involves decomposition of the ICl_2^- formed by a rapid water–complex reaction

$$IpyCl_2 + 2H_2O = IpyOH + H_3O^+ + ICl_2^- \quad \text{(rapid)}$$

$$ICl_2^- \overset{k_1}{\rightleftharpoons} I^- + Cl_2 \quad \text{(rate determining)}$$

Long and Skoog[32] reported a similar aqueous hydrolysis for $I(SCN)_2^-$

$$I(SCN)_2^- \rightleftharpoons I^- + (SCN)_2$$

which is contrary to the mechanism proposed by Creemer and Duncan[33] for thermal and aqueous dissociation of polyhalide ions

$$IX_2^- \rightleftharpoons IX + X^-$$

This reaction rather than $IX_2^- \rightleftharpoons I^- + X_2$ would be expected to predominate in acid solution since X^- is generally a stronger base than I^-. On the other hand, for the pH range of this study, the latter mode is consistent with the above rate-determining proposal and is in line with the view of Long and Skoog.[32]

The second hydrolysis stage, also first order, is unlikely to concern ICl_2^-, and the iodine may form by decomposition of IpyOH

$$IpyOH \overset{k_2}{\rightleftharpoons} IOH + py \quad \text{(rate determining)}$$

$$5IOH = 2I_2 + HIO_3 + 2H_2O \quad \text{(rapid)}$$

These reactions involve the formation of the weak acid HIO, and thus k_2 should be, and is, pH independent. An activation energy of -3.53 kcal mol^{-1} has been calculated for this stage from a k_2 *vs.* $1/T$ plot.

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The Thermodynamic Properties of the Perbromate and Bromate Ions[1]

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The energies of decomposition of $KBrO_4$(c) and $KBrO_3$(c) to KBr(c) plus O_2(g) were measured in a bomb calorimeter. These data were used to derive the standard enthalpy of formation ($\Delta H_f{}^\circ{}_{298.15}$) of $KBrO_4$(c), -68.74 ± 0.14 kcal mol^{-1}, and of $KBrO_3$(c), -86.02 ± 0.12 kcal mol^{-1}. The enthalpies of solution of $KBrO_4$(c) in 2144 mol of water and of $KBrO_3$(c) in 1808 mol of water were measured to be $11,606 \pm 20$ and 9765 ± 42 cal mol^{-1}, respectively, at 25°. The above values were combined with other data to derive standard thermodynamic properties at 25° for the perbromate ion: $\Delta H_f{}^\circ = 3.19 \pm 0.15$ kcal mol^{-1}, $S^\circ = 44.7 \pm 2.0$ cal deg^{-1} mol^{-1}, and $\Delta G_f{}^\circ = 29.18 \pm 0.63$ kcal mol^{-1}; and for the bromate ion: $\Delta H_f{}^\circ = -15.95 \pm 0.13$ kcal mol^{-1}, $S^\circ = 38.6 \pm 0.3$ cal deg^{-1} mol^{-1}, and $\Delta G_f{}^\circ = 4.55 \pm 0.14$ kcal mol^{-1}. The standard electrode potential of the bromate–perbromate couple in acid solution was calculated to be 1.763 ± 0.014 V at 25°. Selected values for the thermodynamic properties of the halates and perhalates of chlorine and iodine are also tabulated. Although the perbromate ion is more oxidizing than either perchlorate or periodate ion, the difference is not great enough to explain why the synthesis of perbromates has been so difficult.

Introduction

The recent discovery of preparative methods[2,3] for perbromic acid and perbromates has ended a long search for these compounds. This study was undertaken to determine some of the key thermochemical data for potassium perbromate and the perbromate ion. Such information should be helpful in exploiting these new and interesting compounds and may help to explain past difficulties encountered in their synthesis. The results of this study also bear on the contention that the highest oxidation states of the nonmetals of the first long period are less stable than the corresponding oxidation states of the preceding and succeeding periods.

Of the possible reactions of $KBrO_4$ suited to calorimetric study, thermal decomposition of the solid was chosen. The simplicity and directness of the reaction

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

leads to a reliable value for the enthalpy of formation of $KBrO_4$(c); the only auxiliary information required is the enthalpy of formation of KBr(c), which is well established. By also determining the enthalpy of solution of $KBrO_4$(c) in water, the standard thermodynamic properties of the perbromate ion could be computed.

Similar measurements were made on $KBrO_3$ to enable comparison of the bromate and perbromate ion stabilities, after finding that the existing thermodynamic data for the bromate ion, which had been obtained by aqueous-reaction calorimetry, were excessively discordant. In addition, it was desired to compare the results for the bromate and perbromate ions with those for the halates and perhalates of iodine and chlorine. Accordingly, a review and selection of data for these additional systems was made. A few calorimetric measurements of the thermal decomposition of $KClO_3$(c) were made to aid us in selecting from among the various values published for the enthalpies of formation of $KClO_3$(c) and $KClO_4$(c).

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

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Experimental Section

Preliminary Observations.—The thermal decomposition of $KBrO_4$ to KBr(c) and O_2(g) proceeds in two steps:[3] decomposition of $KBrO_4$(c) to $KBrO_3$(c) at ~275° and decomposition of $KBrO_3$(c) to KBr(c) at ~390°. The thermal decompositions of $KClO_4$(c) and $KClO_3$(c) to KCl(c) plus O_2(g) have previously been studied by two calorimetric methods: the energy required to raise the sample to its decomposition temperature was supplied either by the combustion[4-6] of an auxiliary substance (benzoic acid) or by a heater.[6,7] A method similar to the former was chosen for this investigation, but graphite rather than benzoic acid was used for the auxiliary source of energy so as to avoid uncertainties associated with the effect of water[8] on the products of reaction.

