contained tetramethylsilane (29.0 mg, 0.329 mmol; identified by infrared spectrum).[9] The −196 °C trap contained N_2O and ethane (identified by infrared spectrum).[10]

Reaction of Tetramethylsilane with CO_2. The same procedure was used for the carbon dioxide reactions.

Reaction of Tetramethylsilane with Water. Deionized distilled water (15.5 mg, 0.861 mmol) and tetramethylsilane (99.4 mg, 1.13 mmol) were condensed into a gold metal tube which was sealed and held at 250 °C (4000 atm) for 18 h. The tube was opened and methane was recovered as a noncondensable gas at −196 °C (identified by infrared spectrum). The material which condensed at −196 °C was passed through a trap cooled to −78 °C (solid CO_2/acetone mixture) into a −196 °C trap. The former trap contained a mixture of hexamethyldisiloxane, (identified by infrared spectrum and confirmed by mass spectrum) and water (identified by infrared spectrum). The mixture was then condensed into a tube containing a small amount of anhydrous magnesium sulfate to remove the water from the hexamethyldisiloxane (44.7 mg, 0.276 mmol). The −196 °C trap contained tetramethylsilane (42.0 mg, 0.487 mmol, identified by infrared spectrum).

Reaction of Dimethyldifluorosilane with N_2O. Commercial N_2O (85.3 mg, 1.94 mmol) and Me_2SiF_2 (103 mg, 1.08 mmol) were condensed into a gold metal tube at −196 °C which was sealed and then held at 360 °C (4000 atm) for 18 h. The tube was opened and a noncondensable gas was observed at −196 °C. The condensable material was passed through traps cooled to −196 °C. The condensable material was passed through traps cooled to −117 °C (ethanol slush) and −130 °C (*n*-pentane slush) into a trap cooled to −196 °C. The −196 °C trap contained a mixture of ethane and nitrous oxide (identified by infrared spectrum)[10] and the −130 °C trap contained Me_2SiF_2. The −117 °C trap contained $(MeSiF_2)_2O$ (85.4 mg, 0.480 mmol; 90% conversion based on Me_2SiF_2 employed; bp −38 to −40 °C). Ir: 2995 (w), 1278 (s), 1150 (vs), 980 (vs), 940 (vs), 820 (s) cm^{-1}. Gas-phase mol wt: calcd, 178.2; found, 177.1. Mass spectrum (*m*/*e*): 163 (11), 161 (6), 160 (13), 159 (100), 131 (12), 129 (16), 81 (23), 77 (17), 51 (4), 49 (12), 47 (30), 43 (6).

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Registry No. $(CH_3)_4Si$, 75-76-3; $(CH_3)SiF_3$, 373-74-0; $(CH_3)_2SiF_2$, 353-66-2; $(CH_3)_3SiF$, 420-56-4; $[(CH_3)_3Si]_2O$, 107-46-0; $(MeSiF_2)_2O$, 63089-45-2; N_2O, 10024-97-2; CO_2, 124-38-9; H_2O, 7732-18-5.

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Contribution from Chemistry Division, Argonne National Laboratory,
Argonne, Illinois 60439

Kinetic Study of the Reduction of Neptunium(VII) and Americium(VI) by Bromide Ion in Aqueous Perchlorate Media[1]

