complexes and supports the theory[15] that bond making plays a more important role in the transition state than does bond breaking.

The one significant observation regarding the rate constant k_3 at 25° is that it is more than 50 times lower than k_1. A large part of the difference is due to the high $\Delta H^{\ddagger}$ for the latter reaction. There is also a considerable difference between the $\Delta S^{\ddagger}$ values, especially if it is considered that in both cases an ionic complex bearing a unit negative charge reacts with water to give the product. In the report of $PtCl_4^{2-}$ aquation studies,[7] it was remarked that the rate of aquation of $PtCl_3(H_2O)^-$ was also much slower than that of $PtCl_4^{2-}$ itself.

Finally, the rate constant k_4, describing the chloride anation reaction of $AuCl_2(H_2O)(OH)$, seems to be quite "normal" for the system with a $\Delta H^{\ddagger}$ value of 15.4 kcal/mole and $\Delta S^{\ddagger}$ = 13 e.u. There is some evidence for the existence of a cationic species, probably $AuCl_2(H_2O)_2^+$, in acid medium (pH 4) as seen from the ion-exchange experiments using a radioactive gold tracer.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
ROYAL HOLLOWAY COLLEGE, ENGLEFIELD GREEN, SURREY, UNITED KINGDOM

The Thermochemistry of Some Phosphorus Halide–Boron Halide Complexes

BY ARTHUR FINCH, P. J. GARDNER, AND K. K. SEN GUPTA

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The standard enthalpies of formation of four complexes of the general formula $PX_3 \cdot BY_3$ (X, Y = Br or I) are reported. These data are discussed in terms of the strength of the donor–acceptor bond. Estimates of this bond strength are: $PI_3 \cdot BI_3$, 22; $PI_3 \cdot BBr_3$, 65; $PBr_3 \cdot BI_3$, 34 and $PBr_3 \cdot PBr_3$, 7 kcal mole^{-1}.

Introduction

The 1:1 complexes formed from boron trihalides and phosphorus trihalides have been studied in connection with their stability with respect to dissociation,[1] their halogen-exchange reactions,[1] and their solid-phase structure.[2,3] Only the complexes involving the heavier halogen atoms are stable with respect to disproportionation or dissociation at room temperature. These complexes are presumably σ bonded from the phosphorus to the boron atom. This is in contrast to the phosphoryl halide–boron halide adducts, which have also been examined thermochemically,[4] where bonding is most probably from oxygen to boron.

Experimental Section

Materials.—Carbon disulfide used as solvent in the syntheses was British Drug Houses AnalaR grade, successively shaken with aqueous potassium permanganate and mercury followed by distillation immediately prior to use. The boron and phosphorus tribromides were supplied by BDH and distilled prior to use. Boron triiodide was supplied by L. Light and Co. and phosphorus triiodide (mp 60–61°, lit.[5] 60.5°) was synthesized by the method of Germann and Traxler[5] and recrystallized from carbon disulfide. Handling was performed in a nitrogen-filled drybox as the compounds are sensitive to both oxidation and hydrolysis.

Syntheses.—All complexes were synthesized by mixing equimolar quantities of the boron and phosphorus halides dissolved in carbon disulfide. The adducts were yellow solids (white, in the case of PBr_3BBr_3) and precipitated from carbon disulfide.

Phosphorus Triiodide–Boron Triiodide.—This was prepared by the method of Mitchell, *et al.*,[2] and vacuum dried; mp 250°. *Anal.* Calcd for PI_3BI_3: I, 94.8. Found: I, 95.7. Halogen analyses were performed by silver nitrate titrations using adsorption indicators.

Phosphorus Triiodide–Boron Tribromide.—This adduct was prepared by the method of Cowley and Cohen[3] and crystallized from carbon disulfide; mp 159–160°; lit.[3] 160°. *Anal.* Calcd for PI_3BBr_3: Br, 36.2; I, 57.6; mol wt, 662. Found: Br, 37.0; I, 56.5; mol wt (by cryoscopy in benzene), 651.

