Crystal Structure of $K_2[C_2O_6]$—First Proof of Existence and Constitution of a Peroxodicarbonate Ion**

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The characteristics of homonuclear bonds between second-row elements are predominantly determined by the strong π overlap of 2p-type wave functions. These interactions can, on one hand, cause considerable strengthening through multiple bond formation, and on the other, weakening of the bonds through lone pair/lone pair repulsion, as soon as the number of p electrons involved per atom exceeds three. The general trend is significantly modulated by the nature of the substituents and the conformation across the homonuclear bond. Those substituents lacking lone pairs and exhibiting high electronegativities appear to reinforce the X–X homonuclear single bonds, by increasing the s contribution to the sigma bond, and by removing electron density from the repulsive lone pairs. This is immediately evident upon comparing the O–O bond lengths in O_2F_2, $O_2(SiMe_3)_2$, and O_2^{2-} (in K_2O_2) which cover the impressively wide range from 122 to 150 and 154 pm.[1] Fully in line with these considerations, among the known diperoxo anions, peroxodisulfate is more stable than peroxodiphosphate, and similar anions of Group 14 elements, such as peroxodisilicate, are not known at all.[2] Since their discovery in the 19th century, percarbonates have been studied repeatedly, in order to reveal constitutions and bonding properties, and to inspect their potential for application as bleaching agents in the detergent industry.[3] In spite of these efforts, the extent of reliable insights has remained limited.[4] Major problems arise from the fact that peroxide functions in the structures can also originate from hydrogen peroxide of crystallization,[6] and because of the thermal lability preventing complete removal of water by drying. It has been shown recently by single-crystal X-ray structure analysis that $KHCO_4 \cdot H_2O_2$, and the respective rubidium compound, unambiguously constitute hydrogenmonoperoxocarbonates.[7] For a peroxodicarbonate, however, conclusive evidence for its constitution,[8] and even existence, has been lacking. Therefore we have reinvestigated a material with the bulk composition of $K_2C_2O_6$ which, according to vibrational spectroscopy,[3e] contains peroxide functions. By means of a crystal structure determination using high-resolution X-ray powder diffraction data (Figure 1) we show that this compound is free of water and hydrogen peroxide of crystallization, and contains the fully deprotonated peroxodicarbonate anion.[9]

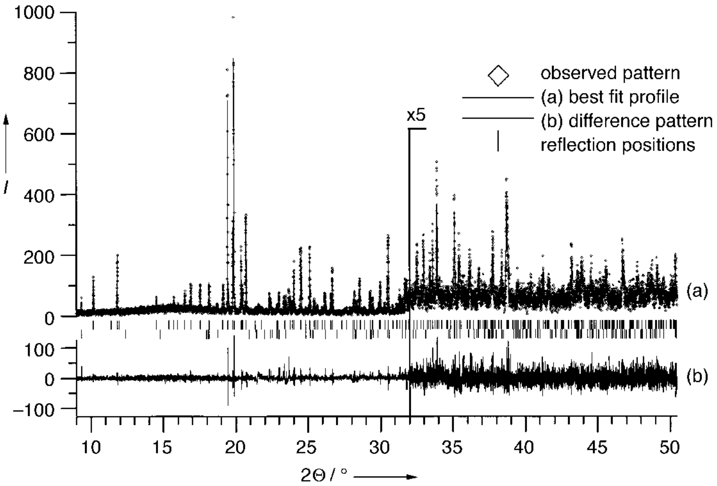

Figure 1. Scattered X-ray intensity for potassium peroxodicarbonate at $T = -123\,^{\circ}C$ as a function of diffraction angle 2Θ. Shown are the observed pattern (diamonds), the best Rietveld-fit profile in $P2_1/c$ (line a), the difference curve between observed and calculated profile (line b), and the reflection markers (vertical bars). The wavelength was $\lambda = 1.12074(2)$ Å. The higher angle part starting at $2\Theta = 32°$ is enlarged by a factor of 5.

