cm^{-1}). Also present in the spectrum of I are absorptions at 2590 (s, BH stretch), 635 (s), and 670 (s) cm^{-1} and a CH_3 stretch (mw) at 2930 cm^{-1}, the remaining bands being broad and not well resolved.

The 32.1-MHz ^{11}B nmr spectrum of pure liquid I consists of two overlapping doublets at low field plus a high-field doublet, all of equal area (δ −7.4 ppm relative to $BF_3 \cdot O(C_2H_5)_2$, J = 140 cps; δ −1.0, $J \approx$ 140; δ +132, J = 195). By analogy with the spectra of parent 2,3,4-$C_3B_3H_7$[9] and its methyl derivatives,[10] the high-field resonance is attributed to the apex B(1)–H group while the low-field doublets are assigned to the nonequivalent B(5)–H and B(6)–H groups. Interpretation of the very large chemical shift of the B(1)–H resonance will not be attempted here except to note that B(1) is the only cage atom not bonded to the metal (a unique situation among known carborane–transition metal complexes). Chemical shifts of several hundred parts per million have been observed in the ^{11}B spectra of paramagnetic iron(III) dicarbollyl complexes,[1b] but such effects have not been reported for diamagnetic carborane–metal π complexes.

The ^1H nmr spectrum of pure I is similar to that of 2-$CH_3C_3B_3H_6$[10] and exhibits single resonances at τ 4.60, 6.80, and 8.94 (relative to external tetramethylsilane) with relative areas of approximately 1:1:3, assigned to C(3)–H, C(4)–H, and CH_3, respectively. The expected quartets arising from three nonequivalent B–H groups are too weak to be clearly identified.

The proposed structure is strongly indicated by the spectroscopic data, volatility, and conditions of synthesis, but an X-ray structure determination is clearly desirable and is planned for the near future. It seems likely that additional transition metal complexes of the small *nido*-carboranes can be prepared, and further studies in this area are in progress.

Acknowledgment. This work was supported by the Office of Naval Research.

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Received July 19, 1969

Heats of Formation of Potassium Perbromate and of the Perbromate Ion, and the Potential of the BrO_3^-–BrO_4^- Electrode

Sir:

The preparation of perbromates by various methods was recently reported.[1,2] There has been some speculation on whether thermodynamic or kinetic effects make it necessary to use extreme oxidizing conditions in preparing bromine in its highest oxidation state.[2] In order to shed further light on this problem, this communication reports the results of our preliminary studies of the heats of formation of potassium perbromate and the perbromate ion.

Potassium perbromate was prepared by a method described elsewhere[2] and repeatedly recrystallized from conductance water before being dried to constant weight at 105° and stored in a desiccator over anhydrous phosphorus pentoxide. The purity of the compound was confirmed by elemental analysis (*Anal.* Calcd: K, 21.37; Br, 43.66; O, 34.97. Found: K, 21.27; Br, 43.67; O, 35.06), determination of oxidizing power (7.98 equiv/mole when reduced to bromide), and comparison of infrared and laser–Raman spectra.[2]

The heat of decomposition of potassium perbromate was determined in an oxygen bomb calorimeter (Parr Instrument Co., Moline, Ill., Catalog No. 1300) equipped with an 18–31° calorimetric thermometer readable to ±0.002° and certified by the National Bureau of Standards. The energy equivalent of the calorimeter was determined in the usual way with 1.00 ml of water in the bomb at 25° and 30.0 atm of oxygen pressure by combustion of benzoic acid pellets, and was found to be −2414.9 ± 12.3 cal/deg. Parr 45C10 standard fuse wire was used to ignite each sample.

Three determinations of the heat of combustion of mineral oil (York Pharmacal Co., Brookfield, Mo.) gave an average value of −11,006 ± 2 cal/g. The bomb was flushed twice with oxygen at 20 atm before filling to a final pressure of 30.0 atm for each calorimetric run. Under these conditions there was no need for a nitric acid correction of the data.

Four measurements have been done to determine the heat of decomposition of crystalline potassium perbromate. Mineral oil was mixed with the $KBrO_4$ in the sample cup of the calorimeter. Experimental conditions were identical with those described for the combustion of the oil. In each case the ignition was violent enough to be audible throughout the room. After each run the bomb washings were collected and aliquots titrated with standard silver nitrate solution at a silver billet electrode to obtain a bromide balance.

