ELECTRONIC STRUCTURE OF $H_2B_2O_3$ AND $H_2B_2S_3$, BORON-CONTAINING SYSTEMS

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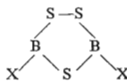Semiempirical MO study of reactivity and physical properties of the title compounds.

This paper presents theoretical considerations on the nature of systems *Ia*, *Ib*, *IIa*, and the derivatives *IIb* and *IIc*. The reactivity of these systems has been examined, in particular the decomposition of *Ia* to B_2O_3 and H_2, and the electronic spectra have been interpreted.
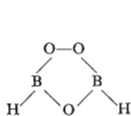
Ia   *Ib*   *IIa*: X = H
IIb: X = n-C_3H_7
IIc: X = Br

The cyclic system *I* has been studied both experimentally and theoretically[1-3]. The sulfur-containing compounds *IIb* and *IIc* have been synthesized recently[4] and their ultraviolet spectra have been recorded[5].

METHODS AND PARAMETRIZATIONS

As the unusual structure of the systems studied makes a quantum chemical interpretation difficult, we have made use of various π electron and all-valence electron methods: besides the standard PPP method[6] (for parameters *cf.* Table I) we employed its modified versions[7] assuming all β integrals nonvanishing and disregarding or accounting for the δ bond polarization. The systems *Ia* and *Ib* have also been calculated by the CNDO/2 method[8] and the CNDO version of Del Bene and Jaffé with and without the configuration interaction[9].

RESULTS AND DISCUSSION

There is some experimental evidence[2] which prefers the planar structure *Ia* to the previously[1] considered trigonal bipyramid structure *Ib*. The CNDO/2 calculations based on the experimental geometries[2,10,11] give the same result, favouring the planar structure by about 11 eV over the *Ib* structure.

We have attempted to interpret the observed decomposition of *Ia* to B_2O_3 and H_2 by adopting a model (Fig. 1) of simultaneous prolongation of the peroxy and B—H bonds (stage A) followed by the H_2 formation and the optimization of the B—O—B angle towards the geometry of B_2O_3 (stage B). The steps considered in the two stages are characterized in Table II and the corresponding energies given by the CNDO/2 method are presented in Fig. 2 (*cf.* Fig. 3). The geometries assumed for the starting and final states of reaction are given in Fig. 1. For the starting state the geometry
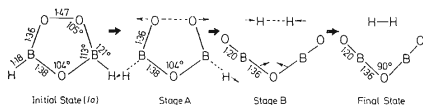

FIG. 1

Model Decomposition Path of $H_2B_2O_3$ (*cf.* Table II)
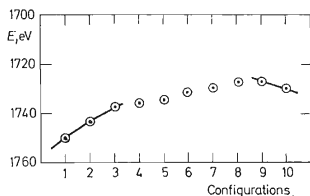   Bond lengths and angles are indicated.

FIG. 2

CNDO/2 Energies of Configurations *1—10* in Decomposition of $H_2B_2O_3$

    The full line passing through the points indicates the region where the SCF approach is justifiable (for numbering of configurations see Table II).
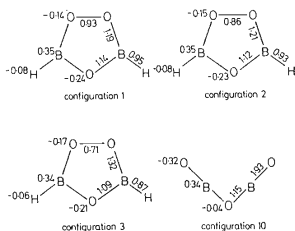

FIG. 3

Charges and Wiberg Bond Indices of Initial Configurations and of the Final State in the *Ia* Decomposition (*cf.* Table II)

TABLE I

Parameters Used in the PPP Calculations

I_μ Valence state ionization potential; A_μ valence state electron affinity; $\beta_{\mu\nu}$ resonance integral between atoms μ, ν which are joined by the chemical bond (its calculation cf. ref.[7]); $r_{\mu\nu}$ average bond length between atoms μ, ν of studied molecules.

Atom (μ)	I_μ, eV	A_μ, eV	$\beta_{\mu\nu}$, eV	$r_{\mu\nu}$, Å	Atom (ν)
B	6·00	− 3·84	−1·88	1·37	O
	6·00	− 3·84	−1·65	1·80	S
	6·00	− 3·84	−0·93	1·87	Br
O	32·90	10·00	−2·42	1·47	O
S	20·27	10·47	−1·15	2·07	S
Br	22·07	14·50	—	—	—

TABLE II

The Model Decomposition Path of $H_2B_2O_3$ (cf. Fig. 1)

(Stage) A configurations $1-8$, (stage) B configurations 9 and 10.