Phosphorus Tribromide–Boron Tribromide.—The method of Tarible[6] was used to synthesize this adduct; mp 59–61°, lit.[1] 61°. *Anal.* Calcd for PBr_3BBr_3: Br, 91.9. Found: Br, 91.0.

Phosphorus Tribromide–Boron Triiodide.—The method of Armington, *et al.*,[7] was used to prepare this adduct; mp 178–182°. *Anal.* Calcd for PBr_3BI_3: Br, 36.2; I, 57.6; mol wt, 662. Found: Br, 37.2; I, 55.7; mol wt (by cryoscopy in benzene), 646.

Calorimetry.—The calorimeter was of the constant-temperature environment type fully immersed in a thermostat maintained at 25 ± 0.01°. A full description may be found elsewhere.[8] The precision and accuracy of the equipment were checked by two standard reactions, one endothermic and the other exothermic. For the dissolution of potassium chloride in water, ΔH ($N = 200$, $T = 25°$) = 4.23 ± 0.03 kcal mole^{-1} (mean of five determinations), and for the neutralization of tris(hydroxymethyl)aminomethane in excess 0.1 M hydrochloric acid, ΔH ($N = 600$, $T =$

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TABLE I

ENTHALPIES OF HYDROLYSIS AND FORMATION OF PX_3BX_3 AND PX_3BY_3 ADDUCTS (KCAL MOLE^{-1})

Compound	N^a	T, °C	$\Delta H_{obsd}(X)$	$\Delta H_f°_T$
PI_3BI_3 (I)	10,692	24.7	−111.2	
	10,985	24.8	−112.3	
	13,271	24.8	−110.7	-44.1 ± 1.2^c
	12,539	25.0	−111.7	
	11,801	24.8	−110.6	
			Mean -111.3 ± 0.85^b	
PBr_3BBr_3 (IV)	8,177	24.7	−132.1	−115.1
	5,031	24.7	−134.6	−112.5
	11,913	24.6	−133.2	-114.1_5
	11,880	24.6	−134.4	-112.9_5
	6,253	25.0	−133.5	−113.7
	7,342	25.0	−132.1	−115.1
				Mean -113.9 ± 1.5^c
			$\Delta H_{obsd}(X, Y)$	
PI_3BBr_3 (II)	14,469	24.6	−64.5	−137.1
	10,874	24.8	−62.4	−139.1
	6,806	24.8	−62.5	−138.9
	4,334	24.7	−62.3	−139.0
	7,871	24.9	−63.6	−137.9
	6,946	24.8	−63.0	−138.4
				Mean -138.4 ± 1.3^c
PBr_3BI_3 (III)	5,716	24.5	−110.8	−90.6
	6,915	24.7	−111.4	-90.0_5
	10,419	24.8	−111.2	−90.3
	12,025	24.9	−110.4	−90.2
	17,174	25.0	−110.7	−90.9
	16,402	24.8	−112.6	−89.0
				Mean -90.3 ± 1.4^c

[a] N is the mole ratio of water to adduct. [b] In this case, ΔH_{obsd} was averaged rather than $\Delta H_f°$ because the values of N were sufficiently close for only one value of $\Delta H_f°(HX \cdot nH_2O)$ to be used. [c] The error in ΔH_{obsd} was taken as the spread; this was combined with the errors in the ancillary data to give the root of sum of the squares as the over-all error.

25°) = −7.15 ± 0.05 kcal mole^{-1} (mean of seven determinations). Literature data for these reactions are: ΔH ($N = 200$, $T = 25°$)[9] = 4.206 kcal mole^{-1} and ΔH ($N = 1330$, $T = 25°$)[10] = −7.104 kcal mole^{-1}, respectively. All enthalpies are quoted in terms of the defined thermochemical calorie, 1 cal = 4.1840 abs joules.

