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Preparation, crystal structure, and thermal behaviour of potassium ozonide

by

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Dedicated to Professor Albrecht Rabenau on the occasion of his 65th birthday.

ABSTRACT. – The preparation of pure samples of potassium ozonide (KO_3) in gramm-amounts was achieved by reaction of gaseous ozone/oxygen mixtures (2 Vol.$-\%O_3$) with potassium hyperoxide in a temperature-controlled ($T = +10$ to $-50°C$) fluidized bed reactor followed by extraction with liquid ammonia. According to thermal (DT, TG) investigations KO_3 is metastable at ambient conditions. Longtime storage is possible in a dry inert atmosphere below $-20°C$. The crystal structure of KO_3 was solved by single-crystal X-ray techniques. Lattice constants were determined from the X-ray powder pattern of KO_3 which was indexed in agreement with the single-crystal results.

Bond angle and distance in the ozonide anion (O_3^-) are 113.5(1)° and 134.6(2) pm, respectively. The crystal structures of KO_3, RbO_3, $H-CsO_3$, $T-CsO_3$, $CsNO_2$ and BaS_3 are related to each other and derive from the CsCl-type of structure.

RÉSUMÉ. – Des échantillons purs d'ozonure de potassium (KO_3), dans des gammes de masse de l'ordre du gramme, ont été préparés par réaction d'un mélange gazeux ozone/oxygène ($2\%O_3$ en volume) avec l'hyperoxyde de potassium dans un réacteur en couche fluide à température variable ($T = +10$ à $-50°C$), suivie d'une extraction avec de l'ammoniac liquide. D'après les études thermiques (ATD, TG) KO_3 est métastable dans les conditions normales de température et de pression. La conservation est possible dans une atmosphère sèche et inerte en dessous de $-20°C$. La structure cristalline de KO_3 a été déterminée par diffraction des rayons X sur un monocristal. Les paramètres du réseau ont été déterminé d'après le diagramme de poudre de KO_3, indexé en accord avec les résultats de la technique du monocristal.

La distance entre les atomes d'oxygène et l'angle des liaisons dans les anions ozonide (O_3^-) sont respectivement 134.6(2) pm et 113.5(1)°. Les structures cristallines de KO_3, RbO_3, $H-CsO_3$, $T-CsO_3$, $CsNO_2$ and BaS_3 sont corrélées et dérivent de la structure CsCl.

INTRODUCTION

Since the first reports by Wurtz [1] and Baeyer and Villiger [2] on the formation of new compounds during the reaction of ozone with alkalihydroxides, several attempts have been undertaken to clarify their

nature [3, 4]. These efforts however, have been only partly successful. So far, no reliable structural data has become available and no synthetic route has been developed, which allows syntheses of pure samples on a preparative scale.

Concerning the crystal structure of KO_3, two proposals have been made, based on X-ray powder data on samples containing KOH and KO_2 as impurities. Zhdanova and Zvonkova suggested that KO_3 is isostructural to KN_3 and is likely to contain a linear O_3^--group [4]. Azàroff and Corvin report a similar unit cell, a bent anion with an angle of 100° and a separation between adjacent oxygen atoms of 119 pm which is smaller than in ozone itself and is thus rather unreasonable [3 *a*].

In advance of testing a more general application of the ozonides in preparative inorganic or organic chemistry and for further discussion of the bonding properties, it seemed neccessary to us to develop and optimize a procedure for the preparation of pure ozonides in gramm-amounts and to determine the crystal structures with single crystal methods. In this paper we report our results on preparation, crystal structure, and properties of potassium ozonide.

EXPERIMENTAL

Synthesis

From the methods proposed earlier for synthesizing KO_3 using KOH [5] or KO_2 [3 g] as starting material, ozonisation of powdered hyperoxide with gaseous O_3/O_2-mixtures ($\sim$2 Vol.$-\%\,O_3$) was deemed most suitable. Potassium hyperoxide was prepared by direct oxidation of pure potassium metal with molecular oxygen according to the method given by Helms and Klemm [6]. Peroxide-free samples were only obtained after treating the crude product at 450°C under elevated O_2-pressure (6.10^7 Pa, reaction-time: 3 *d*) in an autoclave.