J. N. COOPER, M. WOODS, R. SJOBLOM, and J. C. SULLIVAN*

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The oxidation of Br^- to bromine by the actinides, Am(VI) and Np(VII), has been found to proceed by the rate laws $-1/2(d \ln [Am(VI)]/dt) = k_1[Br^-] + k_2[Br^-]^2$ and $-d \ln [Np(VII)]/dt = [Br^-](k_1[H^+] + k_2[H^+]^2)$. The apparent activation parameters are $\Delta H_1^\ddagger = 15.7 \pm 0.1$ kcal/mol, $\Delta H_2^\ddagger = 12.5 \pm 0.1$ kcal/mol, $\Delta S_1^\ddagger = 2.5 \pm 2.7$ eu, and $\Delta S_2^\ddagger = -1.5 \pm 1.6$ eu for Am(VI) and $\Delta H_1^\ddagger = 9.4 \pm 0.3$ kcal/mol, $\Delta H_2^\ddagger = 3.9 \pm 0.5$ kcal/mol, $\Delta S_1^\ddagger = -8.8 \pm 1.1$ eu, and $\Delta S_2^\ddagger = -26.3 \pm 1.8$ eu for Np(VII). The rate laws are accounted for by mechanisms consistent with other oxidations of Br^- and are compared with similar rate laws observed for the dioxo cation, VO_2^+.

Introduction

The previous kinetic studies of the reactions between Np(VII) and a variety of reagents have led to an apparent correlation between the order with respect to $[H^+]$ in the rate law and the pK_a's of the reductants.[2] The present investigation was undertaken, in part, to explore the consequences in the $[H^+]$ dependency when a nonacidic species is the reductant. Additional considerations that prompted this study were to determine the role of hydrogen ion in the oxidation of Br^- by AmO_2^{2+} (a metal ion that undergoes a 1-equiv reduction to the isostructural AmO_2^+), and add to the phenomenological description of the dynamics for the production of Br_2 using 1-equiv oxidants.[3]

Experimental Section

Reagents and Analysis. The preparation and standardization of Np(VII), $LiClO_4$, and $HClO_4$ have been described previously.[4] Stock solutions of Am(III) were prepared as described previously[5] and for each kinetic run Am(VI), free of Am(V) and Am(III), was prepared by ozonizing a dispersion of Am(III) hydroxide in 0.1 M $NaHCO_3$, followed by acidification with $HClO_4$. Extinction coefficients for Am(VI) and Am(V) in 1.0 M $HClO_4$ were established by a photometric titration of Am(VI) with Np(V) according to the reaction

$$\mathrm{Am(VI)} + \mathrm{Np(V)} = \mathrm{Am(V)} + \mathrm{Np(VI)} \qquad (1)$$

following both the decrease in absorbance at 996 nm due to loss of Am(VI) and the increase in absorbance at 980.5 nm after the endpoint due to unreacted Np(V). The resulting extinction coefficients at the principal maxima are listed in Table I.

Table I. Extinction Coefficients of Am(III), Am(V), and Am(VI) at Principal Maxima[a]

	λ, nm	ε, M^{-1} cm^{-1}
Am(III)	503.5	450 ± 4
Am(V)	514	50 ± 1
	718	66 ± 1
Am(VI)	667	30 ± 1
	996	107 ± 2

[a] At 1.00 M $HClO_4$, T = 25 °C.

Reagent LiBr was triply recrystallized from triply distilled water and standardized with silver nitrate using an eosin indicator. Bromine production was estimated with the strong absorption at 267 nm due to Br_3^- formation in large excess Br^- ($\epsilon \sim 3.8 \times 10^4$ M^{-1} cm^{-1}). In all cases, the effective extinction coefficient of Br_3^- was determined independently at the same $[Br^-]$ using the BrO_3^-–Br^- reaction and a standard BrO_3^- solution.

Equipment and Procedures. The computer-interfaced, stopped-flow instrumentation, as well as the basic procedures used in this work, have been detailed previously.[6] The reduction of Np(VII) was followed at 440 nm where the molar extinction coefficient of Np(VII) (ca. 410

M^{-1} cm^{-1}) is much larger than that of any of the other species in the solution. Within a series of consecutive, repetitive experiments, the continuously decreasing $[Np(VII)]_0$ and concomitantly increasing $[Np(VI)]_0$, due to Np(VII) reduction by water, had no effect on the observed rate parameters of the Np(VII) reduction. The Am(VI) reduction was followed by the production of Br_3^- at 330 nm at $[Br^-]$ in large excess over that of the bromine formally produced. Under these conditions, the effective extinction coefficient for the total bromine produced, $M_{Br2} = [Br_2] + [Br_3^-]$, is a constant throughout the course of a given experiment. Unless otherwise noted, all kinetic data were obtained at $\mu = 1.00$ M ($LiClO_4$).

