interesting feature of the spectra is the "crossover" which occurs with respect to the highest frequency mode. In $Se_2Cl_6^{2-}$ the highest frequency absorption seen is a Raman-active mode, $\nu_1(A_{1g})$, while for $Se_2Br_6^{2-}$ infrared-active mode or modes lie at highest frequency. This sort of inversion has been observed previously in compounds containing linear X-M-X [M = Se, Te; X = Cl, Br] systems[10,18] and supports the existence of such groupings in the present case.

Solution Structure. Solution Raman spectral data for $(C_2H_5)_4NSeCl_3$ and $(C_2H_5)NSeBr_3$ may be found in Table IV while the solid-state and acetonitrile solution spectra of $(C_2H_5)_4NSeCl_3$ are reproduced in Figure 1. A comparison of the observed frequencies and relative intensities for the trihaloselenate(II) salts in solution *vs.* the solid state shows that substantial changes in the number of peaks observed and the absorption frequencies occur. In addition, conductivity data indicate that the trihaloselenate(II) salts behave as 1:1 electrolytes in nitromethane solution. The Raman spectra and conductivity data may be easily interpreted if it is assumed that the dimeric anion in the solid state dissociates in solution (eq 5). The SeX_3^- ion so produced is expected to

$$[Se_2X_6]^{2-}(s) \rightarrow 2[SeX_3]^-(solv) \qquad (5)$$

be a T-shaped molecule (C_{2v}) exhibiting six fundamental absorptions, 3 A_1, 2 B_1, and B_2. Of these, three high-frequency modes are expected, 2 A_1 and B_1.

Despite solubility problems, the observed spectrum for $(C_2H_5)_4NSeCl_3$ in nitromethane and acetonitrile (Figure 1) solution corresponds closely to that expected assuming the presence of $[SeCl_3]^-$(solv). Two polarized and one depolarized absorptions are seen in the Se-Cl stretching region and are reasonably assigned to the unique Se-Cl (ν_1, A_1), symmetric Cl-Se-Cl (ν_2, A_1), and antisymmetric Cl-Se-Cl (ν_4, B_1) stretching modes, respectively (Table IV). The remainder of the observed peaks are assigned to the tetraethylammonium ion.

Solubility problems were more severe for $(C_2H_5)_4NSeBr_3$ and spectral data could only be obtained in nitromethane solution. Nevertheless it is readily seen (Table IV) that a much simpler spectrum is observed in solution relative to the solid state and that the observed solution spectrum is readily interpreted in terms of a T-shaped C_{2v} structure.

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Registry No. $(CH_3)_4NSeCN$, 31386-68-2; $(C_2H_5)_4NSeCN$, 42531-78-2; $(C_3H_7)_4NSeCN$, 42531-79-3; $(C_4H_9)_4NSeCN$, 7677-15-8; $(CH_3)_4NSeCl_2CN$, 42531-60-2; $(C_3H_7)_4NSeCl_2CN$, 42531-61-3; $(C_3H_7)_4NSeBr_2CN$, 42531-62-4; $(C_2H_5)_4NSeCl_3$, 42531-63-5; $(C_2H_5)_4NSeBr_3$, 42531-64-6.

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Contribution from the Department of Chemistry,
University of Rhode Island, Kingston, Rhode Island

Thermal Decomposition of the Higher Oxides of Cesium in the Temperature Range 320-500°[1]

S. P. BERARDINELLI, Sr.,* and D. L. KRAUS

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The thermal decomposition of solid cesium superoxide was investigated over the temperature range 320 to 440° and covered the composition range $Cs_2O_{2.06}$ to $Cs_2O_{3.96}$.[2] As a result of this work it is concluded that there is no solid solution formation, or sesquioxide formation, over the indicated composition range. The reaction path was experimentally determined to be: $2CsO_2(s) = Cs_2O_2(s) + O_2(g)$. The values for $\Delta u°$, $\Delta H°$, $\Delta S°$, and K_p were calculated at the mean temperature of 380°. Also, the thermal decomposition of cesium peroxide was studied between 320 and 500°, covering the composition range $Cs_2O_{1.15}$ to $Cs_2O_{1.94}$. The reaction path may be written as: $2Cs_2O_2(s) = 2Cs_2O(s) + O_2(g)$. The values of $\Delta u°$, $\Delta H°$, $\Delta S°$, and K_p were calculated at the mean temperature of 410°.

