divided into two classes. The first class includes those reactions which produce an insoluble alkali metal halide by-product. These reactions produce at a 1:1 $MAlH_4 + MgX_2$ stoichiometry an isolatable $XMgAlH_4$ compound and upon addition of more $MAlH_4$ produce $Mg(AlH_4)_2$ in good yield. An exception to this is the MgI_2 case in THF. Here the "$IMgAlH_4$" disproportionates to MgI_2 and $Mg(AlH_4)_2$ immediately so that "$IMgAlH_4$" cannot be isolated from tetrahydrofuran solution. The second class includes those reactions where the alkali metal by-product is soluble. Here an equilibrium is produced according to

$$MAlH_4 + MgX_2 \rightleftharpoons XMgAlH_4 + MX \qquad (20)$$

Magnesium aluminum hydride is not formed even when $MAlH_4$ is added in excess.

Acknowledgments.—We are indebted to the National Aeronautics and Space Administration (Grant NAG-657) and the Office of Naval Research (Contract N0014-67-A-0159-0005) for their support of this work. We also wish to thank Dr. J. A. Bertrand for the use of his X-ray powder diffraction instrumentation.

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The Thermochemistry of Aqueous Xenon Trioxide[1]

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Received September 4, 1969

Solution calorimetric measurements of the enthalpies of the reactions of $XeO_3(aq)$ with HI(aq) and of $I_2(c)$ with HI(aq) have been used to determine a value of 99.94 ± 0.24 kcal mol^{-1} for $\Delta H_f°(XeO_3 \cdot 96.15H_2O)$ at 298.15°K. The electrode potentials of the Xe–XeO_3 couple in acidic solution and of the Xe–$HXeO_4^-$ couple in basic solution were deduced to be 2.10 ± 0.01 and 1.24 ± 0.01 V, respectively.

Introduction

Xenon trioxide, XeO_3, and its derivatives are perhaps the most unexpected of the noble gas compounds. Solid xenon trioxide is explosively unstable and has an enthalpy of formation of 96 ± 2 kcal mol^{-1}.[2] Solutions of XeO_3 in dilute aqueous acid, although they are potent oxidizers,[3] show no evidence of spontaneous decomposition, and because of this, they have received more experimental attention than has the dangerous solid. A reliable quantitative determination of the thermodynamic oxidizing power of these solutions is therefore of considerable practical value. Inasmuch as reactions of aqueous XeO_3 are irreversible, this oxidizing power can only be measured thermodynamically.

The present investigation was undertaken to obtain a precise value for the enthalpy of formation at 298.15°K of aqueous XeO_3, $\Delta H_f°_{298.15}[XeO_3(aq)]$, from calorimetric measurements of the enthalpies of the reactions between $XeO_3(aq)$ and HI(aq) and between $I_2(c)$ and HI(aq) according to the processes

$$XeO_3(aq) + 9I^-(aq) + 6H^+(aq) \longrightarrow Xe(g) + 3I_3^-(aq) + 3H_2O(l) \qquad (1)$$

$$I_2(c) + I^-(aq) \longrightarrow I_3^-(aq) \qquad (2)$$

These results, when combined with auxiliary thermochemical data from the literature, yielded a precise value for $\Delta H_f°(XeO_3 \cdot 96.15H_2O)$.

Experimental Section

Materials. **XeO_3(aq).**—Xenon trioxide was prepared by hydrolysis of XeF_6, which was synthesized by the reaction of xenon with a large excess of fluorine at 300° and about 100 atm pressure.[4] Hydrolysis was effected by passing a stream of argon over the XeF_6 and then through water.[5] The product was purified by treatment with magnesium oxide, hydrous zirconium phosphate, and hydrous zirconium oxide.[3] A rotary evaporator was used to concentrate the resulting solution at room temperature. The XeO_3 assay, 3.1394 ± 0.0006 (standard deviation) equiv kg^{-1} (*in vacuo*), was determined by iodometric titration,[3] using a thiosulfate solution that had been standardized against Mallinckrodt Primary Standard grade KIO_3 (manufacturer's assay, 99.95–100.05%).