The reaction of ozone with KO_2 according to the equation (i)

$$KO_2 + O_3 \rightarrow KO_3 + O_2 \qquad \text{(i)}$$

may be subdivided into the dissociation of ozone

$$O_3 \rightarrow O_2 + O \qquad \text{(ii)}$$

producing monooxygen diradicals, which immediately react with hyperoxide forming ozonide

$$O + KO_2 \rightarrow KO_3 \qquad \text{(iii)}$$

Because dissociation of ozone (ii), as a metastable compound, is kinetically controlled raising the temperature increases the production rate of O-radicals which themselves recombine to dioxygen in an exothermic reaction competitive to the ozonide formation.

With respect to decomposition into KO_2 and O_2, potassium ozonide is metastable. At about 45°C the rate of O_2 evolution reaches a maximum (see below). So, during ozonisation, heating of the sample due to the exothermic reactions mentioned above must be suppressed by external cooling. On the other hand heterogeneous reaction and diffusion in the solid state are necessary steps during the formation of KO_3 according to equation (i), and need a

minimum temperature of about 10°C for acceptable reaction rates. These two conflicting aspects demand a proper temperature control. This was achieved by using a small cylindrical fluidized bed reactor ($\varnothing = 30$ mm) equipped with a cooling jacket, which allowed a temperature control in the range -75 to $+30$°C. When starting the reaction at room temperature the red colour of KO_3 appeared almost immediately; because of the self-heating reaction, however, the initially formed KO_3 decomposed soon. Upon cooling formation of KO_3 started again in the outer parts of the samples (next to the cooled wall); within 1 hour the reaction zone moved through the sample while the temperature was reduced stepwise to -50°C. As in no case complete reaction of the hyperoxide was observed, enrichment and purification by extraction with and recrystallization from liquid ammonia was carried out. The remaining hyperoxide may be ozonized so that, by repeated ozonization and subsequent extraction, quantitative yields on the basis of the initial amount of KO_2 are possible. All substances were handled during the whole procedure under carefully inert conditions. A detailed description of the equipment used is given elsewhere [7 *a*, *b*].

Viable crystals for single-crystal X-ray investigations were obtained by very slow evaporation (2 hrs.) of liquid ammonia from the potassium ozonide solution. The product crystallized in transparent dark red crystals, which are extremely reactive upon contact with water and carbon dioxide.

Analyses

The active oxygen of the ozonide samples was determined by measuring the loss of weight during thermal decomposition to hyperoxide. The content of active oxygen was found to be 98,7 (13) % of the theoretical value (esd in brackets). The samples were then dissolved in water and potassium was determined by precipitation as potassium-tetraphenylborate according to the method given by Geilmann and Gebauhr [8]. The potassium content was found to be 45.0% (theoretically: 44.9%).

Thermal decomposition

The thermal behavior of potassium ozonide was studied applying DTA-TG-methods and various heating rates. It was thus found that KO_3 decomposes exothermally at ambient conditions. Extrapolated to a heating rate of 0 K/min the decomposition rate reaches its maximum at 45°C under 1 atmosphere Argon (cf. Fig. 1). Thermal decomposition of KO_3 leads quantitatively to the corresponding hyperoxide.

Structure determination

A single crystal of KO_3 was wedged in a capillary tube under dry argon. After sealing, the tube was mounted on an AED2 Siemens-Stoe four-circle-diffractometer. Because of its thermal instability (see before) all X-ray measurements on the KO_3-crystal were undertaken at -20°C using the Stoe low temperature attachment.

Preliminary examinations indicated the crystal to be tetragonal, space group $I4/m\,c\,m$. The unit cell dimensions (-20°C) were obtained by least-squares-fit to the setting angles of 56 reflections measured in positive and negative 2θ. The data are summarized in Table I along with the details of the treatment of the intensity data.

