

## 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<sup>[1]</sup>, 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  $100^\circ$ <sup>[1a]</sup>. Theoretically, values of between 128 and 135 pm are predicted for the bond lengths and between  $108$  and  $120^\circ$  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<sup>[1c]</sup>, 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  $O_2$ <sup>[2]</sup>, 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<sup>[3]</sup> 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<sup>[3]</sup>. 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<sup>[1c]</sup> ( $RbO_3$ : 142(9) pm,  $101(5)^\circ$ ,  $KO_3$ : 119 pm,  $100^\circ$ ), there are considerable discrepancies.

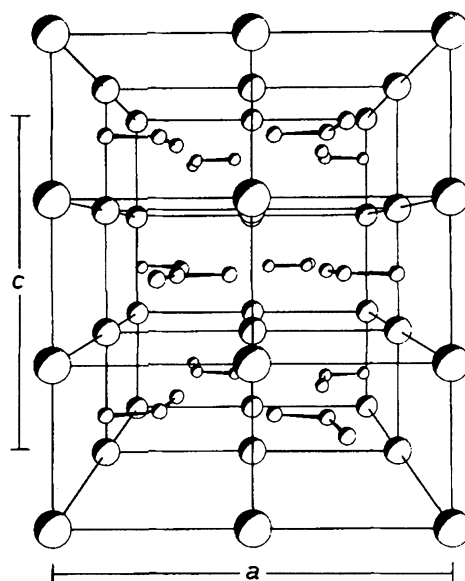


Fig. 1. Perspective diagram of the crystal structure of  $KO_3$ , viewed along  $[100]$ ; large circles denote potassium, small circles oxygen.

The O-O bonds are longer than in ozone (127.8 pm)<sup>[4]</sup>. Since the additional electron occupies an antibonding molecular orbital, this tendency is consistent with expectation. The bond angle is reduced slightly from  $116.8^\circ$  to  $114.0^\circ$ . 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  $\text{RbNO}_2$ <sup>[5]</sup>. Intermolecular interactions between the ozonide ions (dimerization) can be ruled out on the grounds of the large intermolecular distances<sup>[3]</sup>. Also still inexplicable are the marked differences in the stability of the compounds with 19-electron systems ( $\text{NF}_2$ ,  $\text{SO}_2^-$ ,  $\text{O}_3^-$ ,  $\text{S}_3^-$ ,  $\text{ClO}_2$ ) towards dimerization. Whichever of the conceivable criteria is analyzed for an explanation (repulsion of non-bonding electron pairs, differences in electronegativity<sup>[6]</sup>, charge of the monomer, state of aggregation) there are inconsistencies.

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- [3]  $\text{KO}_3$ : 14/mcm,  $a = 864.80(12)$ ,  $c = 716.40(14)$  pm ( $-25^\circ\text{C}$ ),  $V = 535.78 \times 10^6$  pm<sup>3</sup>,  $Z = 8$ . Siemens AED2 diffractometer,  $\text{MoK}\alpha$  radiation, graphite monochromator, scan width  $2.0^\circ$ ,  $\omega$ -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).— $\text{RbO}_3$ :  $P2_1/c$ ,  $a = 644.10(22)$ ,  $b = 603.00(35)$ ,  $c = 874.60(36)$  pm ( $-25^\circ\text{C}$ ),  $\beta = 122.25(2)^\circ$ ,  $V = 287.28 \times 10^6$  pm<sup>3</sup>,  $Z = 4$ . Siemens AED2 diffractometer,  $\text{MoK}\alpha$  radiation, graphite monochromator, scan width  $2.8^\circ$ ,  $\omega$ -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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