Calorimetric Systems.—The bomb calorimeter[9] (laboratory designation ANL-R-3) and the platinum-lined combustion bomb[10] (laboratory designation Pt-1) were previously described, as was the method of measuring and recording calorimetric temperatures by quartz-crystal thermometry.[11] The system was calibrated by the combustion in oxygen of National Bureau of Standards benzoic acid (Sample 39i), whose energy of combustion under prescribed conditions was certified as 26,434 ± 3 J g^{-1}. A series of ten calibration experiments yielded a value for ϵ(calor), the energy equivalent of the calorimetric system, of 3413.38 ± 0.21 (std dev) cal deg^{-1}.

The measurements of the enthalpies of solution of $KBrO_4$ and $KBrO_3$ in water were carried out in an LKB-8700 precision calorimetric system.[12] The glass reaction vessel was modified by the addition of an extra reentry well, into which the sensor of a quartz-crystal thermometer was placed. The over-all performance of the solution calorimetric system was tested by measuring the enthalpy of the reaction of "THAM" [tris(hydroxymethyl)aminomethane, National Bureau of Standards Sample 724] with excess 0.1 *M* HCl; seven such experiments at 25° and at a concentration of 5 g of "THAM"/l. yielded $\Delta H_r = -7109.6 \pm 1.1$ cal mol^{-1}, in good agreement with the results[13,14] of other investigators.

Analytical Procedures.—Iodometric methods were employed to assay perbromate, bromate, and chlorate when present in large amounts, *e.g.*, in the calorimetric specimens and in some of the reaction products. Perbromate and chlorate were first reduced with bromide, the former in 12 *M* HBr[3] and the latter in 8 *M* HCl;[15] the resulting Br_3^- solution was diluted with an iodide solution containing NaH_2PO_4 in excess of that required to react with the free acid. Bromate was allowed to react directly with iodide in dilute acid in the presence of a molybdate catalyst.[15] The I_3^- formed in all three reductions was titrated with a $Na_2S_2O_3$ solution that had been standardized against Mallinckrodt Primary Standard grade KIO_3 (manufacturer's assay, 99.95–100.05%).

Very small amounts of bromate and perbromate were determined spectrophotometrically[3] after reduction to Br_3^-; the bromate was reduced by 0.5 *M* HBr, and the perbromate, by 12 *M* HBr.

Water in the calorimetric specimens was determined by heating to 450° in a stream of oxygen. The effluent oxygen was passed through hot silver wool to remove any elemental bromine formed and then through a cold trap at −78° to condense the water. The trapped water was vaporized and measured manometrically at 100°.

The fluoride impurity in the $KBrO_4$ specimen was determined with a fluoride-sensitive electrode (Orion Research, Inc.).

Materials. $KBrO_4$.—The preparation and recrystallization of $KBrO_4$ has been described in detail elsewhere.[3] The material made was dried to constant weight under vacuum at 100°, after which it was analyzed, with the following results: water, 0.029 ± 0.003%; bromate, 0.004 mol %; fluoride, about 0.001 mol %. Spectrographic analysis indicated less than 10 ppm of metallic impurities. The oxidizing power of the material was equivalent to an assay of 99.94 ± 0.03 mol % $KBrO_4$.

At 24.97 ± 0.02°, the solubility of the specimen in water was determined to be 0.2305 ± 0.0002 *M;* the pH of this solution was approximately 5.0.

$KBrO_3$.—Merck Reagent grade $KBrO_3$ was recrystallized from distilled water. The material was dried, ground in an agate mortar, and redried at 120° in a vacuum oven for 3 days. Its water content was determined to be 0.054 ± 0.002%. Spectrographic analysis indicated less than 10 ppm of metallic impurities. The oxidizing power of the material was equivalent to an assay of 100.0 ± 0.05 mol % $KBrO_3$.

$KClO_3$.—Mallinckrodt Analytical Reagent grade $KClO_3$ was recrystallized from distilled water, ground in an agate mortar, and dried for 3 days under vacuum at 120°.

Graphite.—The combustion of National Carbon Co. WCB grade graphite cloth provided the energy necessary to decompose $KBrO_4$, $KBrO_3$, and $KClO_3$, in the calorimetric experiments. The cloth had a nominal purity of 99.9%, and its energy of combustion in oxygen, as determined by a separate series of 11 combustion experiments, was −7853.19 ± 0.53 (std dev) cal g^{-1}.

Oxygen.—Air Reduction Co. USP grade oxygen was purified by passage through successive tubes packed with hot copper oxide, "Ascarite," magnesium perchlorate, and phosphorus pentoxide.

Calorimetric Procedures.—Preliminary experiments had established that decomposition of a 4-g sample of $KBrO_4$, an amount suited to the physical arrangements within the bomb, would require approximately 4000 cal of energy. Thus, approximately 0.5 g of the graphite cloth was weighed into a tared platinum crucible, and the crucible was suspended from a platinum ring in the center of the bomb. The $KBrO_4$ was weighed into another tared platinum crucible, with cover, and this crucible was suspended from a platinum ring directly over the first crucible. The bomb was then assembled, flushed several times with oxygen, and charged to 30 atm pressure with oxygen. The graphite cloth was ignited by the combustion of a graphite thread, one end of which had been in contact with the cloth and the other end with a short length of platinum wire through which electric current was passed. Decompositions of $KBrO_3$ and $KClO_3$ were conducted in an identical manner.