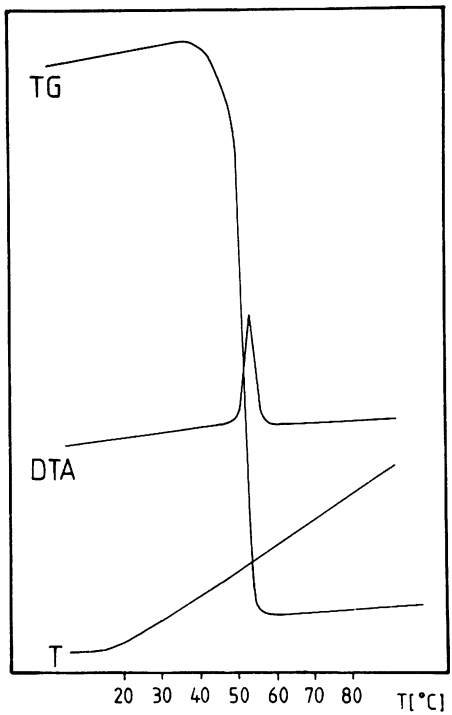

Fig. 1. – DTA-TG-Curve for KO_3; heating rate : 1K/min.

Four standard reflections were measured every 60 minutes and showed no significant change in intensity. A total of 2,509 reflections were measured. The reflections were considered unobserved for $|F_0|$ less than $\sigma(F_0)$. The intensities were corrected for Lorentz and polarization effects. Numerical absorption correction was applied.

The initial positions of potassium- and oxygen-atoms were determined by direct methods [9] and refined by a least-squares procedure minimizing the functions $\Sigma w \| F_0 | - | F_c \|^2$ with final convergence to

$$R = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 | = 0.035$$

and

$$R_w = \Sigma \sqrt{w} \| F_0 | - | F_c \| / \Sigma \sqrt{w} | F_0 | = 0.02 \, (w = 1/\sigma^2(F_0)).$$

Scattering factors for all atoms were taken from ref. [10]. The final parameters are given in Table II and selected bond distances and angles in Table III.

TABLE I

Data for crystal structure analysis.

Formula	KO_3
M	87.1
Crystal system	Tetragonal
Space group	$I4/m\,c\,m$
a/pm	863.58(10)
c/pm	714.06(8)
$V/pm^3 . 10^{+6}$	532.52
Z	8
$D_c/g . cm^{-3}$	2.173
$\mu(Mo-K_\alpha)/cm^{-1}$	16.10
2θ range/°	$2 \leqq 2\theta \leqq 70$
Transmission coefficient	0.78-0.87
Approx. crystal size/mm	$0.06 \times 0.07 \times 0.06$
Data collection instrument	Siemens-Stoe AED2
Measuring mode	ω-Scan
Temperature/°C	−20
No. of data measured	2509
No. of unique reflections	341
No. of observed data	309
Criterion for observed	$n = 1.0$
$I \geqq n\sigma(I)$	
Merging r-value	0.062
No. of parameters refined	15
R	0.035
R_w; $w = 1/\sigma^2(F)$	0.020

Powder diffraction

In order to determine accurate lattice constants of KO_3 the X-ray powder diffraction pattern of this compound was recorded by using a Guinier-Simon [11] camera (T = −25°C) and monochromated $Cu\,K_{\alpha 1}$ radiation ($\lambda = 154.056$ pm). If a tetragonal cell with $a = b = 864.5$ (6) pm and $c = 714.43$ (8) pm, is chosen, the pattern can be indexed as shown in Table IV. All observed d-spacings and intensities are in good agreement with the values calculated from the results of the single-crystal-investigations. The uncertainties concerning the powder diffraction pattern of KO_3 due to the contradictory results of prior investigations [3 *a*, 4], can now be eliminated.

