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Concerning the Thermal Stability of Potassium Ozonide

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An investigation of the characteristics of the thermal decomposition of potassium ozonide has been performed. Discrepancies in the open literature concerning the presence of an induction period preceding the active decomposition of potassium ozonide have been resolved. Under extremely dry conditions, the induction period is observed, the length of which is dependent upon the temperature to which the sample is exposed. Studies have also confirmed that at temperatures of 0° and below the rate of decomposition of potassium superoxide is sufficiently slow so as to make the long term storage of these materials practical. The heat of decomposition of potassium ozonide was determined to be 3.2 Kcal/mole in the temperature range from 325 to 373°K using differential scanning calorimetric techniques.

Introduction

Potassium ozonide undergoes spontaneous decomposition at room temperature to potassium superoxide and molecular oxygen accordingly:

$$KO_3 = KO_2 + \tfrac{1}{2}O_2 \qquad (1)$$

The thermal stability of this material is of concern when applied to air regeneration of closed environments, such as space cabins. The rate(s) at which decomposition occurs in temperature ranges of interest and the temperature(s) at which the rate is slow enough to allow long-term storage of the material without fear of significant amounts of decomposition must be determined if potassium ozonide is to be used in these applications.

Certain discrepancies have appeared in the literature between American and Soviet investigators with regard to the stability characteristics of potassium ozonide. We have investigated the thermal decomposition of potassium ozonide using the methods of thermogravimetry and differential scanning calorimetry to resolve the discrepancies appearing in the literature. Typical kinetic data obtained in these laboratories along with the results reported in the literature by other investigators are summarized in Table I.

The Russian invesigators have reported that the decomposition reaction is complete in approximately 10 days at room temperature, while at 50-60° the decomposition is over in 30 minutes.[1,2] To illustrate further the dramatic effect on stability obtained by a decrease in temperature, the Russian investigators[2] report that at −18° the induction period was 205 days and a decomposition of less than 1% of potassium ozonide took place during this entire period. This corresponded to a loss of only 0.2% of the active oxygen. The Russian data also disclose the existence of an « induction period », *i.e.*, an initial time period during which the decomposition rate is very much slower than the rate of active decomposition of the sample.

Kacmarek[3] has expressed disagreement with the Russian data with regard to the presence of an induction period. Induction periods were not observed by Kacmarek for kinetic studies of the thermal decomposition of potassium ozonide at 20 and 25°. He does not, however, report whether the ozonide was in the form of a powder or a pellet. In addition, in contrast to the excellent reproducibility of the Russian data, Kacmarek's results, at a given temperature, showed very wide differences in the rate of decomposition. For example, for eight runs at 25°, the rate of active decomposition ranged from 4.9 to 50%/hour.

A kinetic study of the thermal decomposition of potassium ozonide was carried out, therefore, to resolve the apparent discrepancies concerning the stability characteristics of the potassium ozonide.

Experimental Section

The apparatus used for these studies has been described elsewhere[4] and was designed to follow the rate of oxygen evolution gasometrically as the sample decomposed via reaction (1) in a thermostated bath. The potassium ozonide sample was loaded into a vial in a dry box, quickly transferred to the sample chamber, the gas burette equilibrated, and the volume of oxygen evolved recorded as a function of time.

Potassium ozonide was prepared by the passage of gaseous ozone over solid potassium hydroxide[5] followed by extraction of the solid mixture with liquid ammonia.[2] Analysis of the recovered product was ac-

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(1) I.A. Kazarnovskii, *et al.*, *Doklady Akad. Nauk SSSR*, *64*, 69 (1949).
(2) I.A. Kazarnovskii, *et al.*, *Doklady Akad. Nauk SSSR*, *108*, 641 (1956).
(3) A.J. Kacmarek, AFOSR 2984; Final Report, June, 1962.
(4) J.A. Marriott, A. Capotosto, Jr., R T. Uno, and A.W. Petrocelli, *Thermochim. Acta*, *2*, 135 (1971).
(5) T.P. Whaley and J. Kleinberg, *J. Amer. Chem. Soc.*, *73*, 79 (1951).

Table I. Summary of kinetic data for the thermal decomposition of potassium ozonide

Sample	Temperature (°C)	Rate of Decomposition (%/hr) Introduction Period	Rate of Decomposition (%/hr) Active Period	Time Introduction Period	Time Total Decomposition
KO_3 Pellet					
Data of Kazarnovskii[2]	19	0.23	2.3	40h	240h
		0.28*	3.2*	—	—
	0	—	—	20d	101d
	—9	0.03	1.5	54d	230d
	—18	—	—	205d	—
Data of Kacmarek[3]	25	—	4.9-50.0	None	—
KO_3 Powder	40	—	20.2	None	3.5h
(N_2 Dry)	30	—	7.0	None	10h
	22	—	4.5	None	15.5h
	0	—	0.5	None	139h
KO_3 Pellet	40	11.8	54.2	4h	11h
(N_2 dry)	30	5.1	17.5	9h	30h
	23	1.8	7.5	24h	60-80h
	0	0.6	—	—	—
KO_3 Pellet	30	1.2	35.4	12h	25h
(P_4O_{10} dry)	23	0.8	16.7	28h	50h