Potassium peroxodicarbonate was synthesized electrochemically from a saturated aqueous solution of K_2CO_3 at $T = -20\,^{\circ}C$. The samples as obtained are microcrystalline and white, with a faint sky blue color. We have been able to prepare single-phase material; however, most charges contain small amounts of $KHCO_3$, the first decomposition product of $K_2C_2O_6$ in an aqueous environment, as an impurity.

The peroxodicarbonate anion (Figure 2) consists of two carbonate groups that are connected through two of its oxygen atoms to form a peroxo group. The molecular symmetry was found to be C_2 within the limits of experimental error.[13] The carbon atoms are surrounded by oxygen atoms in a near trigonal-planar arrangement and in general, the

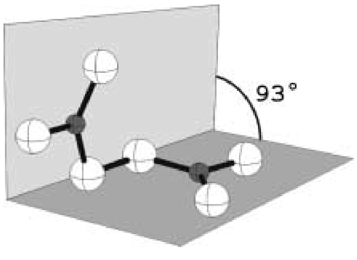

Figure 2. Conformation of the peroxodicabonate anion as found in $K_2C_2O_6$ at $T = -123\,^{\circ}C$. The torsion angle between the two carbonate groups is given.

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intramolecular bond lengths and angles of the carbonate group are within the typical range found for this class of molecules (Table 1). Remarkably, the bond length between the carbon atom and the peroxo-oxygen atom is only 3% longer than the lengths of the terminal C–O bonds. Therefore, this bond contains some degree of double-bond character. The deviations from planarity for the carbonate groups including the second peroxo-oxygen atom are below the precision of the measurement. The O–O bond length in the peroxo group (147(1) pm) is virtually the same as for the related peroxomonohydrogencarbonate anion (146 pm).[7] The C-O-O-C dihedral angle of 93(1)° corresponds to that for dicyclohexylperoxodicarbonate (90°)[15c] and for solid H_2O_2 (93°).[15a] According to the experimental findings (short bonds, planarity of $OOCO_2$ moiety) the C–O(peroxo) bonds show double-bond character and the peroxo-oxygen atoms can be regarded as sp^2 hybridized which leads to an occupied p_z orbital orthogonal to the $O_2C–OO$ plane. The strong repulsion of these orbitals across the O–O bond favors the staggered conformation of O_2C-O-O-CO_2.

Table 1. Selected bond lengths [pm] and torsion angles [°] for $K_2C_2O_6$ and related molecules.

Substance	Ref.	d(O–O)	d(K–O)	d(C–O)	$d(C–O_O)$	C-O-O-C
$K_2C_2O_6$		147(1)	263(1) – 290(1)	126(2) – 129(2)	131(1)	93(1)
$KHCO_4 \cdot H_2O_2$	[7a]	146	275 – 283	123 – 125	138	101_{COOH}
H_2O_2	[15a]	146	–	–	–	93_{HOOH}
K_2CO_3	[15b]	–	264 – 286	127 – 129	–	–
$(C_6H_{11})_2C_2O_6$	[15c]	143	–	118 – 132	138	90

There are two inequivalent potassium sites, but every potassium ion is coordinated to seven oxygen atoms, forming irregular KO_7 polyhedra (Figure 3). The polyhedra can be described as strongly distorted trigonal prisms with an additional oxygen atom above one of the rectangular faces, which forms a long bond to the central cation. The bond lengths between the potassium atoms and the oxygen atoms are in the range 2.63 to 2.9 Å, comparable to that of related compounds (Table 1). The potassium ions are connected to seven oxygen atoms of five different peroxodicarbonate dianions. In the case of the $K(1)O_7$ polyhedron, one edge is equivalent to a peroxo bridge, whereas in the case of the $K(2)O_7$ polyhedron, one edge is equivalent to the triangular edge of a carbonate group. In both cases another peroxodicarbonate group is side-on coordinated (carbonate- and peroxo-oxygen atoms).