RESULTS, DISCUSSION

Applying the improved procedure reported in this paper pure samples (as characterized by chemical analysis and X-ray powder diffraction) of potassium ozonide in large amounts are now accessible. KO_3 is metastable with respect to decomposition into KO_2 and O_2 under ambient conditions.

TABLE II

Refined Positional and Thermal Parameters for KO_3 (with esd's in parantheses) ([a]).

Atom	x	y	z	U_{11}	U_{22}
K(1)	0	0	0.25	0.0260(2)	0.0260(2)
K(2)	0	0.5	0.25	0.0326(3)	0.0326(3)
O(1)	0.2807(1)	0.2193(1)	0	0.0263(5)	0.0263(5)
O(2)	0.2489(1)	0.0667(1)	0	0.0291(5)	0.0263(6)

Atom	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	0.0206 (8)	0	0	0
K(2)	0.0256(10)	0	0	0
O(1)	0.0758(13)	0.0004(6)	0	0
O(2)	0.0398 (6)	−0.0076(5)	0	0

([a]) Anisotropically refined thermal parameters defined as

$$\exp[-2\pi^2[U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2.U_{13}hla^*c^*+2.U_{23}.K.l.b^*c^*]]\text{ Å}^2.$$

TABLE III

Selected Interatomic Distances (pm) and Angles (deg) for KO_3.

O1 − O2	134.6 (2)	O2 − O1 − O2′	113.5 (1)

Shortest intermolecular O − O-distance :

O1 − O2	301.1 (4)	

Potassium-oxygen distances :

K1 − O2	285.3 (3)	(eight times)
K2 − O2	286.7 (3)	(eight times)
K2 − O1	321.9 (4)	(four times)
K1 − O1	355.7 (5)	(eight times)

The decomposition rate decreases with decreasing temperature, so a long-time storage of potassium ozonide is possible at −20°C under dry argon.

The crystal structure of potassium ozonide (cf. Fig. 2) consists of K^+ and O_3^- ions. Based on this investigation and our recent results on RbO_3 [7] definite bond lengths and angles within the O_3^--anion can be given : the mean values from these two independent determinations are 134.4(7) pm and 113.6(5)°, respectively. The small difference between the individual data (KO_3 c.f. Table III, RbO_3 : $d_{O-O}=134.3(7)$ pm, $\sphericalangle O-O-O=113.7(5)°$) indicate that influence of the crystal fields on the geometry of O_3^- are clearly negligible in both cases. As compared to

TABLE IV

Observed and Calculated X-ray Powder Pattern for KO_3 ($T = -25°C$)

$h\ k\ l$	d_c	d_0	I_c	I_0
1 1 0	6,113		0,1	
2 0 0	4,323	4,325	162,7	15
0 0 2	3,572		18,5	
2 1 1	3,400	3,404	348,4	30
1 1 2	3,084		0	
2 2 0	3,058	3,057	188,5	15
2 0 2	2,754	2,754	1 000,0	100
3 1 0	2,734		0,4	
2 2 2	2,3225	2,3220	352,3	30
3 2 1	2,2733	2,2737	85,8	10
3 1 2	2,1712		0,3	
4 0 0	2,1614	2,1621	262,5	25
3 3 0	2,0378		1,2	
2 1 3	2,0277	2,0283	57,3	5
4 1 1	2,0120		5,5	
4 2 0	1,9332	1,9330	138,8	12
4 0 2	1,8493		15,4	
0 0 4	1,7862	1,7863	112,4	10
3 3 2	1,7700		1,3	
1 1 4	1,7147		0	
4 2 2	1,7002	1,7004	151,6	15
5 1 0	1,6956		0,1	
3 2 3	1,6897		25,7	
4 3 1	1,6806		3,0	
2 0 4	1,6507		20,7	
4 1 3	1,5738		1,9	
5 2 1	1,5664		13,9	
2 2 4	1,5421		38,9	
5 1 2	1,5318		0,2	
4 4 0	1,5284		34,5	
3 1 4	1,4953		0,1	
5 3 0	1,4827		1,4	
6 0 0	1,4409		1,0	
4 4 2	1,4051		31,7	
4 3 3	1,3992		1,4	
6 1 1	1,3940		20,4	
4 0 4	1,3768	1,3767	93,7	10
5 3 2	1,3694		2,0	
6 2 0	1,3670	1,3670	52,0	5
3 3 4	1,3432		0,4	
2 1 5	1,3403		9,8	
6 0 2	1,3363	1,3362	107,4	10
5 2 3	1,3312		7,0	
5 4 1	1,3267		3,1	
4 2 4	1,3119	1,3119	69,5	5