* Computed in our laboratories by- a least-squares treatment of the available Russian data.[2]

complished by gravimetric means.[6] Ozonide samples used in these studies ranged between 80 and 90% purity. Superoxide content when required was determined by the method of Seyb and Kleinberg.[7]

Results and Discussion

The results of our studies are also summarized in Table I. The data fell into three classes, depending upon the state of the potassium ozonide sample and the drying procedure employed:

Class I. The first kinetic runs during this study were made using powdered potassium ozonide samples. The reaction chamber was flushed with dry nitrogen prior to introduction of the tared sample vial in an attempt to exclude water vapor from the system. Figure 1 illustrates typical kinetic curves obtained during these studies. In no case was an induction period, as reported by the Russian investigators, observed. Some data reported by Kacmarek[3] do, however, resemble these results, but only with respect to the shape of the curve. The rates of decomposition of powdered potassium ozonide reported in Table I for various temperatures were determined from the straight-line first-order reaction rate plots (obtained by plotting the logarithm of the final volume of evolved oxygen minus the volume of oxygen observed at a given time increment versus time).

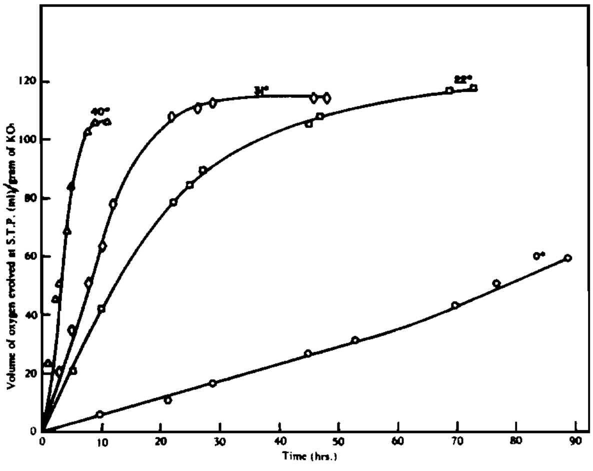

Figure 1. Volume of oxygen evolved at S.T.P. per gram of powdered potassium ozonide as a function of time at various temperatures.

Class II. Following the kinetic studies using powdered potassium ozonide samples, runs were made with the ozonide in pellet form at the same temperatures. A hand pellet press (Parr Instrument Co.) was used and attempts were made to insure the uniformity of pellet dimensions and density by having only one technician prepare the pellets from nearly equal weights of potassium ozonide samples. The reaction chamber was flushed with dry nitrogen prior

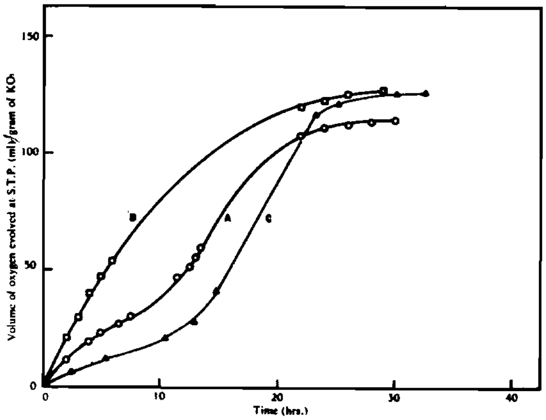

Figure 2. Volume of oxygen evolved at S.T.P. (ml) per gram of pelleted potassium ozonide as a function of time at 30° (N_2 dry - Curves A and B; and P_4O_{10} dry - Curve C).

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(6) A.W. Petrocelli and A. Capotosto, Jr., *Anal. Chem.*, 36, 2509 (1964).

(7) E. Seyb and J. Kleinberg, *Anal. Chem.*, 23, 115 (1951).

to introduction of the sample as in the previous set of runs. The results obtained for these studies are also listed in Table I. Figure 2, curves A and B, shows typical kinetic curve for the thermal decomposition of potassium ozonide in pellet form at 30° In approximately 50% of the cases, an «induction period» was observed (as illustrated by Curve A in Figure 2), similar to that reported by Kazarnovskii, *et al.*[2] Even in our cases where an induction period was not actually evident when the raw kinetic data was plotted, two slopes could still be drawn for the first order reaction rate plot (obtained as noted above); the length of the first rate corresponded to the length of the apparent or visible induction period.

Certain observations were made during these runs which suggested that the nitrogen flushing procedure was not sufficiently effective for removing moisture. The slightest amount of water is apparently capable of catalyzing the decomposition reaction, thus obscuring or destroying the induction period. Examination of the pellets at the end of the kinetic runs confirmed the presence of moisture in the system. The pellet in most cases had a thin white coating, indicative of potassium hydroxide formed by the reaction of the ozonide with water. Further confirmation results when the total volume of oxygen evolved during the decomposition was slightly greater than that calculated for the particular weight of ozonide sample of known purity.

These data also showed significant variance among the runs at a given temperature, possibly due to the non-uniformity of the pellets with respect to thickness, porosity, and density, and/or due to the moisture phenomenon described above.