Potentiometric titration of the XeO_3 solution indicated the presence of 0.010 equiv kg^{-1} of strong acid, presumably perchloric acid introduced during the purification operations.[3] Measurements with a fluoride electrode (Orion Research, Inc.) revealed the presence of 6×10^{-5} mol kg^{-1} of fluoride. No metallic impurities were detected by emission spectrography.

HI(aq).—Constant-boiling hydriodic acid was prepared by fractionation of reagent grade 48% HI, followed by dilution to the required concentration with argon-saturated, twice-distilled water. The distillation and dilution operations were carried out in an inert atmosphere and in subdued light to prevent premature oxidation of the HI. Two HI solutions were made, the concentrations of which were determined to be 0.197 and 0.177 *M* by titration with standardized NaOH. The H_2O:HI molar ratios for these solutions were calculated to be 279.18 and 310.90, respectively, based on the published densities.[6] The solutions were stored in dark bottles in an inert atmosphere.

I_2(c).—Iodine crystals (Electronic Space Products, Inc., Los

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[1] This work was performed under the auspices of the United States Atomic Energy Commission.

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TABLE I

RESULTS FOR THE REACTION OF XeO_3(aq) WITH 0.197 *M* HI

m'[XeO_3(soln)], g	0.79887	0.76569	0.77061	0.77136	0.79607
m'(XeO_3), g	0.074946	0.071833	0.072295	0.072365	0.074683
Δt_c, deg[a]	0.87170	0.83490	0.84039	0.84119	0.86706
$\bar{\mathcal{E}}$(calor), cal deg^{-1}	105.221	105.204	105.270	105.222	105.260
$\bar{\mathcal{E}}$(calor)($-\Delta t_c$), cal	−91.721	−87.835	−88.468	−88.512	−91.267
ΔH_{vap}, cal	−0.137	−0.132	−0.133	−0.133	−0.137
$\Delta H_r/M$, cal g^{-1}	−1225.66	−1224.60	−1225.55	−1224.97	−1223.89

Av $\Delta H_r/M = -1224.93 \pm 0.32^b$ cal g^{-1}

$\Delta H_r = -219.63 \pm 0.06^b$ kcal mol^{-1}

[a] The average initial temperature of the experiment was 24.56°, and the average final temperature was 25.43°. [b] Standard deviation of the mean.

TABLE II

RESULTS FOR THE REACTION OF I_2(c) WITH 0.177 *M* HI

m'[I_2(c)], g	0.31123	0.31188	0.30946	0.30837	0.30942
Δt_c, deg[a]	0.00107	−0.00025	0.00016	−0.00001	0.00033
$\bar{\mathcal{E}}$(calor), cal deg^{-1}	104.21	100.41	99.05	100.82	103.26
$\bar{\mathcal{E}}$(calor)($-\Delta t_c$), cal	−0.112	0.025	−0.016	0.001	−0.034
$\Delta H_{electrical}$, cal	1.525	1.430	1.430	1.430	1.430
ΔH_{vap}, cal	−0.009	−0.009	−0.009	−0.009	−0.009
$\Delta H_r/M$, cal g^{-1}	4.511	4.636	4.540	4.611	4.483

Av $\Delta H_r/M = 4.556 \pm 0.029^b$ cal g^{-1}

$\Delta H_r = 1.156 \pm 0.007^b$ kcal mol^{-1}

[a] The initial and final temperatures of the experiment were approximately 25.0°. [b] Standard deviation of the mean.

Angeles, Calif.), part of a batch of high-purity (99.99%) material used recently in this laboratory,[7] were pulverized in an agate mortar to facilitate their dissolution in the HI. The pulverization and subsequent operations in which the iodine was exposed were performed in an inert atmosphere.

Calorimetric System.—The calorimetric measurements were carried out in an LKB-8700 precision calorimetric system. The glass reaction vessel was modified for quartz-crystal thermometry as described in ref 8. In addition, the gold stirrer and ampoule-holder assembly was replaced with one constructed of Kel-F plastic. All temperature measurements were made with a Hewlett-Packard Model 2801-A quartz-crystal thermometer.