Following each decomposition experiment, the residue in the sample crucible was dissolved in water. The inside of the bomb and the crucible that had contained the graphite were also washed with water to collect any splattered or sublimed material. These solutions were analyzed for unreacted or partially reacted sample, *i.e.*, for perbromate and bromate in the $KBrO_4$ decompositions, for bromate in the $KBrO_3$ decompositions, and for chlorate in the $KClO_3$ decompositions. The pH of each solution was also determined, because the presence of an alkaline solution would suggest that there had been a reaction between the KBr or KCl product and O_2 to produce K_2O_x (or possibly K_2CO_3) and Br_2 or Cl_2; however, no such alkalinity was ever observed. The thermal correction for the formation of K_2O_x or K_2CO_3 is unimportant provided that the amount formed does not exceed 1 μmol per experiment. Preliminary decomposition experiments

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TABLE I

RESULTS OF $KBrO_4$ DECOMPOSITION EXPERIMENTS

$m^i(KBrO_4)$, g	4.00385	4.02331	4.01720	4.01019	4.01991	4.01110
$m^f(KBrO_4)$, g	...	...	0.00139	...	...	0.00143
$m'(KBrO_4)$, g	4.00385	4.02331	4.01581	4.01019	4.01991	4.00967
$m^f(KBrO_3)$, g	0.00005	0.00007	0.00048	0.00003	0.00003	0.00090
m''(graphite), g	0.51022	0.51124	0.51189	0.51204	0.51023	0.51163
Δt_c, deg	1.34629	1.34840	1.34916	1.34905	1.34531	1.34883
ϵ(calor)($-\Delta t_c$), cal	−4595.40	−4602.60	−4605.20	−4604.82	−4592.05	−4604.07
$\Delta E_{\text{contents}}$, cal	−4.73	−4.77	−4.77	−4.76	−4.75	−4.76
$\Delta E_{\text{ignition}}$, cal	0.68	0.89	1.43	0.43	0.69	0.71
ΔE_{gas}, cal	8.17	8.19	8.19	8.19	8.18	8.18
$\Delta E_{\text{graphite}}$, cal	4006.85	4014.86	4019.97	4021.15	4006.93	4017.93
ΔE_{KBrO_3}, cal	...	...	−0.03	...	...	−0.05
$\Delta E_{\text{dec}}°/M$(sample), cal g^{-1}	−145.97	−145.01	−144.53	−144.58	−144.53	−145.16

Av $\Delta E_{\text{dec}}°/M\text{(sample)} = -144.96 \pm 0.23^a$ cal g^{-1}

Impurity correction $= -0.20 \pm 0.02^a$ cal g^{-1}

$\Delta E_{\text{dec}}°/M(KBrO_4) = -145.16 \pm 0.23^a$ cal g^{-1}

[a] The uncertainty given is the standard deviation of the mean.

established that the pH measurement could reliably detect 0.7 μmol of K_2CO_3, which had been deliberately added to $KBrO_3$ samples.

For the enthalpy of solution measurements, the sample of $KBrO_4$ (0.47 g) or $KBrO_3$ (0.51 g) was loaded into a 1-ml glass ampoule. The ampoule was closed with a silicone rubber stopper, sealed with wax, and placed in the reaction vessel containing 99.345 ± 0.002 g of twice-distilled water. At the end of the forerating period, the ampoule was broken and, at the same time, the electrical calibration heater was turned on. The heating rate was chosen to match as closely as possible the endothermal enthalpy of solution; thus the temperature of the calorimeter changed very little during the experiment. A few solution experiments with $KBrO_3$ were performed without electrical heating. Before and after each solution experiment, an electrical calibration experiment was run.

Results

Decomposition Experiments.—The results of six decomposition experiments with $KBrO_4(c)$ and ten with $KBrO_3(c)$ are presented in Tables I and II, respectively. The results are expressed in terms of the defined calorie equal to 4.1840 abs J. The corrections to standard states were applied in the usual manner.[16] The entries in the tables are either self-explanatory or have been explained previously.[16,17]

The following auxiliary data, at 25°, were used in the reduction to standard states: for c_p (cal $\deg^{-1}$ g^{-1}): $KBrO_3$, 0.150;[18] KBr, 0.105;[19] graphite, 0.1697;[20] and Pt, 0.0325;[18] for C_v (cal $\deg^{-1}$ mol^{-1}): O_2, 5.029;[20] and CO_2, 6.883;[20] for the density (g cm^{-3}): $KBrO_4$, 3.08;[21] $KBrO_3$, 3.27; KBr, 2.75; graphite, 2.27; and Pt, 21.45. The heat capacity of $KBrO_4(c)$ was estimated to be 0.15 cal $\deg^{-1}$ g^{-1} based on the assumption that the difference in the molar heat capacities of $KBrO_4(c)$ and $KBrO_3(c)$ is the same as it is for $KClO_4(c)$ and $KClO_3(c)$. The volume of the empty bomb was 330 ml.