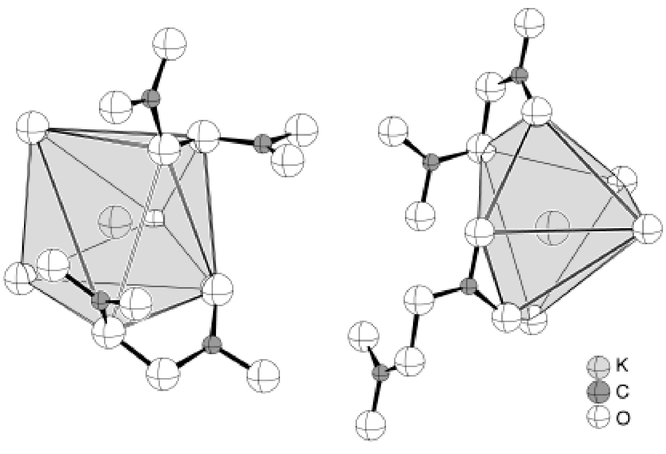

Figure 3. Representation of the two crystallographically distinct KO_7 coordination polyhedra and specially connected peroxodicarbonate groups of potassium peroxodicarbonate at $T = -123$ °C. The other oxygen atoms are carbonate-oxygen atoms of end-on coordinated peroxodicarbonate groups.

The crystal structure of $K_2[C_2O_6]$ is based on a three-dimensional framework of KO_7 polyhedra, interconnected by carbonate groups. For a better understanding, if only the central carbon atoms of the carbonate groups are considered, the crystal structure of $K_2C_2O_6$ can be viewed as a strongly distorted NaCl arrangement with mean KC_6 and CK_6 distances of 350(20) pm (Figure 4).

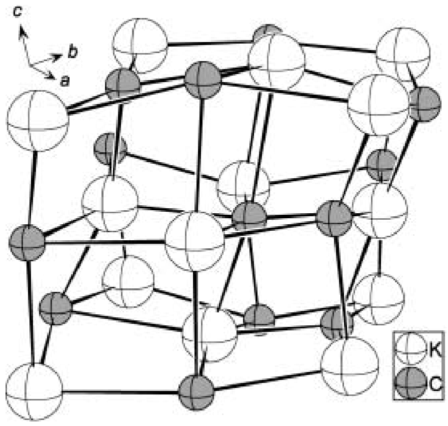

Figure 4. Packing scheme of $K_2C_2O_6$ at $T = -123$ °C in a view perpendicular to the plane spanned by the c axis and the median of a and b axes. The structural relationship to the NaCl type of structure is clearly visible.

Application of peroxodicarbonate as a bleaching component in detergents would liberate harmless carbon dioxide and potassium, besides the desired active oxygen, and would help to maintain favorable pH conditions. Also the onset of rapid decomposition occurs at an appreciably high temperature of 141 °C. Nevertheless all prospects for application in the detergent industry seem to be hindered by its reduced stability during long-term storage.

Experimental Section

$K_2C_2O_6$ was synthesized by anodic oxidation of a saturated aqueous solution of potassium carbonate (p.a., Merck) at $T = -20$ °C. The electrocrystallization was carried out under galvanostatic conditions ($I = 250$ mA, $U > 16$ V) with a potentiostat (EG&G Princeton Applied Research, Type 363). A Pt wire (∅ = 0.5 mm, $l = 40$ mm) was used as an anode, a Pt mesh ($\varnothing_{cyl.} = 40$ mm, $h = 50$ mm, 20 mesh) as cathode. The anodic part was separated by a glassy membrane. Potassium peroxodicarbonate, obtained as a microcrystalline, light blue powder, was filtered and washed with ethanol and diethyl ether. The peroxide content was determined iodometrically.[16] $K_2C_2O_6$ decomposes rather slowly when stored below −20 °C for several weeks (8% per week).