ozone ($d_{O-O} = 128$ pm) the bond distance is enlarged. This is expected, as the additional electron in O_3^- occupies the antibonding $2b_1$ molecular orbital and thus the bond-order n is decreased from $1.5(O_3)$ to $1.25(O_3^-)$.

The relation found between bond order and bond lengths fits well into the scheme of the corresponding relations for other homoatomic bonds of oxygen (Fig. 3). In spite of the decrease of the O–O–O angle to 113.6° (ozone: 116.5°) repulsion between the nonbonded terminal oxygen atoms is relaxed, as can be seen from an increase of their separation by 6 pm. So the variation in the bonding angle is caused mainly by the different electronic structures, an observation which is in accordance with the opinion expressed by Peyerimhoff and Buenker [17] that in triatomic bent molecules with constituent atoms of nearly equal electronegativities such geometrical variations are at most only to a negligible extent due to the repulsive forces mentioned.

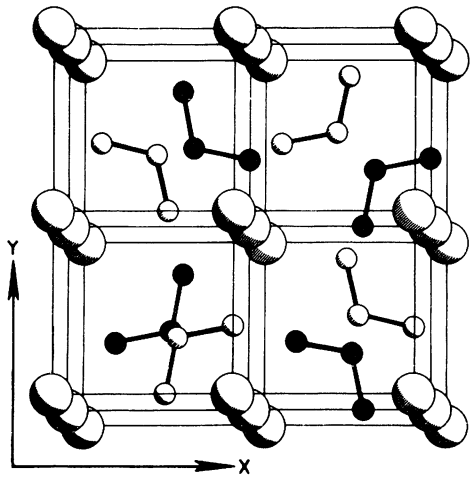

Fig. 2. – Crystal structure of KO_3. View along [001].
Large spheres: K; small spheres: O (shaded at $z=0$, otherwise $z=1/2$).

As can be deduced from Figure 2 the packing of the anions and cations in the crystal structure of potassium ozonide is in principle the same as in cesium chloride. This general arrangement is adopted by several other salts of similar composition, e. g. BaS_3 [18], RbO_3 [7], $H-CsO_3$ [19] and $H-CsNO_2$ [20]. Approximating the triatomic bent anions as spheres the structural relations may be expressed by group-subgroup relationships [21] (cf. Fig. 4). In $H-CsO_3$ and $H-CsNO_2$ which are isostructural the anions are orientationally disordered. So in the average of time and space the crystals exhibit cubic symmetry and the structure of these two representatives may be seen as the « aristotype » of this structural family.