Water was the only impurity in both the $KBrO_4$ and $KBrO_3$ specimens for which a thermal correction was required. The water was assumed to be trapped in the crystal lattice and, after the decomposition, to be present as water vapor. The energy of vaporization of this water from the lattice was taken to be the same as that for free water, 9.9 kcal mol^{-1}.

Two calorimetric experiments on the decomposition of $KClO_3(c)$ [the results are not tabulated] yielded values of −83.75 and −83.70 cal g^{-1} for $\Delta E_{\text{dec}}°/M(KClO_3(c))$, from which $\Delta H_{\text{dec}}° = -9.37$ kcal mol^{-1} is calculated.

Solution Experiments.—The results of six experiments on solution of $KBrO_4$ in water, according to the average reaction

$$KBrO_4(c) + 2144H_2O(l) \longrightarrow KBrO_4 \cdot 2144H_2O(l) \quad (2)$$

and seven experiments on solution of $KBrO_3$ in water, according to the average reaction

$$KBrO_3(c) + 1808H_2O(l) \longrightarrow KBrO_3 \cdot 1808H_2O(l) \quad (3)$$

are presented in Tables III and IV, respectively. $\Delta H_{\text{electrical}}$ is the correction for the electrical energy supplied by the heater during the solution experiment, and ΔH_{vapor} is the correction for the vaporization of solvent into the free volume of the ampoule. The correction for the condensation of water vapor in the reaction vessel, owing to the change in ionic strength during solution, was negligible. The impurity correction is for water.

The derived data for $KBrO_4(c)$ and $KBrO_3(c)$ at 25° are presented in Table V. The formation data refer to the reactions

$$K(c) + {}^1/_2Br_2(l) + 2O_2(g) \longrightarrow KBrO_4(c) \quad (4)$$

$$K(c) + {}^1/_2Br_2(l) + {}^3/_2O_2(g) \longrightarrow KBrO_3(c) \quad (5)$$

and were calculated by combining the enthalpies of decomposition and $\Delta H_f°(KBr(c)) = -94.12 \pm 0.1$ kcal mol^{-1}.[19] The following entropies, $S°_{298.15}$, were used to calculate the $\Delta S_f°$ values (cal $\deg^{-1}$ mol^{-1}): $KBrO_4(c)$, 37.6; $KBrO_3(c)$, 35.65;[18] $Br_2(l)$, 36.38;[19]

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Table II

Results of $KBrO_3$ Decomposition Experiments

$m^i(KBrO_3)$, g	4.00594	4.00605	4.00835	4.00708	4.00830	4.00725	2.06399	2.00466	2.00862	2.02140
$m^f(KBrO_3)$, g	0.00013	0.01169	0.00234	0.00017	0.00010	0.00033	0.00033	0.00008	0.25936	0.00004
$m'(KBrO_3)$, g	4.00581	3.99436	4.00601	4.00691	4.00820	4.00692	2.06366	2.00458	1.74926	2.02136
m''(graphite), g	0.51080	0.51105	0.57104	0.57301	0.57408	0.57234	0.51234	0.57044	0.33117	0.50626
Δt_c, deg	1.23888	1.23923	1.37782	1.38284	1.38445	1.38084	1.21182	1.34497	0.78978	1.19743
ϵ(calor)($-\Delta t_c$), cal	−4228.77	−4229.96	−4703.02	−4720.16	−4725.65	−4713.33	−4136.40	−4590.89	−2695.82	−4087.28
$\Delta E_{\text{contents}}$, cal	−3.85	−3.85	−4.30	−4.32	−4.33	−4.31	−3.54	−3.93	−2.28	−3.49
$\Delta E_{\text{ignition}}$, cal	0.66	0.67	0.72	0.79	0.72	0.76	0.78	0.76	0.75	0.75
ΔE_{gas}, cal	7.33	7.31	7.82	7.84	7.85	7.83	5.48	5.89	3.81	5.40
$\Delta E_{\text{graphite}}$, cal	4011.41	4013.37	4484.49	4499.96	4508.36	4494.69	4023.50	4479.77	2600.74	3975.76
$\Delta E_{\text{dec}}°/M$(sample), cal g^{-1}	−53.23	−53.19	−53.49	−53.88	−53.15	−53.50	−53.39	−54.08	−53.05	−53.85

Av $\Delta E_{\text{dec}}°/M$(sample) = -53.48 ± 0.11^a cal g^{-1}
Impurity correction = -0.33 ± 0.01^a cal g^{-1}
$\Delta E_{\text{dec}}°/M(KBrO_3)$ = -53.81 ± 0.11^a cal g^{-1}

[a] The uncertainty given is the standard deviation of the mean.

Table III

Results of $KBrO_4$ Solution Experiments

$m'(KBrO_4)$, g	0.47104	0.46965	0.47122	0.47122	0.47030	0.47023
Δt_c, deg	−0.00134	0.00069	−0.00122	−0.00115	−0.00055	0.00068
ϵ(calor), cal deg^{-1}	105.717	105.218	105.274	105.196	105.272	104.944
ϵ(calor)($-\Delta t_c$), cal	0.142	−0.073	0.128	0.121	0.058	−0.071
$\Delta H_{\text{electrical}}$, cal	29.790	29.790	29.790	29.790	29.790	29.790
ΔH_{vapor}, cal	−0.006	−0.006	−0.006	−0.006	−0.006	−0.006
$\Delta H_{\text{soln}}/M$(sample), cal g^{-1}	63.53	63.26	63.48	63.46	63.45	63.19

Av $\Delta H_{\text{soln}}/M$(sample) = 63.40 ± 0.05^a cal g^{-1}
Impurity correction = 0.02 cal g^{-1}
$\Delta H_{\text{soln}}/M(KBrO_4)$ = 63.42 ± 0.05^a cal g^{-1}
ΔH_{soln}(in 2144 H_2O)^b = 11606 ± 9^a cal mol^{-1}

[a] The uncertainty given is the standard deviation of the mean. [b] The reaction vessel contained 99.345 ± 0.002 g of water.