Results

The adducts PI_3BI_3 (I), PI_3BBr_3 (II), PBr_3BI_3 (III), and PBr_3BBr_3 (IV) hydrolyze quantitatively and without undue violence in water according to the equation (c = crystal)

$$PX_3BX_3(c) + (n + 6)H_2O(l) = [H_3PO_3 + H_3BO_3 + 6HX] \cdot nH_2O$$

$$PX_3BY_3(c) + (n + 6)H_2O(l) = [H_3PO_3 + H_3BO_3 + 3HX + 3HY] \cdot nH_2O$$

from which we may write

$$\Delta H_f°[PX_3BX_3(c)] = \Delta H_f°(H_3PO_3 \cdot nH_2O) + \Delta H_f°(H_3BO_3 \cdot nH_2O) + 6\Delta H_f°(HX \cdot nH_2O) - 6\Delta H_f°[H_2O(l)] - \Delta H_{obsd}(X)$$

and

$$\Delta H_f°[PX_3BY_3(c)] = \Delta H_f°(H_3PO_3 \cdot nH_2O) + \Delta H_f°(H_3BO_3 \cdot nH_2O) + 3\Delta H_f°(HX \cdot nH_2O) + 3\Delta H_f°(HY \cdot nH_2O) - 6\Delta H_f°[H_2O(l)] - \Delta H_{obsd}(X, Y)$$

Ancillary Data.—The following ancillary thermodynamic data were used

$\Delta H_f°(H_3BO_3 \cdot 1000H_2O) = -256.5 \pm 0.3$ kcal mole^{-1} (ref 11)

$\Delta H_f°[H_3PO_3(aq)] = -226.5 \pm 0.8$ kcal mole^{-1} (ref 12)

$\Delta H_f°(HI \cdot \infty H_2O) = -13.79 \pm 0.1$ kcal mole^{-1} (ref 13)

$\Delta H_f°(HBr \cdot 300H_2O) = -29.05 \pm 0.09$ kcal mole^{-1} (ref 14)

ΔH_{diln}(HBr and HI) and $\Delta H_f°[H_2O(l)] = -68.315$ kcal mole^{-1} (ref 15)

The enthalpy of dilution of boric acid is small[16] and that of phosphorous acid is unknown but probably within the assigned error. The heats of mixing of H_3PO_3, H_3BO_3, HBr, and HI are ignored.

Discussion

The enthalpy changes of the reactions

$$PX_3(ss) + BY_3(ss) = PX_3BY_3(c) \qquad \Delta H°$$

$$PX_3(g) + BY_3(g) = PX_3BY_3(c) \qquad \Delta H_1$$

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TABLE II

ANCILLARY THERMODYNAMIC DATA FOR PX_3 AND BY_3 AT 298°K (KCAL MOLE^{-1})[h]

	PI_3	PBr_3	BI_3	BBr_3
$\Delta H_f°(g)$	7.05 ± 1.7^g	-30.7 ± 1.5^i	4.70 ± 1.0^a	-48.8 ± 0.22^i
$\Delta H_f°(l)$	...	$\underline{-41.7 \pm 2.0^c}$	...	$\underline{-57.0 \pm 0.2^i}$
$\Delta H_f°(c)$	$\underline{-11.45 \pm 0.85^f}$	-45.2 ± 2.5^d	$\underline{-10.8 \pm 0.8^b}$	-61.6 ± 2.0^e

[a] $\Delta H(c \rightarrow g, BI_3)$ due to Tiensuu.[18] [b] Data from ref 19 modified using current $\Delta H_f°[HI(aq)]$ data. [c] $\Delta H(l \rightarrow g, PBr_3)$ due to van Driel and Gerding[20] at ~128°, estimated at 25° using Watson's equation.[21] [d] Assuming $\Delta H(c \rightarrow l, PBr_3) = \Delta H(c \rightarrow l, POBr_3)$. [e] See ref 4. [f] Data from ref 22 modified using current $\Delta H_f°[HI(aq)]$ data. [g] $\Delta H(c \rightarrow g, PI_3) = \Delta H(c \rightarrow l) + \Delta H(l \rightarrow g)$; latter term extrapolated from vaporization data[15,20] for PBr_3 and PCl_3 and former term put equal to $\Delta H(\text{soln}, PI_3 \text{ in } CS_2)$.[22] [h] Appropriate errors have been assigned where estimates are involved. Underlined data are in standard state. [i] Reference 17.