It was found that conversions to bromide averaged 96.0% and ranged from 93.0 to 98.5%. It has been shown[2] that while both bromate and perbromate are reduced to bromine by 12 m HBr, only bromate is reduced by dilute HBr. Adjustment of the pH and the addition of excess KI allows the determination of bromate and perbromate by titration with standard thiosulfate solution. Aliquots of bomb washings treated in this way gave a total bromine balance that agreed within 1–2% with that known from the initial weight of $KBrO_4$.

If it is assumed that the present value for the heat of formation of $KBrO_4$(c) is correct, then the heat of decomposition of $KBrO_4$(c) to $KBrO_3$(c) would be −9.7 kcal. This reaction could contribute 2 or 3 cal to the heat of the 93.0% complete reaction. This would introduce a maximum error of 1.5% for this enthalpy value which is the least exact in the series. This error is small compared with the experimental uncertainty of all the measurements which was calculated to be 2.16 kcal/mole at the 95% confidence level,[3] or 9.01% for this individual result.

The bromine balance error was therefore ignored in subsequent data calculations, but was accounted for in computing over-all experimental uncertainty, which was taken as the product of the measurement uncertainty and the uncertainty in the bromine balance.

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Table I. Results of the Experiments to Determine the Heat of Decomposition of $KBrO_4$(c) at 25°

n^a	m_{oil}, g	E_{oil}, cal	E_t,[b] cal	E_{KBrO_4},[c] cal	Δt, °C	q_f, cal	Δn	ΔnRT, cal	ΔH, kcal/mole
0.01049	0.25240	−2777.9	−3059.9	−282.0	1.275	19.1	0.02098	12.4	−25.70
0.008098	0.15392	−1694.0	−1897.6	−203.6	0.787	2.9	0.01620	9.6	−23.96
0.006432	0.12703	−1398.1	−1549.6	−151.5	0.649	17.7	0.01286	7.6	−22.37
0.008341	0.15607	−1717.7	−1927.6	−209.9	0.802	9.2	0.01668	9.9	−23.98
								Av	−24.00
								Std dev	±1.36

[a] Actual number of moles of $KBrO_4$ decomposed as found by bromine balance of bomb washings. [b] Total energy expended in the calorimeter, $E_t = \Delta t E_S - q_f$. [c] Energy due to decomposition reaction: $KBrO_4(c) = KBr(c) + 2O_2$.

Because the silver nitrate titration was the most reliable, it was used to determine the number of moles of potassium perbromate reacting according to the equation

$$KBrO_4(c) = KBr(c) + 2O_2(g) \qquad (1)$$

The results of these experiments are summarized in Table I.

The average value of the heat of decomposition (ΔH_1) of $KBrO_4$ obtained in this research is −24.00 ± 3.24 kcal/mole. This will be taken as the standard value for subsequent calculations since the Washburn corrections[4] for this experiment are small compared with the uncertainty of the measurements. When the standard heat of formation of potassium bromide is taken as $\Delta H_f^\circ = -93.73$ kcal/mole,[5] then $\Delta H_f^\circ(KBrO_4(c)) = \Delta H_1^\circ(KBrO_4(c)) - 93.73$, and $\Delta H_f^\circ(KBrO_4(c)) = -69.73 \pm 3.24$ kcal/mole.

The heat of solution of three samples of dried, reagent grade potassium chloride was used to calibrate a dewar vessel calorimeter. Temperature changes were detected with the same thermometer that was used with the oxygen bomb calorimeter. The heat of each dissolution was obtained from a plot of data tabulated elsewhere.[6]

Three samples of dry crystalline potassium perbromate were dissolved in the same calorimeter.

$$KBrO_4 + aq = K^+(aq) + BrO_4^-(aq) \qquad (2)$$

The perbromate was recovered quantitatively from these solutions and no evidence of decomposition was found. The results of these studies are summarized in Table II.