I. Introduction

During the thermal decomposition of alkali metal superoxides, oxygen is reversibly released with the formation of a lower oxide.[3-8] Some investigators have claimed that the alkali metal sesquioxide is formed as an intermediate.[9-11] However, recent thermal decomposition studies have shown the process to proceed without sesquioxide formation. The alkali metal superoxide decomposes first to the peroxide then to the monoxide.[5-8]

The thermal decomposition of cesium superoxide at elevated

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(1) Based on work in partial fulfillment of the requirements of the Ph.D. degree of S. P. Berardinelli, Sr.

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temperatures has not been well characterized. The present investigation is concerned with the decomposition process at temperatures up to 440° and various thermodynamic parameters in this region.

II. Experimental Section

Methods. Cesium metal (99.9+% pure), was used to synthesize cesium superoxide. The oxidation process was carried out using 99.9% oxygen. The superoxide synthesis apparatus was similar to that of Morris.[8] The procedure involved the stepwise oxidation of the pure cesium metal to the superoxide. Preliminary to each step, the sample was ground to a fine powder in a controlled atmosphere box using dry nitrogen. Approximately four oxidation steps were necessary to achieve cesium superoxide which analyzed between 85 and 95% CsO_2. The remaining percentage was found to be peroxide. The method of Seyb and Kleinberg was used to analyzed first for superoxide and then for peroxide.[12]

The thermal decomposition was accomplished in a vacuum system capable of pressures less than 1.0×10^{-4} mm and consisted of two McLeod gages, mercury manometer, Cartesian manometer, and reaction chamber. The McLeod gages measured pressures in the range 1.0×10^{-4} to 2.66 mm. The Cartesian manometer was used in the range 2.66 to 10.00 mm with an accuracy of ±0.03 mm. Pressures greater than 10.00 mm were read on the manometer. The reaction chamber was equipped with an *in situ* balance to follow the sample weight with an accuracy of ±0.1 mg.[7] The sample holder was a pure single crystal of magnesium oxide. The temperatures were both indicated and controlled to within ±2.5° by means of a calibrated Leeds and Northrup Speedomax H unit.

About 0.8 g of CsO_2 was placed in sample holder and the system pumped to remove moisture. Trace amounts of moisture have been shown to cause catalytic decomposition of the superoxide.[7] Equilibrium oxygen pressures were measured every 20° from 320 to 400°. The equilibrium oxygen pressure at each temperature was taken as the average of approximately seven cathetometer readings. Later, runs were made at 420 and 440°. This was necessary since cesium superoxide is reported to melt at 432° according to Blumenthal and Centnerszwer[9] but at 450° according to Vol'nov.[4] In the course of this investigation, CsO_2 was found to melt at 450°. The time required to attain equilibrium varied between 5 and 7 hr, the longer times being required at lower temperatures and with samples of lower superoxide content. Compositions were varied by pumping at 300°. From the weight loss, as determined by the *in situ* balance, the empirical formula for each run was calculated.

III. Results

Five different samples of cesium superoxide were used in these studies.

The data for the thermal decomposition of cesium superoxide are presented in Table I. The cesium superoxide-peroxide system is univariant in the temperature range 320-440° and over the composition range studied. There is no evidence for sesquioxide, Cs_2O_3, or solid solution formation. Therefore, the thermal decomposition occurs according to the equation

$$2CsO_2(s) = Cs_2O_2(s) + O_2(g) \qquad (1)$$

The data were fitted to a two-constant equation of the form

$$\log P = A/T + B \qquad (2)$$

where $A = \Delta H^\circ/(2.303R)$ and B = a constant. The computed values of A and B are −4351 and 6.861, respectively; the pressure had been converted to atmospheres. The calculations were performed on an IBM Model 360/30 digital computer. The computer program which evaluated the data utilized the parabolic extrapolation method of least squares.[13]

In Table II, the arithmetic mean pressure, P_m, and the pressure computed by eq 2, P_c, are summarized. The values of the computed dissociation pressure when compared to the experimental mean pressure were within the 99% confidence limit.