TABLE III

DERIVED THERMODYNAMIC DATA FOR THE ADDUCTS AT 298°K (KCAL MOLE^{-1})

	PI_3BI_3	PI_3BBr_3	PBr_3BI_3	PBr_3BBr_3
$\Delta H°$	-21.8 ± 1.7	-69.9 ± 1.6	-37.8 ± 2.5	-15.2 ± 2.5
$\Delta H_1{}^a$	-55.8 ± 2.3	-96.6 ± 2.1	-64.3 ± 2.3	-34.4 ± 2.1
$\Delta H(c \rightarrow g)^b$	$34.0\ (\pm 2.0)$	$31.3\ (\pm 2.0)$	$30.0\ (\pm 2.0)$	$27.3\ (\pm 2.0)$
$D(P-B)$	21.8 ± 3.1	65.3 ± 2.9	34.3 ± 3.0	7.1 ± 2.9

[a] We thank a referee for drawing our attention to some current ΔH(transition) data from which we calculate alternative values for ΔH_1: PI_3BI_3, −56.4; PBr_3BBr_3, −31.4; PI_3BBr_3, −96.6; and PBr_3BI_3, −61.7, kcal mole^{-1}. [b] An arbitrary error of ±2.0 kcal mole^{-1} is assigned to this datum.

may be derived using the ancillary thermodynamic data[17-22] in Table II (ss = standard state). Before considering the thermodynamic stability of the adducts, there is evidence[7] that PBr_3BI_3 and PI_3BBr_3 are discrete compounds and cross halogenation does not occur at ambient temperature.

As a first approximation, if the differences between the entropy changes ($\Delta S°$) are ignored, then relative values of $\Delta H°$ measure the thermodynamic stability of the adducts with respect to dissociation into free donor and acceptor.

An alternative method of considering stability, or relative donor-acceptor power, is to estimate the strength of the donor-acceptor bond. This calculation requires the adduct sublimation enthalpies for which a reasonable approximation is

$$\Delta H(c \longrightarrow g, PX_3 \cdot BY_3) = \Delta H(c \longrightarrow g, PX_3) + \Delta H(c \longrightarrow g, BY_3)$$

Two different estimates of the bond dissociation energy of each adduct are given by the equations

$$D(X_3P-BY_3) = -\Delta H(c \longrightarrow g, PX_3 \cdot BY_3) - \Delta H_1$$

$$D^*(X_3P^*-BY_3{}^*) = D(X_3P-BY_3) + E_r(PX_3) + E_r(BY_3)$$

where the asterisk signifies the molecule in its molecular electronic and molecular hybridization state and E_r is the reorganization energy.[23] It has been shown[4] that the inclusion of E_r in a discussion of donor-acceptor properties of the phosphoryl halide-boron halide systems does not significantly affect the conclusions. Hence we shall consider D rather than D^* in the subsequent discussion.

Corroboratory evidence for $D(I_3P-BI_3)$ comes from a recent estimate[24] of 16 kcal for this datum derived from a vibrational analysis of the adduct.