Data Analysis. The observed A_t–t data from individual kinetic experiments were treated with a standard nonlinear least-squares adjustment to fit the first-order rate expression

$$A_t = (A_0 - A_\infty)\exp(-k_{obsd}t) + A_\infty \qquad (2)$$

allowing k_{obsd}, A_0, and A_∞ to be adjustable parameters. Each kinetic experiment was monitored to at least 80% completion, 800–950 data points being collected during this period. Previously described criteria were applied[6] to show that the observed A_t–t data adequately conform to eq 2 and optimized values of A_0 and A_∞ always agreed with observed A_0 and A_∞ values within experimental error. At least six experimental determinations of k_{obsd} were made for each set of reaction conditions, and we report here the mean of these determinations, $\bar{k}_{obsd}$, and the standard deviation, σ_m. Unless otherwise noted, all uncertainties in this report are standard deviations.

Results

Stoichiometry. The stoichiometry of each of the title reactions was established by determining the amount of bromine produced by a known amount of oxidant in the presence of a large excess of Br^-; in each case, account was taken of the small, independently measured absorptivity of the actinide product at 267 nm. In the case of the Am(VI)–Br^- reaction, the determination of the total bromine produced, led directly to the stoichiometric ratio $\Delta Br_2/\Delta Am(VI) = 0.505 \pm 0.007$ consistent with the reaction

$$2Am(VI) + 2Br^- \rightarrow Br_2 + 2Am(V) \qquad (3)$$

In the case of the Np(VII)–Br^- reaction, the initial, fast reduction of Np(VII) was followed by a slower production of bromine, evidently due to reduction of Np(VI) ($t_{1/2}$ ca. 10 min, $[H^+] = 0.09$ M, $[Br^-] = 1.0$ M). The stoichiometry of the overall reaction $\Delta Br_2/(2Np(VII)_0 + Np(VI)_0) = 0.498 \pm 0.004$, whereas the stoichiometric ratio of the reaction between Np(VI) and Br^- was found to be $\Delta Br_2/\Delta Np(VI) = 0.500 \pm 0.004$. These results plus the analysis of the stock Np(VII) solution, (Np(VII) + Np(VI))/Np(VII) = 1.1, are used to calculate the stoichiometric ratio $\Delta Br_2/Np(VII) = 0.496 \pm 0.006$ consistent with the reactions

$$2Np(VII) + 2Br^- \rightarrow Br_2 + 2Np(VI) \qquad (4)$$

followed by

$$2Np(VI) + 2Br^- \rightarrow Br_2 + 2Np(V) \qquad (5)$$

Kinetics. In the case of the Np(VII)–Br^- reaction, the independence of $\bar{k}_{obsd}$ on $[Np(VII)]_0$ and $[Np(VI)]_0$ and the successful fit of the A_t–t data to eq 2 suffice to show that the rate law governing the Np(VII)–Br^- reaction, when Br^- is in pseudo-first-order excess, is first order in [Np(VII)] and zero order in [Np(VI)]. Over the range of $[Br^-]$, 3.5×10^{-3} to 4.2×10^{-2} M and constant $[H^+]$, the $\bar{k}_{obsd}$ values are dependent on the $[Br^-]$; linear least-squares adjustment of the $\bar{k}_{obsd}$–Br^- data to the polynomial

$$\bar{k}_{obsd} = k_a + k_b[Br^-]$$

for seven different $[Br^-]$ leads to the rate coefficients $k_a = 1.7 \pm 2.0$ s^{-1} and $k_b = (3.69 \times 10^3) \pm 80$ M^{-1} s^{-1} at 25 °C, $[H^+] = 0.16$ M. The k_a term is not statistically significant and the rate law is first order in $[Br^-]$.

