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Abstract

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INVESTIGATION OF THE MECHANISM OF THE REACTION OF SPONTANEOUS DECOMPOSITION OF POTASSIUM OZONIDE USING THE MAGNETIC METHOD

The study of the kinetics of the spontaneous decomposition of potassium ozonide (1) showed that this reaction, proceeding according to the equation

$$2\,KO_3 = 2\,KO_2 + O_2 + 11.6 \text{ kcal},$$

has an autocatalytic character with an induction period amounting, at 18, 0, −9, and −18° respectively, to 1.67; 20; 54 and 205 days. In the subsequent active period the rate of decomposition of potassium ozonide increases sharply; the activation energy is 22–23 kcal/mole.

To elucidate the mechanism of decomposition of potassium ozonide, we undertook magnetic measurements. In the formation of strongly paramagnetic intermediate products one could expect deviations of the magnetic susceptibility from additivity in the direction of an increase; in the case of formation of diamagnetic products—in the direction of a decrease.

The potassium ozonide preparations contained 88–92% KO_3. As an example we give the composition of preparation No. 1: KO_3 89.8%; KOH 8.0%; H_2O (in the form of $KOH \cdot H_2O$) 2.2%.

Magnetic measurements were carried out simultaneously with kinetic measurements at room temperature (18–20°) and at 0°. The measurements were made by the Gouy method on an apparatus with a large laboratory electromagnet. A weighed portion of 0.5–0.6 g of potassium ozonide powder was placed in an ampoule of Jena glass, about 2 mm in diameter and 140 mm long, provided with a stopcock and a ground joint, which made it possible alternately to connect the ampoule to the balance of the magnetic apparatus and to a gas burette, in which the amount of evolved oxygen was measured. Before being filled, the ampoules were heated in vacuum to remove adsorbed moisture.

The operations of taking, weighing, and loading the ampoules were carried out in a special dry chamber. Oscillations in weighing the ampoules on the magnetic balance did not exceed 0.09 mg, whereas the change in the weight of the samples in the magnetic field was from 15 to 45 mg. The results of magnetic measurements with different preparations were reproduced, as a rule, within $±$2%.

In all, nine experiments were carried out: seven at 18–20° and two at 0°. The initial product KO_3 and the final KO_2, as is known, are paramagnetic. At room temperature our potassium ozonide preparations gave $\chi_g \cdot 10^6 = +16.9 \pm 0.15$, and the final product (potassium superoxide) $\chi_g \cdot 10^6 = +25.2 \pm 0.15$. These values, referred to 100% preparations*, agree satisfactorily with previous data (2–4).

Table 1 and Fig. 1 give the results of several kinetic and magnetic measurements at room temperature and at 0°**. The dotted—

* In recalculating the magnetic susceptibility to 100% preparations, the diamagnetism of the KOH and H_2O impurities may be neglected. The same applies to the corrected values of the gram susceptibility of the solid reaction products in Table 1.

** V. I. Smirnova took part in the measurements.

Table 1

Experiment No. 15, preparation No. 1, sample 0.5463 g, temperature 19°

No.	Time from the start of the experiment, h	Degree of decomposition of KO_3 from the oxygen evolved, %	Measured	Corrected	Calculated by the additive rule*	Δ, %
1	0	0	+15.15	+16.89	—	—
2	17	8.1	+15.95	+17.81	+17.60	+1.2
3	23	9.5	+15.90	+17.76	+17.70	+0.3
4	41.5	11.1	+16.10	+17.98	+17.80	+1.0
5	47.5	18.9	+17.60	+19.67	+18.09	+8.7
6	67.3	27.4	+20.30	+22.75	+19.20	+18.5
7	89.5	48.8	+22.50	+25.33	+21.02	+20.5
8	94.5	56.3	+23.15	+26.41	+21.64	+20.7
9	113.5	74.2	+23.50	+26.62	+23.17	+14.9
10	118.5	78.3	+23.20	+26.31	+23.51	+11.9
11	161.5	95.0	+23.05	+26.25	+24.96	+5.2

Fig. 1. Course of the change in magnetic susceptibility during the decomposition of KO3 at 0° (a) and 18-20° (b)

Figure 1: Fig. 1. Course of the change in magnetic susceptibility during the decomposition of KO3 at 0° (a) and 18-20° (b)

No.	Time from the start of the experiment, h	Degree of decomposition of KO_3 from the oxygen evolved, %	Measured	Corrected	Calculated by the additive rule*	Δ, %
12	167.5	96.1	+23.15	+26.38	+25.08	+5.2
13	186.5	98.1	+22.70	+25.88	+25.22	+2.6
14	191	98.1	+22.75	+25.93	+25.22	+2.8
15	220	100	+22.30	+25.44	–	–
16	230	100	+22.20	+25.33	–	–

* Calculated using the equation: χ_g (mixture) $= a\chi_g(KO_3) + (1-a)\chi_g(KO_2)$, where a is the fraction of potassium ozonide in the mixture.