Table II. Results of the Heat of Solution Measurements on $KBrO_4$(c) at 25°

m_{KBrO_4}, g	m_{H_2O}, g	Δt, °C	$m \times 10^2$ [a]	ΔH, cal	ΔH, cal/mole
1.7230	399.3	−0.246	2.357	109.3	11,609
1.7158	399.8	−0.240	2.345	106.9	11,402
1.7379	399.6	−0.246	2.376	109.3	11,510
				Av	11,507
				Std dev	±104

[a] Molality of the final solution in the calorimeter.

The average value of the heat of solution obtained in this research at 25° is $\Delta H_2 = 11{,}507 \pm 104$ cal/mole. The ionic strengths of the final solutions were about 0.02 m, and an extended form of the Debye–Hückel theory can be used to make the small correction to infinite dilution. The heat of dilution of the electrolyte, ϕ_L, can be approximated at these concentrations as[7]

$$\phi_L = \frac{\nu}{2} A_H |Z_+Z_-| I^{1/2}\alpha - 2.303RT^2\nu_+\nu_-(dB/dT)m \qquad (3)$$

where

$$\alpha = (1 + I^{1/2})^{-1} - \sigma(I^{1/2})/3 \qquad (4)$$

The function $\sigma I^{1/2}$ has been tabulated elsewhere.[8]

Using values tabulated for similar 1:1 electrolytes,[7] $\nu = 2$, $A_H = 688$, $I^{1/2}\alpha = 0.0909$, $2.303RT^2(dB/dT)m = 7.8$, then $\Delta H_2^\circ = \Delta H_2 - 71$ cal, and $\Delta H_2^\circ = 11.44 \pm 0.25$ kcal/mole.

The standard heat of formation of the aqueous potassium ion, $\Delta H_f^\circ(K^+(aq)) = -60.04$ kcal/mole,[9] may now be combined with the heats of formation and solution of $KBrO_4$ to yield the standard heat of formation of the aqueous perbromate ion, $\Delta H_f^\circ(BrO_4^-(aq)) = \Delta H_2^\circ + \Delta H_f^\circ(KBrO_4(c)) - \Delta H_f^\circ(K^+(aq))$ and $\Delta H_f^\circ(BrO_4^-(aq)) = 1.75 \pm 3.49$ kcal/mole.

The entropy of BrO_4^-(aq) can be estimated from similar ion types to be about 45 ± 5 eu. The $\Delta S_f^\circ(BrO_4^-(aq))$ may be calculated from the other known entropies[4] to give $\Delta S_f^\circ(BrO_4^-(aq)) = -87 \pm 5$ eu. This value may be used to calculate the free energy of formation of the perbromate ion, $\Delta G_f^\circ(BrO_4^-(aq)) = 27.7 \pm 5.0$ kcal/mole.

The standard free energy for the couple

$$H_2O + BrO_3^-(aq) = BrO_4^-(aq) + 2H^+(aq) \qquad (5)$$

can now be calculated using auxiliary thermodynamic data[4] and was found to be $\Delta G_5^\circ = 84.0 \pm 5.0$ kcal/mole. This value can be used to estimate the standard potential of the couple, $E_5^\circ = -1.82 \pm 0.10$ V.

It is evident that the thermodynamic barrier to the formation of perbromate is large, and only the strongest oxidizing agents can be used successfully in its preparation. However, there is still no satisfactory thermodynamic explanation for the apparent failure of oxidants such as peroxydisulfate and ozone, with E° values of −2.01 and −2.07, respectively,[10] to cause perbromate formation. This suggests that kinetic effects may still be important in this oxidation.

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Acknowledgments. The authors wish to thank Professor J. W. Cobble for his helpful suggestions and discussions. They also are grateful to Mr. Gary L. Hatch of this department for making analyzed samples of crystalline potassium perbromate available for these studies. The authors also thank Dr. E. H. Appelman for the use of a preprint of his work[2] before publication. This research was supported in part by a grant from the Faculty Research Committee of Kansas State Teachers College.

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Received May 22, 1969

A Paramagnetic Complex of Palladium(II)[1]

Sir:

While the chemistry of Pd(II) deals almost exclusively with square-planar, diamagnetic species, there are reports in the literature of other coordination geometries. To our knowledge, there are no substantiated reports of a tetrahedral species of Pd(II). In this communication we wish to report a paramagnetic complex of Pd(II) which we believe to be tetrahedral.