The overall performance of the calorimetric system was checked by running a series of reactions of "THAM" [tris(hydroxymethyl)aminomethane, National Bureau of Standards Sample 724] with excess 0.1 *M* HCl. Seven experiments at 25° and a "THAM" concentration of 5 g $l.^{-1}$ yielded a value and standard deviation of -7109.6 ± 1.1 cal mol^{-1}, in excellent agreement with the result (-7109.0 ± 0.7 cal mol^{-1}) obtained by Hill, Öjelund, and Wadsö.[9]

Calorimetric Procedures.—The XeO_3 samples were loaded by means of a glass hypodermic syringe into weighed, 1-cm^3 glass ampoules which were immediately sealed off with a propane–oxygen flame and reweighed.

The iodine was placed in similar weighed ampoules in a helium-filled glovebox. These ampoules were stoppered, removed from the box, promptly sealed with a flame, and weighed.

For the XeO_3–HI and I_2–HI reactions, the filled ampoules were placed in the calorimeter vessel, which contained 99.41 ml of hydriodic acid solution at ~20°. After the forerating period, the ampoules were broken. The exothermic reaction with XeO_3 was very rapid, and iodine was released instantaneously, whereas the endothermic reaction with solid I_2 was slow. In the latter experiments, the calibration heater was turned on simultaneously with the breaking of the ampoule, and the rate of heating was adjusted to parallel as closely as possible the reaction taking place in the calorimeter. Thus, the process was pseudo-adiabatic, and the overall temperature rise was very small. For the enthalpy-of-dilution measurements, several ampoules of XeO_3 were broken in the calorimeter vessel, which contained 99.345 g of H_2O.

The mean energy equivalent of the calorimetric system, $\bar{\mathcal{E}}$(calor), was determined by performing an electrical calibration before and after each reaction experiment.

Results

Calorimetric data for the oxidation of HI(aq) by XeO_3(aq) and for the dissolution of I_2(c) in HI(aq) are given in Tables I and II, respectively, and the calculation of $\Delta H_f°(XeO_3 \cdot 96.15H_2O)$ is detailed in Table III. Energy units are given in terms of the thermochemical calorie equal to 4.1840 abs J. The mass of XeO_3 reacted in each experiment was deduced from the mass of XeO_3 solution placed in the ampoules. The correction denoted by ΔH_{vap} in Table I is for the vaporization of water from the solution to saturate the liberated Xe(g); in Table II, the corresponding correction is for the vaporization of water into the free volume of the ampoule. These corrections are based on a value of 10,519 cal mol^{-1} [10] for the enthalpy of vaporization of water. In Table II, $\Delta H_{electrical}$ is the amount of electrical energy dissipated by the heater during the reaction. Thermal effects of impurities in the xenon trioxide, iodine, and hydriodic acid were deemed to be insignificant. For the conversion of the average enthalpies in Tables I and II to molar quantities, the molecular weights of XeO_3 and I_2 were taken to be 179.298 and 253.8088, respectively.

The enthalpy of dilution of $XeO_3 \cdot 96.15H_2O$ in a large excess (~14,000 mol) of water was found experimentally to be 0 ± 30 cal mol^{-1}. The uncertainty is based on what we consider to be the smallest temperature rise that can be reliably detected by our calorimet-