Using the data in Table III and analogous data for phosphoryl halide-boron halide complexes,[4] the following order of donor ability with respect to a fixed acceptor and the converse may be formulated. Relative donor power (or Lewis basicity) with respect to (a) BCl_3 is $POCl_3 > POBr_3$ ($>PBr_3 > PCl_3$), (b) BBr_3 is $PI_3 > POCl_3 > POBr_3 \sim PBr_3$ ($>PCl_3$), and (c) BI_3 is $PBr_3 > PI_3$. Relative acceptor power (or Lewis acidity) with respect to (d) PCl_3 is ($BBr_3 > BCl_3$), (e) PBr_3 is $BI_3 > BBr_3$ ($>BCl_3$), (f) $POBr_3$ is $BCl_3 > BBr_3$, (g) $POCl_3$ is $BBr_3 > BCl_3$, and (h) PI_3 is $BBr_3 > BI_3$. The data in parentheses are deduced from Holmes' description of the stabilities with respect to dissociation of the adducts "PCl_3BCl_3," "PBr_3BCl_3," and PCl_3-BBr_3. The order of acceptor power of boron trihalides relative to organic bases, both in solution[25] and in the gas phase,[26] has been established as $BF_3 < BCl_3 < BBr_3$ and extended to include $BBr_3 < BI_3$ by Cook[27] (this latter work relative to xanthone and by frequency shifts in the vibrational spectrum). This order is followed in (d), (e), and (g) but reversed in (f) and (h). Also, orders of donor power are self-consistent except for (c). The anomalous complexes are $POBr_3BBr_3$, $POBr_3$-BCl_3, PI_3BBr_3, and PI_3BI_3. It is readily seen that PI_3-BI_3 is the most sterically hindered with respect to halogen-halogen interaction (or F and B strain)[28] of the PX_3BY_3 series. Further, the POB angle in the POX_3BY_3 complexes is considerably expanded from

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the tetrahedral angle (probably[29] between 140 and 150°) and examination of molecular models reveals that $POBr_3BBr_3$ is considerably more sterically strained, with respect to POB angle distortion than $POBr_3BCl_3$. This explanation is not entirely satisfactory in that the $POCl_3$ complexes exhibit the usual order. However, with the present limited evidence, it is probably the most realistic.

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CONTRIBUTION FROM THE OLIN MATHIESON
RESEARCH CENTER, NEW HAVEN, CONNECTICUT

Complexes Derived from 1,3-Diiminoisoindoline-Containing Ligands. II. The Stepwise Formation of Nickel Phthalocyanine

BY THOMAS J. HURLEY, MARTIN A. ROBINSON, AND SAMUEL I. TROTZ

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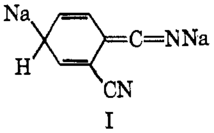
The stepwise formation of nickel phthalocyanine is traced through the initial complexation of 1,3-diiminoisoindoline with nickel chloride, its condensation with 2 additional moles of 1,3-diiminoisoindoline, and the formation of a unique six-membered isoindolinenine complex. This latter compound readily converts to the metalated phthalocyanine upon heating.

Introduction

Since the discovery of phthalocyanine, in 1907,[1] this molecule and its metalated analogs have been the subject of extensive investigation. In spite of the fact that many preparative methods have been uncovered and the physical and chemical properties of these compounds elucidated, the mechanisms of formation are less clearly defined. A pertinent example involves the preparation of sodium phthalocyanine by the action of sodium metal, sodamide, or sodium hydride on a solution of phthalonitrile in butyl alcohol.[2-4] Sander[5] postulated that phthalonitrile and sodium metal react to form the labile addition product I, which then polymerizes with the addition of three phthalonitrile molecules to form the stable tetramer ring system. However, Borodkin[6] was not in agreement with the formulation of the intermediate since the phthalocyanine molecule was not produced in the absence of alcohol. He theorized that, in the example under discussion, it is the sodium butylate that reacts with phthalonitrile, forming an unstable addition product (II), which gives the phthalocyanine derivative either by reaction with other phthalonitrile molecules or through the intermediate isoindolinenine species (III). The course of the reaction in methanol was also studied. When a mixture of sodium metal and phthalonitrile was refluxed in methanol, the metalated phthalocyanine formed. If, however, the temperature was maintained at 40°, then colorless crystals deposited. Isolation and purification of these crystals followed by elemental analyses indicated that the substance was the sodium derivative of methoxyiminoisoindolinenine (IV).[6]



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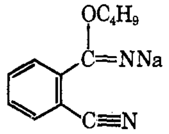

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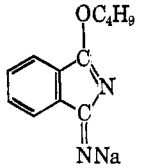

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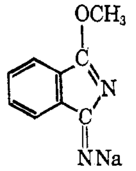

IV

In the work reported here, the stepwise formation of nickel phthalocyanine from nickel(II) chloride and

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