

Crystal Structures of Potassium Ozonide and Rubidium Ozonide**

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In the case of main group elements, bond systems with uneven numbers of electrons are an exception to the rule; on the other hand, a host of such systems appears to exist in the case of triatomic units with 19 valence electrons. This may be a coincidence. But there are also indications of such systems being especially stable: for example, the markedly low tendency for chlorine dioxide to dimerize. As further supporting evidence of this concept, one could mention the tendency of N_2F_4 to dissociate into NF_2 radicals, or the exceptionally long S-S bond in the dithionite ion (239 pm, bond order noticeably less than one), indicating a tendency for decomposition into two SO_2^- moieties. The group of 19-electron systems also includes the ozonide ion O_3^- . However, despite intensive studies over the past twenty years and more^[1], the existence of this anion has still not been unequivocally settled. In particular, there has been lack of reliable data on its geometry: thus, the data on experimentally determined O-O bond lengths vary between 119 and 142 pm, with the O-O-O angle being quoted as 100° ^[1a]. Theoretically, values of between 128 and 135 pm are predicted for the bond lengths and between 108 and 120° for the bond angle. We have now determined the dimensions of the ozonide ion by X-ray structure analyses on single crystals of KO_3 and RbO_3 .

Of the possible strategies available for the preparation of alkali-metal ozonides^[1c], it was found from detailed preliminary investigations that the reaction of solid potassium or rubidium hyperoxide with O_2/O_3 mixtures was the most suitable. The hyperoxides of potassium and rubidium, obtained by oxidation of the alkali metals with O_2 ^[2], were

ozonized for 1 h in a fluidized bed reactor (capacity ca. 100 mL) with O_2/O_3 mixtures (6 vol.-% ozone). About 0.02 mol of hyperoxide was converted per run. Optimal reaction temperatures are $5^\circ C$ and $20^\circ C$ for KO_3 and RbO_3 , respectively. The reaction can be monitored by the change in color of the reaction mixture from yellow to intense red.

For the growth of single crystals the ozonides were extracted at $-40^\circ C$ with liquid ammonia, while unreacted hyperoxide remained undissolved. The solvent was then removed under argon with cooling; the alkali-metal ozonides precipitated as transparent deep-red crystals. The single crystals for the X-ray structure analysis were prepared under an inert gas at $10^\circ C$.

The X-ray structure analyses^[3] confirm the predicted composition of the alkali-metal ozonides. Isolated angular O_3^- ions are present whose dimensions in RbO_3 (O-O (averaged) 134.1(15) pm, bond angle $114.6(13)^\circ$) and KO_3 (135.7(5) pm, bond angle $113.4(8)^\circ$) agree within the standard deviations^[3]. Thus, packing effects seem to have no significant impact on the geometry of the anion. With respect to the bond lengths and angles previously determined on the basis of inadequate data^[1c] (RbO_3 : 142(9) pm, $101(5)^\circ$, KO_3 : 119 pm, 100°), there are considerable discrepancies.

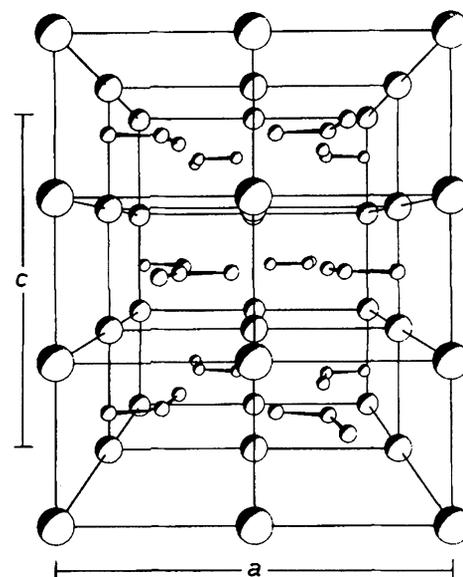


Fig. 1. Perspective diagram of the crystal structure of KO_3 , viewed along $[100]$; large circles denote potassium, small circles oxygen.