According to the results of thermal analysis (DTA/TG/MS; Metzsch STA 429; 20 °C – 800 °C; 2 °C min^{-1}) and in agreement with previous experiments,[3e] $K_2C_2O_6$ decomposes at 141 °C by generation of oxygen and carbon dioxide.

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[8] Interpretation of the IR data was based on the wrong molecular symmetry; however, the postulation of a peroxodicarbonate anion was correct.[3e]

[9] a) Crystal structure data of $K_2C_2O_6$: monoclinic, space group $P2_1/c$ (no. 14), $a = 838.05(1)$, $b = 1076.41(2)$, $c = 711.67(1)$ pm, $\beta = 111.24(0)^\circ$ $V = 598.4(2) \times 10^6$ pm^3, $\rho_{\text{calcd}} = 2.200$ g cm^{-3}, $\rho_{\text{measured}} = 2.14(1)$ g cm^{-3} (He pycnometer, Micrometritics AccuPyc 1330 GB), $Z = 4$, $\mu = 55.04$ cm^{-1}. b) Devices for X-ray diffraction experiments: Suny X3B1 beamline at National Synchroton Light Source, Brookhaven National Laboratory, USA, double Si(111) monochromator, and Ge(111) crystal analyzer, $\lambda = 115.011(2)$ pm, Na(Tl)I scintillation counter with pulse height discriminator, $T = -73\,^\circ$C, $5.0^\circ < 2\Theta < 43.679^\circ$ in steps of $0.003^\circ 2\Theta$, glass capillary of 0.7 mm diameter; due to decomposition even at low temperature, a second measurement for structure refinement was performed at beamline B2 at the Hamburger Synchrotronstrahlungslabor (HASYLAB) immediately after synthesis of the material: Three-circle Huber goniometer, Ge(111) double crystal monochromator, and Ge(111) crystal analyzer, $\lambda = 112.074(2)$ pm, Na(Tl)I scintillation counter, $T = -123\,^\circ$C, $9.0^\circ < 2\Theta < 50.5^\circ$ in steps of $0.003^\circ 2\Theta$, glass capillary of 0.7 mm diameter. c) Structure determination process: Data reduction and background modeling by using the GUFI program,[10] crystal structure solution by global optimization with 15 parameters by using the DASH program package,[11] two phases of Rietveld refinements by employing a model for anisotropic micro-strain with potassium hydrogencarbonate as second phase by using the GSAS program package,[12] $R_p = 0.193$, $R_{wp} = 0.246$, $R_F = 0.080$, $\chi^2 = 0.84$, number of reflections 281, number of variables 35, number of refined atoms 10. The relatively high weighted-profile R factor is due to the statistics of the observed step scan intensities caused by limited time for measurement. d) Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412335.

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Self-Assembled Receptors for Enantioselective Recognition of Chiral Carboxylic Acids in a Highly Cooperative Manner

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One of the ultimate aims in molecular recognition is to understand fully and mimic the exquisite selectivities so eminently observed in natural receptors, such as antibodies and enzymes. A first approach is to build synthetic receptors by using rigid covalent scaffolds, to which are attached functional groups that can bind their guest molecules by multiple noncovalent interactions, such as hydrogen bonding, π–π stacking, or metal coordination.[1] However, covalent systems are often too rigid and unable to adapt their shape to that of the guest, which can result in less than optimal binding affinities and selectivities. Another important drawback of covalent receptor molecules is their labor-intensive synthesis, which leaves little potential for structural variations in the scaffold.[2]

A different approach to shaping the binding site of an artificial receptor is to bring together the different components by multiple noncovalent interactions.[3, 4] This approach, which more closely resembles Nature's strategy, is currently being investigated as a potential alternative to covalent receptor molecules. A number of systems based on coordinative metal–ligand interactions[5] or hydrogen-bonding interactions[6] have been investigated, and some show significant structural selectivities.[7] However, in the majority of cases, substrate selectivity is the result of shape complementarity

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