bond by only ca. 0.2 Å due to the relativistic effect. Therefore, the overlapping of 6p orbitals in dibismuthene is not so unfavorable compared with the case of 5p orbitals in distibene. On the contrary to the shrinkage of 6s orbitals, the size of 6p orbitals is larger than those of 5p orbital since p orbitals are not so affected by the relativistic effect.[8] Thus, the unfavorable factor of (1) should be almost cancelled by the favorable factor of (2) in the case of a Bi=Bi bond as compared with an Sb=Sb bond. That is, the energy gap between π and π^* orbitals may be nearly the same in the case of Sb=Sb and Bi=Bi. It was supported by theoretical calculations for the overlap of *np* orbitals in HE=EH (E = P, As, Sb, and Bi) since the integrals of overlapping of 5p orbitals in HSb=SbH is almost the same as those of 6p orbitals in HBi=BiH (Figure 3). We came to a conclusion that the π^* energy level of a dibismuthene is higher than that of a distibene since the energy levels of 6p is higher than those of 5p as depicted in Figure 4. It should be noted that the experimental results observed here in cyclic voltammetry could be recognized as an experimental evidence of "relativistic effects of the 6th row elements."

On the other hand, irreversible oxidation waves were

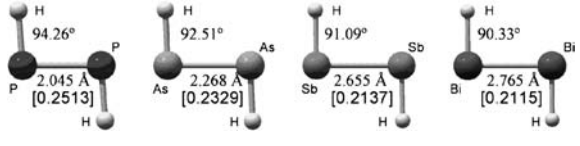


Figure 3. Optimized structural parameters[7] and integrals of overlapping of np orbitals (in parenthesis, HF/Lanl2mb for E; STO-3G for H) of HE=EH (E = P, As, Sb, Bi).

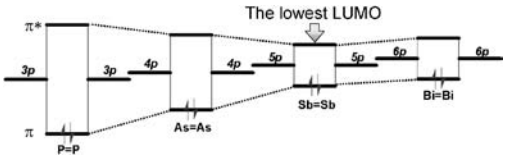


Figure 4. Depiction of interaction of np orbitals.

observed for **1**, **2**, and **3** around $E_{pa} = +1.01$, $+1.02$, and $+0.74$ V vs Ag/Ag^+, respectively (Figure 1b), suggesting that the corresponding radical cations and/or dications of **1**, **2**, and **3** are unstable under these conditions. It is somewhat difficult to draw a conclusion based on such ambiguous experimental data in spite of all our efforts to observe precise oxidation potentials. Theoretical studies on HOMO levels of E=E bonds are somewhat unreliable because the energy levels of their π orbitals are close to those of n_+ orbital (in phase integration of lone pairs).

In summary, we have revealed the redox behavior of the distibene and dibismuthene for the first time using cyclic voltammetry. The systematic comparison of the redox properties of dipnictenes led us to demonstrate an experimental evidence for the relativistic effect of bismuth.

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