The O-O bonds are longer than in ozone (127.8 pm)^[4]. Since the additional electron occupies an antibonding molecular orbital, this tendency is consistent with expectation. The bond angle is reduced slightly from 116.8° to 114.0° . The distance between the two terminal oxygen atoms increases significantly from 218 to 226 pm.

With considerable simplification the packing of K^+ or Rb^+ and O_3^- to a three-dimensional crystal array can be rationalized as the CsCl-type structure (Fig. 1). The shortest contacts between oxygen and alkali-metal ions are, in the case of KO_3 exclusively and in the case of RbO_3 predominantly, those at the terminal O-atoms of the anion. This structural feature enables qualitative conclusions to be drawn about the polarity of the ozonide ion. Common to both ozonides is a marked deviation (86 pm (KO_3), 58 pm (RbO_3)) of the anion from the center of the polyhedron that is formed by the eight alkali-metal ions. There is still

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no satisfactory explanation for the complete order of the ozonide anions at room temperature, which is in contrast with the comparable RbNO_2 ^[5]. Intermolecular interactions between the ozonide ions (dimerization) can be ruled out on the grounds of the large intermolecular distances^[3]. Also still inexplicable are the marked differences in the stability of the compounds with 19-electron systems (NF_2 , SO_2^- , O_3^- , S_3^- , ClO_2) towards dimerization. Whichever of the conceivable criteria is analyzed for an explanation (repulsion of non-bonding electron pairs, differences in electronegativity^[6], charge of the monomer, state of aggregation) there are inconsistencies.

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- [3] KO_3 : 14/mcm, $a = 864.80(12)$, $c = 716.40(14)$ pm (-25°C), $V = 535.78 \times 10^6$ pm³, $Z = 8$. Siemens AED2 diffractometer, $\text{MoK}\alpha$ radiation, graphite monochromator, scan width 2.0° , ω -scan, 2084 measured reflections with $6.7^\circ < 2\theta < 65^\circ$, 147 symmetry independent reflections with $F > 3\sigma(F)$, anisotropic refinement, $R = 0.063$ for 15 free parameters, $R_w = 0.046$, $w = 4.15/(\sigma^2(F))$ selected bond lengths [pm] and angles [$^\circ$] (standard deviations in brackets): O1–O2 135.7(5) ($2\times$), O2–O2' 226.9(11), O1–O2' 300.5(11) intermolecular, K–O2 285.3(6) ($8\times$); O2–O1–O2' 113.4(8).— RbO_3 : $P2_1/c$, $a = 644.10(22)$, $b = 603.00(35)$, $c = 874.60(36)$ pm (-25°C), $\beta = 122.25(2)^\circ$, $V = 287.28 \times 10^6$ pm³, $Z = 4$. Siemens AED2 diffractometer, $\text{MoK}\alpha$ radiation, graphite monochromator, scan width 2.8° , ω -scan, 1953 measured reflections with $7.5^\circ < 2\theta < 50^\circ$, 373 symmetry independent reflections with $F > 3\sigma(F)$, anisotropic refinement, $R = 0.059$ for 37 free parameters, $R_w = 0.047$, $w = 3.48/(\sigma^2(F))$. Selected bond lengths [pm] and angles [$^\circ$] (standard deviation in brackets): O1–O2 134.7(15), O1–O3 133.4(17), O2–O2' 225.6(16), O1–O3' 299.2(11) intermolecular, O2–O1–O3 114.6(13), Rb–O2 292.2(10), Rb–O3 296.7(11), Rb–O3' 300.3(12), Rb–O3'' 300.9(12); Rb–O1 305.8(11), Rb–O2' 306.4(17), Rb–O3''' 307.0(11), Rb–O2'' 308.5(12). Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depositary number CSD 51112, the names of the authors, and the journal citation.
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