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TABLE III

CALCULATION OF $\Delta H_f{}^\circ{}_{298.15}[XeO_3(aq)]^{a,b}$

1.	$Xe(g) + [3I_3^- \cdot 41.974H^+ \cdot 38.974I^- \cdot 13{,}492.53H_2O] \rightarrow XeO_3 \cdot 96.15H_2O + 47.974(HI \cdot 279.18H_2O)$	$\Delta H_1 = 219.63 \pm 0.18$ kcal mol^{-1} [c]
2.	$3I_2(c) + 43.209(HI \cdot 310.90H_2O) \rightarrow [3I_3^- \cdot 43.209H^+ \cdot 40.209I^- \cdot 13{,}433.68H_2O]$	$\Delta H_2 = 3.47 \pm 0.05$ kcal mol^{-1} [c]
3.	$[3I_3^- \cdot 43.209H^+ \cdot 40.209I^- \cdot 13{,}492.53H_2O] \rightarrow [3I_5^- \cdot 41.974H^+ \cdot 38.974I^- \cdot 13{,}492.53H_2O] + 0.6175H_2(g) + 0.6175I_2(c)$	$\Delta H_3 = 16.84 \pm 0.04$ kcal mol^{-1} [d]
4.	$[3I_3 \cdot {}^-43.209H^+ \cdot 40.209I^- \cdot 13{,}433.68H_2O] + 58.85H_2O(l) \rightarrow [3I_3^- \cdot 43.209H^+ \cdot 40.209I^- \cdot 13{,}492.53H_2O]$	$\Delta H_4 = 0.00 \pm 0.00$ kcal mol^{-1} [d]
5.	$4.765(HI \cdot 279.18H_2O) \rightarrow 2.3825H_2(g) + 2.3825I_2(c) + 1330.29H_2O(l)$	$\Delta H_5 = 65.12 \pm 0.14$ kcal mol^{-1} [e,f]
6.	$43.209(HI \cdot 279.18H_2O) + 1370.59H_2O(l) \rightarrow 43.209(HI \cdot 310.90H_2O)$	$\Delta H_6 = -0.18 \pm 0.02$ kcal mol^{-1} [e]
7.	$3H_2(g) + {}^3/{}_2O_2(g) \rightarrow 3H_2O(l)$	$\Delta H_7 = -204.94 \pm 0.03$ kcal mol^{-1} [g]
	$Xe(g) + {}^3/{}_2O_2(g) + 96.15H_2O(l) \rightarrow XeO_3 \cdot 96.15H_2O$	$\Delta H_f{}^\circ{}_{298.15}(XeO_3 \cdot 96.15H_2O) = 99.94 \pm 0.24$ kcal mol^{-1}

[a] Species in this table are in the aqueous state, unless designated otherwise. [b] Uncertainties are given as twice the overall standard deviation. [c] This work. [d] This result is based on the assumption that, with respect to enthalpies of dilution, I_3^- is identical with I^-. Reaction 3 can then be broken down into the following component reactions: (i) $41.974(HI \cdot 321.45H_2O) \rightarrow 41.974(HI \cdot 312.26H_2O) + 385.74H_2O(l)$, ΔH (from ref *e*) = 0.042 kcal mol^{-1}; (ii) $0.6175H_2(g) + 0.6175I_2(c) + 385.74H_2O(l) \rightarrow 1.235(HI \cdot 312.26H_2O)$, ΔH (from ref *e* and *f*) = -16.88 ± 0.04 kcal mol^{-1}. Similarly, reaction 4 becomes $43.209(HI \cdot 312.26H_2O) \rightarrow 43.209(HI \cdot 310.92H_2O) + 58.85H_2O(l)$, ΔH taken from ref *e*. [e] V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," Report NSRDS-NBS-2, National Bureau of Standards, Washington, D. C., 1965. [f] P. B. Howard and H. A. Skinner, *J. Chem. Soc., A*, 1536 (1966). [g] Reference 10.

ric equipment. Thus, we conclude that $\Delta H_f{}^\circ(XeO_3 \cdot \infty H_2O) = 99.94 \pm 0.24$ kcal mol^{-1}. For the reaction

$$XeO_3(c) + \infty H_2O(l) \longrightarrow XeO_3 \cdot \infty H_2O(aq) \qquad (3)$$

we calculate $\Delta H_{soln} = 3.9 \pm 2.0$ kcal mol^{-1}, based on the literature value[2] for $\Delta H_f{}^\circ[XeO_3(c)]$.