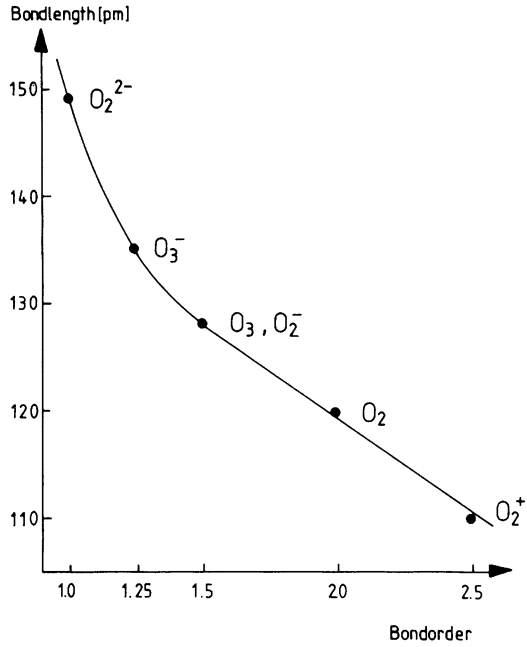

Fig. 3. – Relation between bond length d and bond order n in homoatomic oxygen molecules: O_2^+ [12], O_2 [13], O_2^- [14], O_3 [15], O_2^{2-} [16], and O_3^-.

In KO_3 the shortest contacts between oxygen and potassium are those at the terminal O-atoms of the ozonide group, with the resulting distances (285 and 287 pm) corresponding to the sum of the ionic radii of potassium and oxygen (289 pm) [22]. This structural feature allows qualitative conclusions on the polarity of the ozonide anion to be drawn: in agreement with SCF-MO-calculations by Cosgrove and Collins [23], the terminal oxygen atoms seem to be polarized negatively. The calculated electron density coefficients of the $2b_1$-molecular orbital, which accomodates the nineteenth valence electron were found to be 0.372 for the terminal and 0.255 for the central oxygen atoms. Striving towards K – O bonding contacts mentioned above, the ozonide ions are shifted from the centre of the polyhedron formed by the eight nearest potassium ions by the considerable amount of 86.7 pm.

According to the group-subgroup-relations between the crystal structures of KO_3 and RbO_3 the rubidium compound is a more distorted variant of the CsCl-type structure. This distortion may be caused by the fact that

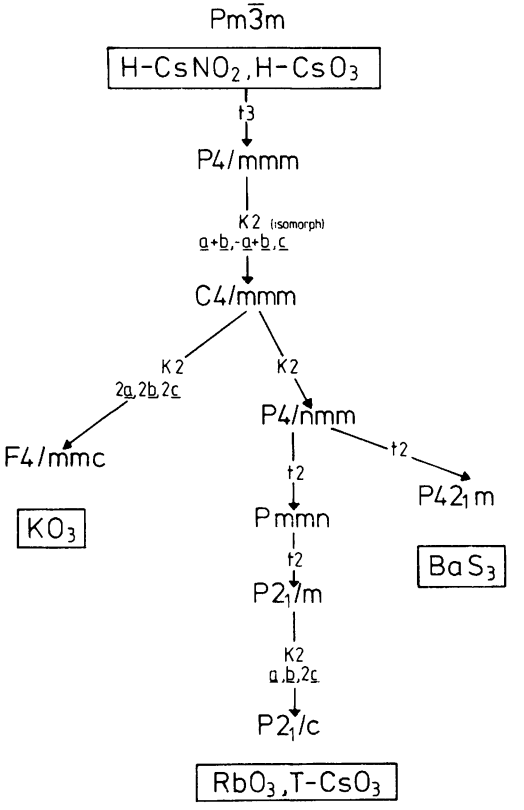

Fig. 4. – Group-subgroup relations between the crystal structures of KO_3, RbO_3, H–CsO_3, T–CsO_3, $CsNO_2$, and BaS_3.

the larger Rb-cations require and obtain a higher coordination number by adjacent oxygen atoms (KO_3: 8; RbO_3: 9).

The ozonide groups are arranged in a strictly ordered manner forming layers parallel to (001) (cf. Fig. 2). This type of ordering causes a tetragonal distortion of the CsCl analogous units from "c/a" = 1.0 to 0.83 and is understandable in terms of polar interactions between positively and negatively polarized oxygen atoms of adjacent O_3^--ions. Covalent inter-actions along with spin pairing can be ruled out as the shortest intermolecular O–O-separations between neighbouring O_3^--ions are 301 pm, and thus in the range of van der Waals contacts [24]. Moreover, preliminary measurements of the magnetic susceptibility show paramagnetic behavior down to 21 K [25].

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