Table IV

Results of $KBrO_3$ Solution Experiments

$m'(KBrO_3)$, g	0.50907	0.51195	0.50458	0.50842	0.51071	0.51091	0.51078	0.50757
Δt_c, deg	−0.27996	−0.28513	0.00277	0.00079	−0.28408	−0.00290	−0.00015	0.00201
ϵ(calor), cal deg^{-1}	105.595	105.055	105.087	105.308	105.292	105.226	105.230	105.272
ϵ(calor)($-\Delta t_c$), cal	29.562	29.954	−0.291	−0.083	29.911	0.305	0.016	−0.212
$\Delta H_{\text{electrical}}$, cal	...	...	29.790	29.790	...	29.790	29.790	29.790
ΔH_{vapor}, cal	−0.006	−0.006	−0.006	−0.006	−0.006	−0.006	−0.006	−0.006
$\Delta H_{\text{soln}}/M$(sample), cal g^{-1}	58.06	58.50	58.45	58.42	58.56	58.89	58.34	58.26

Av $\Delta H_{\text{soln}}/M$(sample) = 58.44 ± 0.09^a cal g^{-1}
Impurity correction = 0.03 cal g^{-1}
$\Delta H_{\text{soln}}/M(KBrO_3)$ = 58.47 ± 0.09^a cal g^{-1}
ΔH_{soln}(in 1808 H_2O)^b = 9765 ± 15^a cal mol^{-1}

[a] The uncertainty given is the standard deviation of the mean. [b] The reaction vessel contained 99.345 ± 0.002 g of water.

O_2(g), 49.00;[19] K(c), 15.46.[19] The entropy of $KBrO_4$(c) was estimated by assuming that the difference in entropy between $KBrO_4$(c) and $KBrO_3$(c) was identical with the entropy difference between $KClO_4$(c) and $KClO_3$(c) and was assigned an uncertainty of 2.0 cal deg^{-1} mol^{-1}. The atomic weights[22] of bromine, potassium, and oxygen were taken as 79.904, 39.102, and 15.9994, respectively. The uncertainties given in the table are uncertainty intervals[23] equal to twice the combined standard deviations arising from known sources.

The standard state for a solution was taken to be the hypothetical ideal solution at unit molality. The relative apparent molal heat content of a solute in an infinitely dilute real solution is the same as it is in this standard-state solution. Thus, in order to obtain the standard enthalpies of solution of $KBrO_4$ and $KBrO_3$, it is necessary to know the enthalpies of dilution from the measured concentrations to infinite dilution. For $KBrO_3$, the enthalpy of dilution from 1808 H_2O to ∞ H_2O was taken as -19 ± 20 cal mol^{-1} from Parker's compilation,[24] to yield $\Delta H_{\mathrm{soln}}^\circ(KBrO_3(c)) = 9746 \pm 50$ cal mol^{-1}. For $KBrO_4$, the enthalpy of dilution from 2144 H_2O to ∞ H_2O was estimated to be 0 ± 30 cal mol^{-1} by a comparison with the enthalpies of dilution of other sodium and potassium halates and perhalates.[24] Moreover, measurements were made of the enthalpy of solution of $KBrO_4$ at several concentrations more dilute than given in Table III. These measurements, which yielded enthalpies of dilution as the difference in the measured enthalpies of solution, tended to substantiate the above estimate. Thus, $\Delta H_{\mathrm{soln}}^\circ(KBrO_4(c))$ is $11{,}606 \pm 40$ cal mol^{-1}.

Discussion

Perbromate and Bromate Ions.—The values obtained in this investigation for the standard enthalpies of formation of $KBrO_4$(c) and $KBrO_3$(c) are -68.74 ± 0.14 and -86.02 ± 0.12 kcal mol^{-1}, respectively. These data, when combined with the standard enthalpies of solution of the salts and $\Delta H_f^\circ(K^+(aq))$, -60.32 kcal mol^{-1},[20] yield $\Delta H_f^\circ(BrO_4^-(aq)) = 3.19 \pm 0.15$ kcal mol^{-1} and $\Delta H_f^\circ(BrO_3^-(aq)) = -15.95 \pm 0.13$ kcal mol^{-1}. These ionic values are relative to that for hydrogen ion, H^+, for which ΔH_f°, S°, and ΔG_f° are taken equal to zero.