Class III. As a result of the observations made during the second set of kinetic studies, it was decided to dry the reaction chamber with phosphorus pentoxide prior to sample loading. The operating procedures remained the same in all other respects. The results were dramatic. In these runs, induction periods were consistently observed. Figure 2, Curve C, illustrates the typical kinetic curves obtained for these data. For example, at about 31°, an induction period of 12 hours and average decomposition rates of 1.1 and 35.4%/hr for the induction and active periods, respectively, were observed. These data are contrasted to an induction period of nine hours and average decomposition rates of 5.1 and 17.5%/hr when nitrogen flushing was used. These results confirm the indications that nitrogen flushing was not effective in removing water vapor from the reaction system.

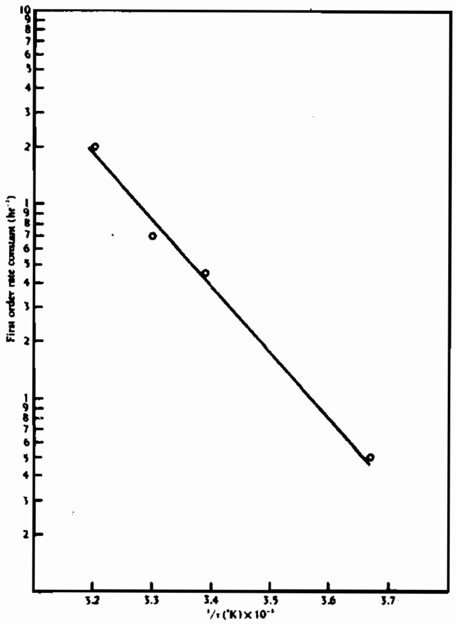

Figure 3. Plot of the logarithm of the first-order rate constant as a function of 1/T for the thermal decomposition of powdered potassium ozonide.

More important, our results indicate that under extremely dry conditions, we are in essential agreement with the Soviet investigators. Moreover, the results serve to point out that, although, the ozonides tend to gradually decompose upon standing to the superoxide and oxygen, the rates of their decomposition at temperatures 0° and below are sufficiently slow so as to make the long term storage of these materials practical.

Estimations of the activation energy of the thermal decomposition of potassium ozonide were made from Arrhenius plots of the kinetic data presented in Table I. Figure 3 illustrates the curve obtained for the case in which the potassium ozonide sample was a powder. A value of 15.6 kcal was obtained for the activation energy. Estimates of the activation energy were also made for the other cases. The data obtained for pelleted samples yielded values of 17.8 kcal when the reaction chamber was flushed with nitrogen and 13.5 kcal when phosphorus pentoxide was used as the drying agent as compared to values of 21.6-23.4 kcal for the temperature range of 18° to 50° reported by the Soviet investigators.[2]

In order to obtain a measure of the heat of reaction associated with the thermal decomposition of potassium ozonide to the superoxide and molecular oxygen, reaction (1), a differential thermal analysis of a sample of potassium ozonide was made using a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1. The measurements were made at the Perkin-Elmer facilities in Norwalk, Connecticut.

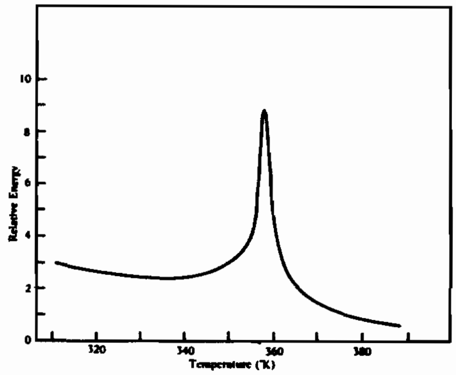

Figure 4. Differential calorimetric recording obtained for a 10.56 mg sample of potassium ozonide (86.6% pure).

The differential calorimetric scan recorded for a 10.56 mg wafer sample of potassium ozonide (86.6%

pure) is shown in Figure 4. Qualitatively, this curve shows that a measurable decomposition rate is not observed until a temperature of about 52° is reached and that the energy change for the decomposition reaction is exothermic. Quantitatively, the heat of the decomposition reaction is related to the area under the curve obtained. An external standard was used to calibrate the instrument. Indium metal was chosen because it has a well-known transition energy of 6.8 cal/gram and is available in high purity. The heat evolved during the decomposition of the potassium ozonide sample was thus determined to be 3.2 kcal/mole in the temperature range from 325 to 373°K.

In determining the heat of the decomposition reaction, the purity, of the potassium ozonide sample was taken into account. The assumption was made that the impurities in the sample did not undergo any transitions or reactions which would contribute to the energy change observed in the temperature range at which the measurements were made.

Our value is in qualitative agreement with the value of 5.8 kcal/mole at 298.16°K reported by Kazarnovskii, *et. al.*[2] Upon completion of the differential calorimetric scan, the decomposed potassium ozonide was cooled and reweighed. On the basis of the weight lost upon decomposition, the purity of the ozonide sample was determined to be 86.0%. This figure is in agreement with the original analysis (86.6%) made following our standard procedure.[4]

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