The straight dashed line represents the values of χ_g calculated according to the additivity rule.

The deviations from additivity that were found, lying far beyond the limits of measurement error, indicate the intermediate formation of a strongly paramagnetic product. It is natural to suppose that this product is atomic oxygen, whose magnetic susceptibility is several times greater than that of KO_3 and KO_2, since an oxygen atom in the ground state (^3P) has two unpaired electrons.

Fig. 1. Course of the change in magnetic susceptibility during the decomposition of KO_3 at 0° (a) and 18-20° (b)

The intermediate formation of oxygen atoms is also confirmed by the observed evolution of traces of ozone, which was manifested in oxidation of the mercury surface in the manometric tube of the apparatus.

The amount of atomic oxygen at various stages of the process can be estimated from the magnetic data and the weight of the solid reaction products.

Proceeding from the fact that the latter consist of KO_3, KO_2, and atomic oxygen, the following three equations may be written:

$$x + y + z = g_t \tag{1}$$

$$0.4489x + 0.5499y = 0.4489g_0 \tag{2}$$

$$\chi_g(\mathrm{KO_3})x + \chi_g(\mathrm{KO_2})y + \chi_g(\mathrm{O})z = g_t\chi_g \text{ (mixture)} \tag{3}$$

where g_0 is the amount of KO_3 in the initial charge, g_t is the weight of the solid reaction products, x is the amount of KO_3, y is the amount of KO_2, and z is the amount of atomic oxygen after t hours (all in grams); $\chi_g(KO_3)$, $\chi_g(KO_2)$, $\chi_g(O)$, and χ_g(mixture) are the gram magnetic susceptibilities at the temperature of the experiment*.

Equation (2) is based on the constancy of the amount of potassium in the reaction mixture. Solving equations (1), (2), and (3) with the numerical values $\chi_g(KO_3) \cdot 10^6 = +16.89$; $\chi_g(KO_2) \cdot 10^6 = +25.33$, and $\chi_g(O) \cdot 10^6 = +211.88$, we find:

$$x = 4.9484\, g_t - 3.5539g_0 - 0.0234g_t\chi_g \text{ (mixture)}$$

$$y = 3.7175\, g_0 - 4.0395g_t + 0.0191g_t\chi_g \text{ (mixture)}$$

$$z = 0.0911\, g_t - 0.1636g_0 + 0.0043g_t\chi_g \text{ (mixture)}$$

These equations make it possible to calculate the amounts of KO_3, KO_2, and atomic oxygen at various stages of the KO_3 decomposition process. Table 2 gives the values obtained for experiment No. 15.

Table 2

Amount of atomic oxygen in the solid products of the decomposition reaction of potassium ozonide (experiment No. 15)

No.	Time from beginning of experiment, h	Degree of decomposition of released oxygen, %	Weight of solid reaction products (g_t), g	Amount of KO_3 (x), g	Amount of KO_2 (y), g	Amount of atomic oxygen (z), g	True degree of decomposition of KO_3, %	Amount of atomic oxygen, g-at per 100 mol initial KO_3	Amount of atomic oxygen, g-at per 100 mol decomposed KO_3
1	0	0	0.4901	0.4901	—	—	—	—	—
2	17	8.1	0.4828	0.4461	0.0357	0.0008	9.0	0.9	9.9
3	23	9.5	0.4815	0.4408	0.0402	0.0005	10.1	0.6	5.5
4	41.5	11.1	0.4801	0.4319	0.0473	0.0006	11.8	0.7	5.6
5	47.5	13.9	0.4775	0.4013	0.0724	0.0037	18.2	4.1	22.7
6	67.3	27.4	0.4654	0.3134	0.1441	0.0077	36.4	8.5	23.7
7	89.5	48.8	0.4461	0.2013	0.2357	0.0090	60.3	10.0	16.9
8	94.5	56.3	0.4393	0.1636	0.2664	0.0091	65.3	10.1	15.2
9	113.5	74.2	0.4231	0.0883	0.3279	0.0067	81.9	7.5	9.1
10	118.5	78.3	0.4195	0.0758	0.3381	0.0055	84.4	6.0	7.2
11	161.5	95.0	0.4044	0.0109	0.3911	0.0022	97.9	2.5	2.5
12	167.5	96.1	0.4034	0.0054	0.3957	0.0023	99.3	2.5	2.6
13	186.5	98.1	0.4016	0.0023	0.3982	0.0011	100	1.2	1.3
14	191	98.1	0.4016	0.0018	0.3986	0.0012	100	1.4	1.4
15	220	100	0.3988	—	0.3986	—	100	—	—
16	230	100	0.3988	—	0.3986	—	100	—	—