Table II. Np(VII) Reduction by Br^-

	$\bar{k}_{obsd}/[Br^-] = k_0' + k_1'[H^+] + k_2'[H^+]^2$		
T, °C	k_0', M^{-1} s^{-1}	$10^{-3}k_1'$, M^{-2} s^{-1}	$10^{-4}k_2'$, M^{-3} s^{-1}
1.2	−6.5 ± 14	4.82 ± 0.25	1.45 ± 0.07
12.7	−29 ± 18	8.58 ± 0.30	2.30 ± 0.08
25.0	−116 ± 83	20.3 ± 1.3	2.75 ± 0.30

Table III. Np(VII) Reduction by Br^-–Ionic Strength Dependence[a]

μ, M	$\bar{k}_{obsd}$, s^{-1}	μ, M	$\bar{k}_{obsd}$, s^{-1}
0.30	21.27 ± 0.26	1.50	37.44 ± 1.0
0.70	23.57 ± 0.45	2.00	53.05 ± 1.7
1.00	28.37 ± 0.56		

[a] $[H^+] = 0.16$ M, $[Br^-] = 7.06 \times 10^{-3}$ M, $T = 25$ °C.

In the presence of excess Br^-, the $\bar{k}_{obsd}/[Br^-]$ values are dependent on the $[H^+]$ over the range of $[H^+]$, 0.060–0.526 M; linear least-squares adjustment of the $\bar{k}_{obsd}/[Br^-]$ data to the polynomial

$$\bar{k}_{obsd}/[Br^-] = k_0' + k_1'[H^+] + k_2'[H^+]^2$$

with a minimum of six different $[H^+]$ at each temperature, leads to the coefficients listed in Table II. For each temperature, the k_0' term is statistically insignificant at the 95% confidence level and thus the rate law governing the Np(VII) reduction may be expressed as

$$-d\ln[Np(VII)]/dt = \bar{k}_{obsd} = k_1[H^+][Br^-] + k_2[H^+]^2[Br^-]$$

at each temperature. Nonlinear least-squares analysis[7] fitting all 35 $\bar{k}_{obsd}/[Br^-]$ data points to the Eyring equation

$$\bar{k}_{obsd}/[Br^-] = 2\frac{k_BT}{h}\sum_m[H^+]^m\exp\left(\frac{\Delta S_m^\ddagger}{R}\right)\exp\left(\frac{-\Delta H_m^\ddagger}{RT}\right) \qquad (6)$$

with $m = 1$ and 2, leads to the apparent activation parameters, $\Delta H_1^\ddagger = 9.41 \pm 0.33$ kcal/mol, $\Delta H_2^\ddagger = 3.92 \pm 0.52$ kcal/mol, $\Delta S_1^\ddagger = -8.8 \pm 1.1$ eu, and $\Delta S_2^\ddagger = -26.3 \pm 1.8$ eu. The average percent difference between $\bar{k}_{obsd}$ and the rate parameter calculated from these optimized activation parameters is 3.1 and the maximum deviation is 7.9%. The data in Table III show that at $[H^+] = 0.16$, where about 80% of the reaction proceeds by the k_1 path, $\bar{k}_{obsd}$ exhibits a strong positive salt effect over the range of ionic strengths 0.30–2.0 M ($LiClO_4$).

The reduction of Np(VII) by Cl^- in $HClO_4$ was also observed qualitatively. The reaction was sufficiently slow ($t_{1/2}$ ca. 45 s, $[H^+] = 0.10$ M, $[Cl^-] = 0.18$ M, $\mu = 0.33$ M, $T = 25$ °C) that no attempt was made to evaluate the stoichiometry or kinetics due to the competing Np(VII) reduction by water.