The ligand N,N-ethylenedimorpholine (EDM), $C_{10}H_{20}N_2O_2$ (Figure 1), has been shown to force tetrahedral coordination geometry with divalent first-row transition metal halides.[2] The reaction of EDM with palladium halides does not lead to such simple results. The reaction of $PdCl_2$ with EDM in acetone gives a yellow complex with the stoichiometry $PdCl_2EDM$ (**1**). The complex is insoluble in an extremely wide variety of solvents and is diamagnetic.[3] Similar results are obtained with $PdBr_2$, prepared through the reaction of $PdCl_2$ with KBr. The insolubility of these complexes is attributed to a polymeric structure with the nitrogens of the EDM moiety bridging adjacent palladiums.

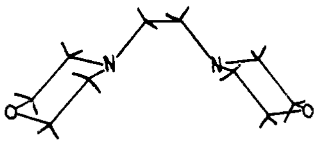

Figure 1.

The reaction of PdI_2 with EDM in acetone leads to no apparent reaction. However, the reaction of K_2PdI_4 (prepared by the reaction of $PdCl_2$ with excess KI) with a 50-fold molar excess of EDM in acetone produces a red solution. Evaporation of the acetone and trituration of the resulting solid with ether gives a product with the approximate stoichiometry PdI_2EDM (**2**). The solid is diamagnetic. When dissolved in acetone **2** originally gives a light red solution (**3**) which darkens over a period of 2 hr to give **4**. Upon addition of a large excess of EDM to **4**, the solution again reverts to a light red color (**5**). Solutions **3** and **4** are diamagnetic while solution **5** is paramagnetic. The magnetic moment is 3.4 ± 0.1 BM at 305°K.

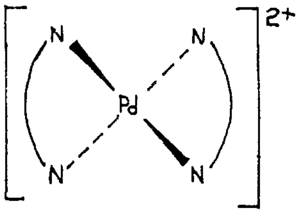

Figure 2.

Conductivity studies show the solutions **4** and **5** are 2:1 electrolytes while solution **3** is a nonelectrolyte. Upon the conversion of **4** to **5** a band grows into the electronic spectrum at 19,200 cm^{-1} (ϵ 200). Kinetic studies on the conversion of **3** to **4** show that the two species are in equilibrium; **3** $\rightleftharpoons$ **4**. The equilibrium constant is 25 ± 5 at 298°K. Addition of a large amount of EDM to either **3** or **4** leads to the appearance of a paramagnetic species in the time required to make the susceptibility measurement, about 2 min. These results lead to the following reaction scheme.

$$\begin{tikzcd}
\underset{\text{solid}}{\mathbf{2}} \arrow[r] & \mathbf{3} \arrow[rr, shift left] \arrow[dr, "\text{EDM}"'] & & \mathbf{4} \arrow[ll, shift left] \arrow[dl, "\text{EDM}"] \\
& & \mathbf{5} &
\end{tikzcd}$$

The species **2**–**5** can be assigned reasonable structures on the basis of the above data and a knowledge of the steric requirements of the ligand. **2** and **3** most probably are square-planar monomeric species. Species **4** can reasonably be assigned a dimeric structure with bridging iodides. Since the paramagnetic species **5** is only formed in the presence of a large excess of EDM, it is reasonable to assign a structure to **5** which contains more EDM than the solid **2**. The observed paramagnetism does not, *a priori*, rule out a square-planar structure[4] but makes it unlikely. The steric requirements of the ligand tend to rule out an octahedral structure.[5] On the basis of the above and the conductivity studies on **5**, a tetrahedral species is postulated (Figure 2). If this is the case a band in the electronic spectrum between 8,000 and 10,000 cm^{-1} might be expected. No band, however, was observed in this region. Upon evaporation of the solvent and trituration with ether, **5** yields **2**. Complex **5** has not been isolated in the solid state at this time, but work on the system is continuing.

The difference in behavior between the chloride and bromide complexes, on the one hand, and the iodide complex, on the other, can be rationalized on the basis of the coordinating power of the species involved and the size of the anion present. Chloride and bromide are better coordinating ligands than iodide. As a result of this the nitrogens of the EDM moiety are better able to compete with the halide ions for the available coordination sites in the case of iodide. The size of the anion is also a factor. With the large iodide ion the

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(1) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 14–18, 1969.

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