From the data of Table 2 it follows that, at the beginning of decomposition, the content of atomic oxygen in the solid phase increases, passes through a maximum at a degree of decomposition of potassium ozonide of about 60%, and then falls to zero at 100% decom-

* The magnetic susceptibility of atomic oxygen has not yet been measured. A theoretical calculation using the Van Vleck equations gives, for room temperature (293°K), the value
$\chi_g(\mathrm{O}) \cdot 10^6 = 5000/16 = 312.5$ (5). Since in our case the orbital component of the magnetic moment is apparently frozen by the field of the lattice ions, for the susceptibility of atomic oxygen located in the solid phase a theoretical value was taken corresponding to only one spin moment. Then we have at 293°K: $\chi_g(\mathrm{O}) \cdot 10^6 = 3390/16 = 211.88$; at 273°K: $\chi_g(\mathrm{O}) \cdot 10^6 = 227.5$. The values of the amount of atomic oxygen calculated below with these values possibly represent an upper limit.

Fig. 2. Rate of evolution of molecular oxygen (1) and amount of atomic oxygen (2). Temperature 0°. (Experiment No. 16).

Figure 2: Fig. 2. Rate of evolution of molecular oxygen (1) and amount of atomic oxygen (2). Temperature 0°. (Experiment No. 16).

Fig. 3. Rate of formation of atomic oxygen (1) and evolution of molecular oxygen (2). Temperature 19-20°. (Experiment No. 22).

Figure 3: Fig. 3. Rate of formation of atomic oxygen (1) and evolution of molecular oxygen (2). Temperature 19-20°. (Experiment No. 22).

decline. At the maximum, the solid phase contains about 15% of all the oxygen formed in the form of atoms. The largest relative amount of atomic oxygen (up to 25%) is observed at the end of the induction period or at the beginning of the active period.

This result is an argument in favor of the hypothesis put forward[ˆ1] concerning the nature of the induction period, based on the theory of defective crystalline structures. According to this hypothesis, the induction period is characterized by the accumulation of defects in the crystal lattice of potassium ozonide, i.e., of O_2^- ions and oxygen atoms; upon reaching a certain critical number of these defects, the initial structure decomposes into a phase saturated with defects and nuclei of a new phase, KO_2. This moment corresponds to the beginning of the active period of the reaction, which proceeds predominantly at the boundary of the two phases.

Fig. 2. Rate of evolution of molecular oxygen (1) and amount of atomic oxygen (2). Temperature 0°. (Experiment No. 16).

To clarify the mechanism of molecular oxygen evolution, the rate of this process (w_{O_2}) was compared with the amount of atomic oxygen in the solid phase (z). In Fig. 2, as an example, data are presented

Fig. 3. Rate of formation of atomic oxygen (1) and evolution of molecular oxygen (2). Temperature 19-20°. (Experiment No. 22).

from experiment No. 16. They indicate that the formation of molecular oxygen is a first-order reaction with respect to atomic oxygen. This makes the recombination mechanism unlikely and argues in favor of the reaction of oxygen atoms with ozonide ions:

$$O + O_3^- = O_2^- + O_2.$$

Further kinetic analysis revealed for the rate of formation of atomic oxygen the same regularity as for the rate of evolution of molecular oxygen, namely—a curve with a clearly expressed topochemical maximum (Fig. 3). Consequently,

both principal elementary acts in the decomposition of potassium ozonide into potassium superoxide and oxygen,

$$KO_3 = KO_2 + O$$

$$KO_3 + O = KO_2 + O_2 \uparrow$$

proceed predominantly at the phase boundary.

It is possible that an analogous mechanism occurs in the decomposition of other metal oxides, as well as of salts of oxygen acids. To test this hypothesis, studies using atomic oxygen are planned.

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Note: Figure translations are in progress. See original paper for figures.