In the case of Am(VI)–Br^- reaction, the A_t–t data were well fit by eq 2 for $[Am(VI)]_0$ ranging from (2.1 to 4.2) $\times 10^{-4}$ M showing that the rate law governing this reaction is first-order in [(Am(VI)] in the presence of a pseudo-first-order excess of $[H^+]$ and $[Br^-]$. Over the range of $[H^+]$, 0.05–0.50 M, $\bar{k}_{obsd}$ is independent of $[H^+]$.

Over the range of $[Br^-]$, 0.0070–0.286 M, $\bar{k}_{obsd}$ values reveal a complex dependence on $[Br^-]$. In 0.50 M $[H^+]$, $\bar{k}_{obsd}$ values were fit by a linear least-squares adjustment to the polynomial

$$\bar{k}_{obsd} = k_0' + k_1'[Br^-] + k_2'[Br^-]^2$$

at each of three different temperatures with a minimum of five different $[Br^-]$. The coefficients obtained are listed in Table IV. All of the k_0' are small and negative; only that at 1.8° is significantly different from zero at the 95% confidence

Table IV. Am(VI) Reduction by Br^- [a]

	$\bar{k}_{obsd} = k_0' + k_1'[Br^-] + k_2'[Br^-]^2$		
T, °C	k', s^{-1}	$10^{-1}k_1'$, $M^{-1}\,s^{-1}$	$10^{-2}k_2'$, $M^{-2}\,s^{-1}$
1.8	−0.63 ± 0.15	3.46 ± 0.51	5.23 ± 0.27
12.8	−0.47 ± 0.60	8.34 ± 1.5	12.83 ± 0.64
25.0	−0.22 ± 0.14	17.3 ± 2.0	36.8 ± 1.9

[a] $[H^+] = 0.50$ M, $\mu = 1.00$ M ($LiClO_4$).

Table V. Rate Parameters for the Reaction of Am(VI) with Br^- [a]

$[Br^-]$, mM	$\bar{k}_{obsd}$, s^{-1}	$[Br^-]$, mM	$\bar{k}_{obsd}$, s^{-1}
$T = 1.8$ °C		$T = 25.0$ °C	
35.8	1.278 ± 0.006	7.15	1.17 ± 0.02
71.5	4.43 ± 0.08	7.15	1.25 ± 0.03
143	15.22 ± 0.18	35.8	10.3 ± 0.2
214.5	31.2 ± 0.9	71.5	31.1 ± 0.9
286	51.0 ± 1.0	71.5	29.6 ± 1.1[b]
$T = 12.8$ °C		107.5	61.7 ± 0.4
		107.5	61.2 ± 0.7
35.8	4.20 ± 0.11	110.8	62.8 ± 1.0[c]
71.5	11.97 ± 0.13	110.8	61.0 ± 1.0[d]
143	38.8 ± 1.2	110.8	61.8 ± 0.9[e]
214.5	78.1 ± 0.9	143	97.4 ± 2.3
286	125.7 ± 1.6	214.5	191.7 ± 4.3

[a] $[Am(VI)]_0$ ranged from (2.1 to 4.5) × 10^{-4} M, $[H^+] = 0.50$ M unless otherwise noted. $\mu = 1.00$ M ($LiClO_4$). λ 330 nm. [b] $[H^+] = 0.05$ M. [c] $[Am(VI)]_0 = 4.2 \times 10^{-4}$, not included in calculation of activation parameters. [d] $[Am(VI)]_0 = 2.10 \times 10^{-4}$, not included in calculation of activation parameters. [e] λ 350 nm.