The entropy and Gibbs energy of formation of the perbromate and bromate ions are obtainable from the general-solution equation

$$KX(c) + \infty H_2O(l) \longrightarrow (K^+ + X^-)\cdot \infty H_2O \qquad (6)$$

for which $\Delta G^\circ(6) = -2RT \ln \gamma_\pm m_\pm$ and $\Delta S^\circ(6) = [\Delta H^\circ(6) - \Delta G^\circ(6)]/T$. The data used for $\gamma_\pm$, the mean ionic activity coefficient, and $m_\pm$, the mean ionic molal concentration in saturated solutions of $KBrO_3$ and $KBrO_4$ at 25°, are given in Table VI along with the derived results for S° and ΔG_f°. The activity coefficient for a saturated solution of $KBrO_4$ was estimated by comparison with those of other univalent electrolytes.[25]

TABLE V

DERIVED DATA AT 25°[a]

	$KBrO_4$(c)	$KBrO_3$(c)
$\Delta E_{\mathrm{dec}}^\circ/M$, cal g^{-1}	-145.16 ± 0.54	-53.81 ± 0.36
$\Delta E_{\mathrm{dec}}^\circ$, kcal mol^{-1}	-26.56 ± 0.10	-8.99 ± 0.06
$\Delta H_{\mathrm{dec}}^\circ$, kcal mol^{-1}	-25.38 ± 0.10	-8.10 ± 0.06
ΔH_f°, kcal mol^{-1}	-68.74 ± 0.14	-86.02 ± 0.12
ΔS_f°, cal deg^{-1} mol^{-1}	-94.0 ± 2.0	-71.50 ± 0.20
ΔG_f°, kcal mol^{-1}	-40.71 ± 0.62	-64.70 ± 0.13
$\Delta H_{\mathrm{soln}}^\circ$, kcal mol^{-1}	11.61 ± 0.04	9.75 ± 0.05

[a] The uncertainty given is an uncertainty interval.

Mel, Jolly, and Latimer[26] obtained $\Delta H_f^\circ(BrO_3^-(aq))$ values of -18.70 and -17.82 kcal mol^{-1}, respectively, from the measured enthalpies of the reactions

$$BrO_3^- + 9I^- + 6H^+ \longrightarrow 3I_3^- + Br^- + 3H_2O \qquad (7)$$

$$BrO_3^- + 8Br^- + 6H^+ \longrightarrow 3Br_3^- + 3H_2O \qquad (8)$$

If the result from reaction 8 is updated by the use of selected data from ref 20, the value for $\Delta H_f^\circ(BrO_3^-(aq))$ becomes -14.1 ± 0.6 kcal mol^{-1}. Howard and Skinner[27] recently determined the enthalpy of formation of HI(aq) from studies of reactions in aqueous hydrazine. Their suggested value for $\Delta H_f^\circ(I^-(aq))$ of -13.79 ± 0.03 kcal mol^{-1} appears to be more reliable than previous assessments.[20] Three studies of the enthalpy of reaction of I_2(c) with I^-(aq) to form I_3^-(aq) have been reported.[28-30] We have selected the ΔH for this reaction as determined by Mercer and Farrar[30] (1.074 ± 0.012 kcal mol^{-1}) which yields $\Delta H_f^\circ(I_3^-(aq)) = -12.72 \pm 0.03$ kcal mol^{-1}. Use of this last value along with Howard and Skinner's value for I^-(aq) in reaction 7 yields $\Delta H_f^\circ(BrO_3^-(aq)) = -16.0 \pm 0.9$ kcal mol^{-1}. This result is close to that obtained from reaction 8 and is in excellent agreement with the result obtained by more direct methods in this study.

Perchlorate and Chlorate Ions.—In selecting thermodynamic values for the perchlorate and chlorate ions, two sources of thermal decomposition data are available. Vorob'ev and coworkers[6,7] measured the thermal decomposition of the chlorates and perchlorates of sodium and potassium using electrical heat as the energy source for the decomposition; Gilliland and coworkers[4,5,31] used heat from the combustion of benzoic acid to effect the decompositions. A consistent difference appears in the results obtained by the two sets of investigators, which is indicative of a systematic bias. Our measurement (see Results, above) of the enthalpy of decomposition of $KClO_3$(c) is much closer to that of Gilliland and Wagman,[4] $\Delta H_{\mathrm{dec}}^\circ = -9.16 \pm$

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TABLE VI

THERMODYNAMIC PROPERTIES OF THE HALATES AND PERHALATES AT 25°

Thermodynamic Properties of the Potassium Salt

	$\Delta H_f°$, kcal mol^{-1}	$S°$, cal deg^{-1} mol^{-1}	$\Delta S_f°$, cal deg^{-1} mol^{-1}	$\Delta G_f°$, kcal mol^{-1}
$KClO_3$(c)	−95.08 ± 0.16	34.17 ± 0.20[a]	−81.44 ± 0.20	−70.80 ± 0.17
$KClO_4$(c)	−103.22 ± 0.21	36.10 ± 0.20[a]	−104.00 ± 0.20	−72.21 ± 0.22
$KBrO_3$(c)	−86.02 ± 0.12	35.65 ± 0.20[a]	−71.50 ± 0.20	−64.70 ± 0.13
$KBrO_4$(c)	−68.74 ± 0.14	37.6 ± 2.0(estd)	−94.0 ± 2.0	−40.71 ± 0.62
KIO_3(c)	−119.46 ± 0.10	36.20 ± 0.20[a]	−66.64 ± 0.20	−99.59 ± 0.12
KIO_4(c)	−110.08 ± 0.50	38.1 ± 2.0(estd)	−89.2 ± 2.0	−83.49 ± 0.78