Discussion

The present study represents the only reported determination of the enthalpy of reaction between aqueous XeO_3 and I^-; however, for the enthalpy of reaction of $I_2(c)$ with I^-, three other determinations are available for comparison. Stern and Passchier[11] obtained 0.893 ± 0.012 kcal mol^{-1}; Wu, Birky, and Hepler[12] obtained 1.34 ± 0.2 kcal mol^{-1}; and Mercer and Farrar[13] obtained 1.074 ± 0.012 kcal mol^{-1}. Our result (1.156 ± 0.015 kcal mol^{-1}) is in reasonable accord with the latter two results.

An approximate value for the oxidation potential of aqueous XeO_3 may be derived from the present research. The standard partial molar entropy, $\bar{S}^\circ[XeO_3(aq)]$, has to be estimated. Powell and Latimer[14] have given the following expression for aqueous nonelectrolytes

$$\bar{S}^\circ = S^{int} + {}^3/{}_2R \ln M + 10 - 0.22V_M \qquad (4)$$

In the above equation, S^{int} is the internal (rotational, vibrational, and electronic) molal entropy of the solute, M is the molecular weight, and V_M is the molar volume in the pure liquid state. For the purposes of the present calculation, it has been assumed that the internal entropy is equal to the difference between the total entropy and the translational entropy of XeO_3 in the ideal gas state. Thus

$$S^{int} = S^\circ[XeO_3(g)] - 6.86 \log M - 11.44 \log 298.15 + 2.31 \qquad (5)$$

A value of 68.69 cal deg^{-1} mol^{-1} [15] was taken for $S^\circ[XeO_3(g)]$, making S^{int} 27 cal deg^{-1} mol^{-1}. V_M was assumed to be 39.4 cm^3 mol^{-1}, the same as for solid XeO_3.[16] In this way, we calculate $\bar{S}^\circ[XeO_3(aq)] = 44 \pm 4$ cal deg^{-1} mol^{-1}. We may combine this value with S° values[10] of 40.53 and 49.00 cal deg^{-1} mol^{-1} for Xe(g) and $O_2(g)$, respectively, to obtain $\Delta S_f{}^\circ = -70 \pm 4$ cal deg^{-1} mol^{-1} and $\Delta G_f{}^\circ = 120.8 \pm 1.2$ kcal mol^{-1}, for aqueous XeO_3. Combination of $\Delta G_f{}^\circ[XeO_3(aq)]$ with $\Delta G_f{}^\circ[H_2O(l)] = -56.69 \pm 0.01$ kcal mol^{-1} [10] leads to $E^\circ = 2.10 \pm 0.01$ V for the half-reaction

$$Xe(g) + 3H_2O(l) \longrightarrow XeO_3(aq) + 6H^+(aq) + 6e^- \qquad (6)$$

This is significantly higher than the estimate made by Appelman and Malm,[3] who used an unrealistic entropy for $XeO_3(c)$.

The potential $E_B{}^\circ$ for the corresponding reaction in alkaline solution[3]

$$Xe(g) + 7OH^-(aq) \longrightarrow HXeO_4^-(aq) + 3H_2O(l) + 6e^- \qquad (7)$$

may also be deduced. Appelman and Malm[3] reported an equilibrium constant of $(6.7 \pm 0.5) \times 10^{-4}$ for the reaction

$$HXeO_4^-(aq) \longrightarrow XeO_3(aq) + OH^-(aq) \qquad (8)$$

Combination of this constant with $\Delta G_f{}^\circ[OH^-(aq)] = -37.59$ kcal mol^{-1} [10] yields $E_B{}^\circ = 1.24 \pm 0.01$ V.

Our results indicate that XeO_3 is one of the strongest oxidants in aqueous media. Solutions of XeO_3 are thermodynamically unstable toward oxidation of water; the nonoccurrence of this reaction indicates a high activation barrier which probably arises from the absence of any stable intermediate oxidation states of xenon between XeO_3 and the free elements.

Acknowledgment.—We wish to thank Regina Shiau for assisting with the preparation of the XeO_3, Jerome Lech for the spectrographic analyses, and Thomas L. Cramer for editorial assistance.

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