level, and no obvious physical significance can be attributed to a negative rate parameter for a reaction whose $E°$ is greater than 0.51 V. For this reason the full set of $\bar{k}_{obsd}$ was analyzed with a nonlinear least-squares[7] treatment fitted to the Eyring equation

$$\bar{k}_{obsd} = 2\frac{k_B T}{h}\sum_m [Br^-]^m \exp\left(\frac{\Delta S_m^{\ddagger}}{R}\right) \exp\left(\frac{\Delta H_m^{\ddagger}}{RT}\right) \qquad (7)$$

with $m = 1$ and 2. The apparent activation parameters obtained were $\Delta H_1^{\ddagger} = 15.7 \pm 0.1$ kcal/mol, $\Delta H_2^{\ddagger} = 12.5 \pm 0.1$ kcal/mol, $\Delta S_1^{\ddagger} = 2.5 \pm 2.7$ eu, and $\Delta S_2^{\ddagger} = -1.5 \pm 1.6$ eu. The average percent difference between $\bar{k}_{obsd}$ and the rate parameter calculated with these optimized activation parameters was 4.5 with the two largest deviations being 15.2 and 9.7%, respectively. Elimination of the datum corresponding to the 15% deviation had no significant effect on the activation parameters.

The reduction of Am(VI) by I^- was also monitored qualitatively at $[I^-] = 1.8 \times 10^{-3}$, $[H^+] = 0.05$, and $[Am(VI)] = 1.16 \times 10^{-3}$ M. The reaction was complete within stopped-flow mixing time (ca. 5 ms) and no attempt was made to evaluate the kinetics or stoichiometry of this reaction.

Discussion

Am(VI)–Br^-. The rate law zero order in $[H^+]$ is consistent with results previously found for reduction of Np(VI) and Pu(VI) ions by I^-.[8] The terms first and second order in $[Br^-]$ are similar to those found in the reduction of Ce(IV) by $[Br^-]$[9] and are consistent with the rapid formation of an AmO_2^{2+}–Br^- complex

$$AmO_2^{2+} + Br^- \rightleftarrows O_2AmBr^+ \qquad (8)$$

followed by the parallel steps

$$O_2AmBr^+ \rightarrow AmO_2^+ + Br\cdot \qquad (9)$$

$$O_2AmBr^+ + Br^- \rightarrow AmO_2^+ Br_2^-\cdot \qquad (10)$$

where the oxidations of $Br\cdot$ and $Br_2^-\cdot$ are presumed to follow rapidly.

Table VI. Rate Parameters for the Reaction of Np(VII) with Br^- [a]

$[H^+]$, M	$\bar{k}_{obsd}$, s^{-1}	$[H^+]$, M	$[Br^-]$, mM	$\bar{k}_{obsd}$, s^{-1}
$T = 1.2$ °C[b]		$T = 25$ °C		
0.060	2.375 ± 0.03	0.0605	7.06	8.50 ± 0.09
0.110	4.92 ± 0.06	0.0605	70.6	93.6 ± 1.4
0.211	11.61 ± 0.16	0.110	7.06	17.4 ± 0.4
0.261	15.95 ± 0.15	0.110	7.16	16.7 ± 0.3
0.362	25.9 ± 0.8	0.160	3.53	12.8 ± 0.1
0.462	37.2 ± 0.5	0.160	7.06	28.4 ± 0.6
$T = 12.7$ °C[b]		0.160	14.12	54.5 ± 0.9
		0.160	21.2	82.7 ± 1.4
0.058	3.90 ± 0.05	0.160	28.2	106.6 ± 2.0
0.108	8.14 ± 0.11	0.160	35.3	127.3 ± 3.2
0.158	13.38 ± 0.18	0.160	42.3	160.3 ± 4.6
0.208	19.45 ± 0.16	0.210	7.16	38.6 ± 0.6
0.258	26.55 ± 0.5	0.261	7.06	50.8 ± 0.6
0.308	33.6 ± 0.9	0.310	7.16	63.5 ± 0.6
0.357	41.9 ± 0.8	0.362	7.06	75.8 ± 1.7
0.456	61.1 ± 0.6	0.410	7.16	90.8 ± 0.5
		0.421	7.06	93.2 ± 1.9
		0.462	7.06	104.6 ± 3.6
		0.510	7.16	120.8 ± 2.0
		0.513	7.06	134.3 ± 2.0
		0.526	7.06	126.6 ± 3.5

[a] $[Np(VII)]_0$ ranged from (6.2 to 8.0) × 10^{-4} M, $\mu = 1.00$ M ($LiClO_4$), λ 440 nm. [b] $[Br^-]_0 = 7.06 \times 10^{-3}$ M.