Configuration	∢ OBO, °	r_{BH}, Å	Configuration	∢ OBO, °	r_{BH}, Å
1	113	1·18	6	160	1·60
2	120	1·20	7	170	2·00
3	130	1·25	8	180	3·00
4	140	1·30	9	104	2·00
5	150	1·40	10	90	0·74

TABLE III

Results of the PPP Calculations on IIa and IIc

Molecule	I^a	A^b	μ^c	Electronic transition[d]
IIa	11·28	3·58	3·46	36·19 (−0·81); 40·82 (−0·48); 46·28 (−0·41); 48·56 (−0·10)
IIc	11·07	3·40	3·07	36·33 (−0·81); 40·14 (−0·47); 45·37 (+0·42); 48·61 (−0·11)

[a] Ionization potential, in eV; [b] Electron affinity, in eV; [c] Dipole moment, in Debye; [d] Wavenumbers in 10^{-3} cm^{-1}, logarithms of oscillator strengths in parentheses.

determined experimentally was employed[2]. With the V-shaped[12,13] B_2O_3, the B—O—B angle assumed was obtained by the CNDO/2 energy minimization using the experimental bond lengths[12]. Also with H_2 the bond length given by the CNDO/2 minimization was employed. We are aware of shortcomings of the SCF method in descriptions of a homolytic bond fission for the region of "long" bonds (this is the case with configurations 4—8, cf. Table II), as well as of certain inconsistency given by the adoption of experimental geometries. Nevertheless, Fig. 2 permits us to draw the following qualitative conclusion: since the energy of products (B_2O_3, H_2) is considerably higher than that of the reactants, the path suggested in Fig. 1 appears to be unlikely for the observed fast and spontaneous decomposition of the cycle Ia. The energy difference is so high that the picture can hardly be changed by taking the entropy change into account. Probably a rather different (bimolecular, catalytic, chain) mechanism is involved which seems also to be the case in connection with the photochemical process reported by Grimm and Porter[3]. These authors have measured the tail absorption of Ia at the end of the near ultraviolet region (Fig. 4), therefore light of about 45000 cm^{-1} should be used to cause a photochemical decomposition. The nature of nodal planes and the expansion coefficients in frontier orbitals, however, do not imply a decomposition of Ia to B_2O_3 and H_2 to be more likely on electron excitation.

The observed tail absorption is reproduced best by the classical PPP calculation (Fig. 4). The CI CNDO calculation after Del Bene and Jaffé assigns the first band to the $n \rightarrow \pi^+$ transition (the electron promotion being from the nonbonding AO localized by 64% on the oxygen in the symmetry plane of Ia), but the predicted transition energy (76 kK) is too high. The first ionization potential and electron affinity are predicted by that method to be 13·3 eV and −1·3 eV, respectively, which confirms a high sensitivity of the system to nucleophilic agents. The PPP calculation taking the σ bond polarization into account predicts the first ionization potential to be at 10·6 eV, the electron affinity at 1·2 eV and the dipole moment at 0·94 debye (experimental value is 0·96 debye[2]).
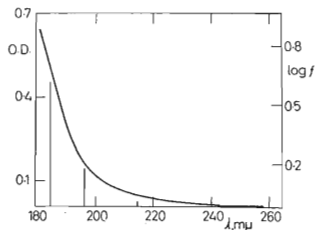

FIG. 4

Electronic Spectrum of Ia

Experimental absorption curve is taken from[3]; theoretical S—S transitions are calculated by the PPP-method. O.D. optical density, log f oscillator strength.
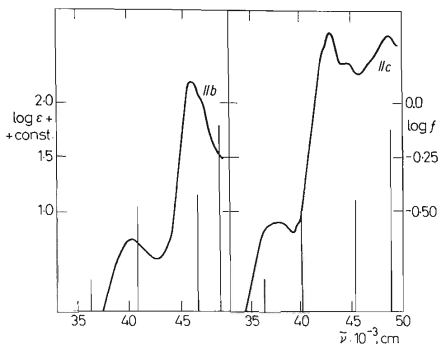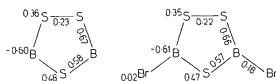
FIG. 6
PPP Charges and Bond Orders of *IIa* and *IIc* Calculated by the PPP Method

The sulfur-containing systems *IIa* and *IIc* have been treated by π electron methods, from which the standard PPP method has proved the most convenient. The results given by that method are presented in Table III. The experimental absorption curves for *IIb* and *IIc* (ref.[5]) are compared, in Fig. 5, with the calculated spectral data. For *IIb* we use the theoretical data of the parent *IIa* system. For the other characteristics there are no experimental data available against which to judge the semiempirical results. Atom charges given by the standard PPP method for the molecules *IIa* and *IIc* are presented in Fig. 6.

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