Table I. Equilibrium Pressures (mm) for the Thermal Decomposition of Cesium Superoxide, 320–440°

	Temperature, °C					
Run	320	340	360	380	400	Composition
1			1.010	1.68	2.51	$Cs_2O_{2.38}$
2			0.950	1.59	2.55	$Cs_2O_{2.29}$
3			0.930	1.65	2.45	$Cs_2O_{2.27}$
4			0.920	1.59	2.32	Cs_2O_{219}
5			0.950	1.58	2.40	$Cs_2O_{3.96}$
6			0.850	1.61	2.15	$Cs_2O_{3.68}$
7	0.431	0.573	0.968	1.58	2.31	$Cs_2O_{2.70}$
8	0.350	0.569	0.961	1.67	2.63	$Cs_2O_{3.75}$
9			0.958	1.54	2.28	$Cs_2O_{2.97}$
10	0.344	0.577	0.970	1.62	2.56	$Cs_2O_{2.83}$
11			0.950	1.59	2.61	$Cs_2O_{2.79}$
12	0.347	0.570	0.940	1.61	2.31	$Cs_2O_{2.63}$
	420	440				
13	3.90	5.55				$Cs_2O_{2.06}$
14	4.25	6.05				$Cs_2O_{3.32}$
15	4.05	5.61				$Cs_2O_{2.39}$
16	4.11	5.63				$Cs_2O_{2.14}$
17	4.13	5.63				$Cs_2O_{3.95}$
18	4.04	5.68				$Cs_2O_{3.85}$
19	4.09	5.72				$Cs_2O_{3.59}$
20	4.05	5.70				$Cs_2O_{3.17}$
21	4.12	5.81				$Cs_2O_{2.76}$

Table II. Pressure–Temperature Data for the Thermal Decomposition of Cesium Superoxide

Temp, °K	$1/T \times 10^{-3}$	P_m, mm	P_c, mm
593.16	1.686	0.346	0.336
613.16	1.631	0.572	0.583
633.16	1.579	0.946	0.976
653.16	1.531	1.61	1.58
673.16	1.485	2.41	2.50
693.16	1.443	4.08	3.84
713.16	1.402	5.71	5.76

The value of the enthalpy change for the dissociation process at 380° is

$$\Delta H^\circ = 19.91 \pm 0.47 \text{ kcal}$$

Assuming oxygen to behave as an ideal gas under the experimental conditions, the change in free energy, Δu°, was calculated to be 8.01 ± 0.89 kcal at the mean temperature, 380°, using the relation

$$\Delta u^\circ = -RT \ln P_{O_2}$$

where P_{O_2} is in atmospheres.[14] ΔS° was then calculated to be 18.29 ± 0.75 eu using the equation

$$\Delta S^\circ = (-\Delta u^\circ + \Delta H^\circ)/T$$

and K_p is $2.08 \pm 0.3 \times 10^{-3}$ atm at 380°.

The thermal decomposition of cesium peroxide was investigated over the temperature range 320-500°. Equilibrium partial pressure measurements were made at 20° intervals covering the composition range $Cs_2O_{1.15}$ to $Cs_2O_{1.94}$. The experimental procedure was essentially that for the thermal decomposition of cesium superoxide. The time required to reach equilibrium, however, was found to vary between 3 and 5 hr, with the longer time being required at lower temperatures and for lower peroxide compositions.

The samples used in this part of the investigation were obtained by pumping cesium superoxide samples at 300° until equilibrium pressures were reached. Mean equilibrium pres-

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Table III. Mean Equilibrium Pressures (mm) for the Thermal Decomposition of Cesium Peroxide, 320–500°

	Temperatures										
Run	320	340	360	380	400	420	440	460	480	500	Composition
1	0.063	0.115	0.166	0.262	0.434	0.570	0.855	1.10	1.62	2.22	$Cs_2O_{1.18}$
2	0.062	0.105	0.161	0.257	0.391	0.551	0.842	1.14	1.71	2.47	$Cs_2O_{1.36}$
3			0.162	0.256	0.399	0.598	0.839	1.14	1.74	2.67	$Cs_2O_{1.94}$
4			0.190	0.266	0.400	0.560	0.873	1.13	1.77	2.53	$Cs_2O_{1.15}$
5	0.063	0.108	0.162	0.259	0.394	0.573	0.861	1.32	1.76	2.51	$Cs_2O_{1.76}$
6			0.167	0.251	0.407	0.575	0.874	1.15	1.65	2.43	$Cs_2O_{1.31}$
7	0.062	0.117	0.161	0.267	0.411	0.579	0.855	1.16	1.90	2.36	$Cs_2O_{1.65}$
8			0.162	0.285	0.409	0.570	0.865	1.23	1.71	2.58	$Cs_2O_{1.50}$

sures for the thermal decomposition of cesium peroxide are presented in Table III.