Thermodynamic Properties of Solution

	$\Delta H_{soln}°$, kcal mol^{-1}	$\Delta G_{soln}°$, kcal mol^{-1}	$\Delta S_{soln}°$, cal deg^{-1} mol^{-1}	Solubility, m	$\gamma_\pm$
$KClO_3$(c)	9.89 ± 0.05[b]	1.20 ± 0.05	29.15 ± 0.23	0.700[e]	0.518[c]
$KClO_4$(c)	12.20 ± 0.06[b]	2.67 ± 0.10	31.96 ± 0.40	0.150[e]	0.70[g]
$KBrO_3$(c)	9.75 ± 0.05	1.55 ± 0.05	27.50 ± 0.23	0.488[e]	0.556[c]
$KBrO_4$(c)	11.61 ± 0.04	2.19 ± 0.10	31.59 ± 0.37	0.236	0.67(estd)
KIO_3(c)	6.63 ± 0.05[b]	1.69 ± 0.10	16.57 ± 0.37	0.428[e]	0.56(estd)
KIO_4(c)	15.2 ± 0.2[d]	4.70 ± 0.10	35.22 ± 0.74	0.022[e]	0.86(estd)

Standard Thermodynamic Properties of the Ions

	$\Delta H_f°$, kcal mol^{-1}	$S°$, cal deg^{-1} mol^{-1}	$\Delta G_f°$, kcal mol^{-1}
ClO_3^-	−24.87 ± 0.15	38.8 ± 0.3	−1.90 ± 0.18
ClO_4^-	−30.70 ± 0.20	43.6 ± 0.4	−1.84 ± 0.24
BrO_3^-	−15.95 ± 0.13	38.6 ± 0.3	4.55 ± 0.14
BrO_4^-	3.19 ± 0.15	44.7 ± 2.0	29.18 ± 0.63
IO_3^-	−52.51 ± 0.11	28.3 ± 0.4	−30.20 ± 0.16
IO_4^-	−34.56 ± 0.45	48.8 ± 2.1	−11.09 ± 0.79
K^+	−60.32[f]	24.5[f]	−67.70[f]

[a] Reference 18. [b] Reference 24. [c] Reference 25. [d] A. A. Shidlovskii and A. A. Voskresenskii, *Russ. J. Phys. Chem.*, **39**, 810 (1965). [e] H. Stephen and T. Stephen, "Solubilities of Inorganic and Organic Compounds," Vol. 1, Part 1, Pergamon Press Ltd., Oxford, 1963. [f] Reference 20. [g] W. M. Latimer and J. E. Ahlberg, *J. Am. Chem. Soc.*, **52**, 549 (1930).

0.07 kcal mol^{-1}, than to that of Vorob'ev, Privalova, and Huang,[7] $\Delta H_{dec}° = -11.6 \pm 0.4$ kcal mol^{-1}. Accordingly, the results of Gilliland and coworkers were selected for computing the enthalpies of formation of the chlorates and perchlorates. The value obtained for $\Delta H_f°(ClO_3^-(aq))$ from the $KClO_3$ study is −25.00 ± 0.11 kcal mol^{-1} whereas that obtained from the $NaClO_3$ decomposition is −24.74 ± 0.09 kcal mol^{-1}. The value selected for the enthalpy of formation of the chlorate ion is the average of these two results. The decomposition data of Johnson and Gilliland[5] on $KClO_4$ yield $\Delta H_f°(ClO_4^-(aq)) = -30.89 \pm 0.12$ kcal mol^{-1} and the data of Gilliland and Wagman[31] on $NaClO_4$ yield −30.52 ± 0.11 kcal mol^{-1}. The average of these two results was selected for the perchlorate ion. The auxiliary data used in the above calculations were taken from ref 19, 20, and 24. The values for $KClO_3$(c) and $KClO_4$(c) given in Table VI were chosen to be consistent with the values selected for the ions.

Periodate and Iodate Ions.—The selected value for the enthalpy of formation of the iodate ion is based on the work of Howard and Skinner,[32] who measured the enthalpy of reaction of KIO_3(c) with aqueous hydrazine hydrochloride to obtain $\Delta H_f°(KIO_3(c)) = -119.46 \pm 0.10$ kcal mol^{-1}. This value was used to calculate $\Delta H_f°(IO_3^-(aq)) = -52.51 \pm 0.11$ kcal mol^{-1}. The result is consistent with earlier studies[28,29] of the reduction of IO_3^- with I^- when the earlier data are updated by the use of our previously selected values for the enthalpies of formation of I^-(aq) and I_3^-(aq).

The value selected for $\Delta H_f°(IO_4^-(aq))$ is based on the recent work of Mercer and Farrar,[30] who studied the reduction of $NaIO_4$(c) with I^-(aq). They reported $\Delta H_f°(IO_4^-(aq)) = -38.8 \pm 0.4$ kcal mol^{-1}. This value becomes −34.56 ± 0.45 kcal mol^{-1} when corrected by the use of our selected data for I^-(aq) and I_3^-(aq).

The standard electrode potentials for the generalized reaction

$$XO_3^- + H_2O \longrightarrow XO_4^- + 2H^+ + 2e^- \qquad (9)$$

are obtained from the $\Delta G_f°$ values of Table VI and $\Delta G_f°(H_2O(l)) = -56.687$ kcal mol^{-1} [20] by use of the relationship $E = \Delta G°(9)/nF$. The value for F, the Faraday constant, was taken to be 23,060.9 cal (V equiv)$^{-1}$. The derived electrode potentials are 1.230 ± 0.006, 1.763 ± 0.014, and 1.644 ± 0.018 V, where **X** is Cl, Br, and I, respectively.