Alternatively the term first order in $[Br^-]$ may be interpreted as arising from an outer-sphere process

$$AmO_2^{2+} + Br^- \rightarrow AmO_2^+ + Br\cdot \qquad (11)$$

The observed $\Delta G^{\ddagger}$ for the term first order in $[Br^-]$ is 14.96 kcal/mol, whereas the thermodynamic properties of the $Br\cdot$ radical, as estimated by Margerum,[10] lead to a $\Delta G°_{Am(VI)-Br^-}$ for reaction 11 of 10.61 kcal/mol. Using this latter value to estimate $K_{Am(VI)-Br^-}$, and exchange rate constants of $k_{Am(V)-Am(VI)} = 4.7$[11] and $k_{Br^--Br} = 10^{10}$,[12] the Marcus cross relation[13] yields an estimated rate constant for eq 11 of $k_{Am(VI)-Br^-} = 4.6$ $M^{-1}\,s^{-1}$ in poor agreement with the observed $k_1' = 173$ $M^{-1}\,s^{-1}$. These results are consistent with (but do not provide compelling evidence for) the interpretation that an outer-sphere electron transfer mechanism does not provide a major contribution to the overall rate of this reaction, in contrast to the results obtained for Np(VI) and Pu(VI) reduction by I^-.[8]

Np(VII)–Br^-. The rate law first order in the reducing agent is unexceptional in Np(VII) reductions, having been observed in the case of all other monomeric reducing agents studied.[2] What is unusual is the appearance of a kinetically significant term, second order in $[H^+]$. In other oxidations of Br^-, for example, by Co(III),[14] MnO_4^-,[15] Ce(IV),[9] and peroxy acids,[16] involvement of $[H^+]$ in the rate law has been attributed to protolytic equilibria involving the oxidizing agent or an oxidant–reductant complex. It has been observed that, in other reductions of Np(VII), where H^+ is not available from an acidic moiety in the reductant, it is necessarily provided externally by H_2O or free H^+. In general the order of the rate laws with respect to $[H^+]$ increases roughly with the pK_a of the reductant. The zero-order $[H^+]$ dependence for reduction by H_2SeO_3 ($pK \sim 2.6$),[17] the first-order $[H^+]$ dependence for reduction by water ($pK \sim 15.7$),[4] and the second-order dependence for reduction by the nonacidic Br^- ion are consistent with this overall pattern.

It is interesting to note that substantially the same pattern of $[H^+]$ dependence occurs in the reductions of V(V), usually written VO_2^+. Thus for reductions of VO_2^+ inverse order $[H^+]$ dependences are observed only for strongly acidic cations such as Ti(III)[18] and V(III).[19] Less strongly acidic cations such as V(II)[20] and Fe(II)[21] show zero- and first-order $[H^+]$ dependence whereas second-order dependences are observed only in the case of essentially nonacidic reducing agents such as I^-[22] and Br^-.[23] Apparently the same maximum requirement for two H^+ in the activated complex obtains for both VO_2^+ and NpO_2^{3+} in reductions by nonacidic species.

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Registry No. Am(III), 2541-46-4; AmO_2^+, 22878-02-0; AmO_2^{2+}, 12323-66-9; NpO_2^{3+}, 33702-71-5; Br^-, 24959-67-9; H^+, 12408-02-5.