The data indicate that the system is univariant over the range of temperatures and compositions studied. Since it is a two-component system, three phases $Cs_2O_2(s)$, $Cs_2O(s)$, and $O_2(g)$ must be in equilibrium. The equation for the thermal decomposition may be written

$$2Cs_2O_2(s) = 2Cs_2O(s) + O_2(g) \qquad (3)$$

The peroxide data were analyzed by the same method as that used for the superoxide. With a two-constant equation, the best fit is given by

$$\log P_{O_2} = -3982/T + 5.517 \qquad (4)$$

where P_{O_2} had been converted to atmospheres. The computed dissociation pressures, P_c, according to eq 4 as well as the mean experimental partial pressures, P_{O_2}, are given in Table IV.

The calculated values of the thermodynamic parameters at 410° are

$$\Delta H° = 18.23 \pm 0.37 \text{ kcal}$$

$$\Delta u° = 9.98 \pm 0.84 \text{ kcal}$$

$$\Delta S° = 12.08 \pm 0.71 \text{ eu}$$

$$K_p = 6.39 \pm 0.2 \times 10^{-4} \text{ atm}$$

IV. Summary

The thermal decomposition of cesium superoxide was investigated over the temperature range 320–440°. Equilibrium oxygen pressure measurements were made at 20° intervals, 320–440°, over the composition range $Cs_2O_{2.06}$ to $Cs_2O_{3.96}$. From the data, it can be concluded that there is neither solid solution formation nor sesquioxide formation, over the indicated composition range. Further, the system is univariant, being composed of three phases and two components. The equilibrium pressures in the temperature range 320–440° are best fitted to the equation

$$\log P_{O_2} = -4351/T + 6.861$$

The values for $\Delta u°$, $\Delta H°$, $\Delta S°$, and K_p at 380° are calculated for the reaction

$$2CsO_2(s) = Cs_2O_2(s) + O_2(g)$$

In general, the free energy for the thermal decomposition process becomes less negative, less favorable, as one proceeds from lithium superoxide to cesium superoxide. The significance of this can be interpreted on the basis of greater crystal stability between the larger cation and the sizable O_2 anion. Because of this, the partial pressures obtained in the thermal decomposition reaction decrease in the series sodium superoxide to cesium superoxide.

Table IV. Pressure–Temperature Data for the Thermal Decomposition of Cesium Peroxide

Temp, °K	$1/T \times 10^{-3}$	P_m, mm	P_c, mm
593.16	1.686	0.0625	0.0634
613.16	1.631	0.111	0.105
633.16	1.579	0.166	0.168
653.16	1.531	0.263	0.262
673.16	1.468	0.406	0.398
693.16	1.443	0.572	0.590
713.16	1.402	0.858	0.855
733.16	1.364	1.17	1.21
753.16	1.327	1.73	1.69
773.16	1.293	2.47	2.32

The enthalpy change for the thermal decomposition process at 298°K, ΔH_{298}, as calculated by eq 2, is approximately equal to 17 kcal. This enthalpy change compares favorably with the work of Morris.[8] However, ΔH_{298} obtained from the data in ANL 5750 is 40.6 kcal.[15] It should be noted that the enthalpy change, ΔH_{298}, in this work can be attributed to the process as indicated by eq 1. Cesium superoxide is known to be quite hygroscopic.[4,8] If $H_2O(g)$, or $H_2O(l)$, is present, then the reaction is different from eq 1. In the ANL 5750 report, the thermodynamic data attributed to cesium superoxide may be due to trace impurities of water causing irreversible decomposition.

The thermal decomposition of cesium peroxide was studied between 320 and 500°, over the composition range $Cs_2O_{1.15}$ to $Cs_2O_{1.94}$. This region, also, is univariant, without solid solution formation. The pressure-temperature data are best fitted by the expression

$$\log P_{O_2}(\text{mm}) = -3982/T + 5.517$$

The values of $\Delta u°$, $\Delta H°$, $\Delta S°$, and K_p are calculated at 410° for the reaction

$$2\,Cs_2O_2(s) = 2Cs_2O(s) + O_2(g)$$

Registry No. CsO_2, 12018-61-0; Cs_2O_2, 12053-70-2.

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