These electrode potentials establish that perbromate is a stronger oxidant than either perchlorate or periodate. This irregularity would be even more pronounced if we calculated the iodine potentials in terms of the predominant species in acid solution, H_5IO_6.[33] A similar anomaly appears in the series sulfur, selenium, and tellurium,[33] while an effect of the same nature has

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been invoked to account for the nonexistence of $AsCl_5$.[34] This apparent relative instability of the highest oxidation states of the nonmetallic elements of the first long period has been discussed at length, but the explanations offered have been less than convincing.[34] The effect appears real, but its causes are probably complex.

It is important to realize that perbromate ion is only a little more strongly oxidizing than periodate, and the difference is not, in itself, sufficient to explain why perbromates have been so hard to prepare. However, the perbromate ion is only slowly reduced,[3] indicating the presence of a high activation barrier between Br(V) and Br(VII). This barrier plus the fairly high electrode potential could account for the difficulties encountered in the synthesis of perbromates.

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Mechanism of the Reduction of Vanadium(V) by Hexacyanoferrate(II) in Acidic Aqueous Solution

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The rapid reaction between vanadium(V) and hexacyanoferrate(II) proceeds at least partially *via* an inner-sphere mechanism involving an intermediate postulated to be a vanadium(IV)–iron(III) binuclear complex. The oxidation–reduction step follows a rate equation $-d[V(V)]/dt = k_{ox}[VO_2^+][Fe(II)]$ with $k_{ox} = (1.2 \pm 0.3) \times 10^6\ M^{-1}\ sec^{-1}$ at 8° and 0.50 *M* ionic strength. The intermediate decays in a first-order process independent of all concentrations when VO_2^+ is present in excess. The activation parameters for this process are $\Delta H_0^{\ddagger} = 14.1 \pm 0.3$ kcal/mol and $\Delta S_0^{\ddagger} = -4.4 \pm 1.1$ eu, with $k_0 = 34.1\ sec^{-1}$ at 25° and 0.50 *M* ionic strength. With excess iron(II) the rate equation contains an additional term, first-order in the excess iron(II) concentration, which is subject to several interpretations. The associated activation parameters are $\Delta H_1^{\ddagger} = 6.53 \pm 0.55$ kcal/mol and $\Delta S_1^{\ddagger} = -15.8 \pm 1.9$ eu, with $k_1 = 3.51 \times 10^4\ M^{-1}\ sec^{-1}$ at 25°.

Introduction

The reduction of chromium(VI) by hexacyanoferrate(II) and several other substitution-inert iron(II) complexes has recently been shown to follow a different kinetic pattern than that observed with aquoiron(II) and a number of other reducing agents.[1] In particular, the reductions by the cyanoiron(II) complexes were found to proceed, at least partially, by inner-sphere processes in which the bridging ligand originates on the reducing agent, in contrast to the normal situation where the oxidizing agent supplies the bridging ligand. Since vanadium(V) is isoelectronic and probably also isostructural (VO_2^+ or more probably $V(OH)_4^{+\,2}$ or possibly $V(OH)_4OH_2^{+\,3,4}$) with chromium(VI), the reduction of VO_2^+ by $Fe(CN)_6^{4-}$ has been investigated in an attempt to determine whether the rather novel mechanism in which the reducing agent supplies the bridging ligand in fact has a more general existence.

Experimental Section

Solutions of vanadium(V) perchlorate were prepared by dissolution of Fisher purified vanadium pentoxide or Fisher sodium orthovanadate in an excess of perchloric acid. Solutions were analyzed by titration with iron(II) in approximately 6 *M* sulfuric acid to a ferroin end point. These analyses agreed to within 1% with the concentrations determined from the visible spectra and from the weight of material dissolved. Vanadium(IV) perchlorate solutions were prepared by electrolytic reduction of a V_2O_5 suspension in perchloric acid[5] or by reaction of equivalent amounts of barium perchlorate and vanadyl sulfate (Alfa Inorganics). Barium sulfate was removed by centrifugation. Solutions were analyzed by titration with cerium(IV) sulfate to a ferroin end point in acetic acid solution.[6] The hydrogen ion concentration was determined by titration of the acid released from a column of ion-exchange resin in the H^+ form and correction for the acid displaced by VO^{2+}. Solutions of potassium ferrocyanide, potassium ferricyanide, lithium perchlorate, and perchloric acid were prepared and analyzed as previously described.[1]

The kinetics of the reduction of VO_2^+ by $Fe(CN)_6^{4-}$ were determined with a Durrum stopped-flow spectrophotometer, using previously described techniques.[1] Spectra were measured with a Cary 14 recording spectrophotometer. Spectra of the intermediate were calculated from the difference in transmittance between the intermediate (at the time of initial observation) and the products, using stopped-flow oscillograms measured at various wavelengths with an oscilloscope calibrated to determine transmittance changes exactly. Two limiting interpretations were made of the absorbances calculated in this manner. (1) It was assumed that the entire reaction involves the formation of the intermediate so that the calculated absorbance equals the absorbance of the intermediate. This assumption was used to determine the spectrum shown in Figure 2. (2) Assuming that

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