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Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Temperature Dependence of the Extinction Coefficient of Mercuric Iodide Vapor. Heat of Sublimation and Vapor Pressure of Solid HgI_2

BERNARD M. ABRAHAM and ANTHONY JEANNOTTE*

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The temperature dependence of the extinction coefficient of HgI_2 vapor has been determined at a single wavelength of 342 nm where the data can be represented by the equation $\epsilon(\lambda\ 342\ \text{nm}, T) = (0.803 \pm 0.008)T/K - (273.1 \pm 4.1)$. Measurements of the absorbance of the vapor in equilibrium with the solid as a function of temperature yielded the following vapor pressure equation, where the pressure is in millimeters of Hg (reduced to 273.15 K and standard gravity) and the temperature is in Kelvins: $\ln P = -(9959 \pm 71)K/T + (23.28 \pm 0.16)$, $417 \leq T \leq 509$. The heat of sublimation calculated from this equation is 82.80 kJ mol^{-1}. The linear dependence of $\ln P$ vs. $1/T$ also establishes Beer's law for the vapor.

Introduction

It is possible in practice as well as in principle to thermally decompose water well below 3500 K by means of a properly selected sequence of chemical reactions.[1-3] The sequence may be regarded as a machine,[4] powered by heat, which does work on water to decompose it into the elements. Since the reagents are components of the machine, they must be regenerated essentially without loss on traversing the cycle. One such sequence, designated ANL-4, is currently under investigation in the Chemistry Division of the Argonne National Laboratory.[5]

The hydrogen product in the cycle ANL-4 is generated by the reaction of mercury vapor with vaporized ammonium iodide. In preparing to study the kinetics of this reaction, spectroscopically, we found it necessary to reexamine the temperature dependence of the extinction coefficient of HgI_2 vapor. During the course of these measurements we have also been able to determine the vapor pressure of solid HgI_2 and the heat of sublimation. It is these results we report at this time.

The absorption spectrum of HgI_2 vapor has been found by several investigators[6,7] to be continuous with a band commencing at about 400 nm and rising to a maximum at 265 nm. It has also been established that HgI_2 does not thermally decompose in the temperature range of interest to us, viz., up to 775 K.[8] A complicating feature, however, is the temperature dependence of the extinction coefficient.[9] This would present no problem if an experiment were conducted at constant temperature provided Beer's law is obeyed. Herczog and Wieland[9] determined the temperature dependence of the extinction coefficient of HgI_2, but they did not, at the same time, establish the validity of Beer's law for the vapor; they assumed that

$$\log (I_0/I) = \epsilon(\lambda,T)Cl \qquad (1)$$

where C is the concentration of HgI_2 in moles/liter, l is the optical path length in centimeters, and $\epsilon(\lambda,T)$ is the wavelength–temperature-dependent extinction coefficient. Although there is little reason to doubt the soundness of this procedure, it was essential for our purposes to establish experimentally that the monitored species (HgI_2) does indeed follow Beer's law.

Experimental Section

A schematic diagram of the optical train and ancillary equipment, which were assembled to perform these measurements, is presented in Figure 1. Both the xenon arc and the single monochromator were Bausch and Lomb units; the monochromator covered the spectral range 300–700 nm in 5-nm scale graduations. To reduce any long wavelength light which may have been scattered through the exit slit of the monochromator, a UV filter (λ_{max} 360 nm, fwhm = 50 nm) was positioned at the exit slit. The two aspheric condensing lenses produced a nearly parallel beam which was chopped at 325 Hz. This beam was then split into a reference, I_0', and a sample beam, I, by the optically flat quartz plate. The reference beam was directed to a silicon photodetector as was the sample beam after it had traversed the furnace (sample region). The voltage generated by the respective detectors was amplified and phase detected by the PAR lock-in amplifiers and finally fed into a Hewlett-Packard digital voltmeter operating in the ratio mode. The voltmeter output yielded the ratio