$KH(O_2)CO_2 \cdot H_2O_2$—An Oxygen-Rich Salt of Monoperoxocarbonic Acid**

Arnold Adam* and Mathias Mehta

> *"..speculation about the structure of these compounds is less profitable than X-ray crystallographic examination."*
>
> A. F. Wells[1a]

The existence of peroxocarbonate or hydrogen peroxocarbonate anions in saltlike compounds has so far not been proven by structural methods.[1b–e] The reported compositions of alkaline and alkaline earth metal peroxocarbonates and hydrogen peroxocarbonates, for example, have been derived either from analytical methods or from the preparative route and the ability to give off oxygen.[2] Models of the structure of such moieties have been developed by using data from vibrational spectroscopy on microcrystalline materials.[3] The commercially used product incorrectly labeled as "percarbonate" is in fact a hydrogen peroxide adduct of sodium carbonate, $Na_2CO_3 \cdot 1.5\,H_2O_2$.[4]

Our studies on hydrogen carbonates[5] and structurally related carbonic acid derivatives, such as monoalkylcarbonates,[6] led to the following questions for the acidic salts of the unknown peroxocarbonic acid H_2CO_4: what structural characteristics are exhibited by a hydrogen peroxocarbonate ion, how does it participate in hydrogen bonding, and how do the resulting anion blocks fit into the general system of hydrogen carbonates?[7]

$KH(O_2)CO_2 \cdot H_2O_2$ is the first compound of a new class of substances[8] for which "true" peroxocarbonate ions have been shown to exist in the form of $[H(O_2)CO_2]^-$ ions by X-ray crystal structure analysis (Figure 1 and Table 1). These can be formally derived by replacing the OH group of a hydrogen carbonate ion by an OOH group. The C atom is surrounded in an approximately trigonal-planar fashion by O1, O2, and O3 (C–O: 122.9(2)–138.1(2) pm; O-C-O: 110.4(2)–129.6(2)°). The deviations are caused by the fact that O3 belongs to the peroxo grouping. Within experimental error, the C atom is in the plane defined by O1, O2, and O3, while the O4 atom of the peroxo group is displaced from this plane by 18.5(4) pm. The O3–O4 distance (145.7(2) pm) is comparable to that in solid H_2O_2.[9] The C-O3-O4 angle of 111.9(1)° corresponds closely to a tetrahedral angle, while the torsion angle C-O3-O4-H1 is 101(6)°. The angle between the hydrogen-bond donor O4, H1, and the hydrogen-bond acceptor O2 is 138(8)°, while the angle O3-O4-H1 is 88(5)°, again comparable to that found in solid H_2O_2. The hydrogen bond lengths of 268.0(3) pm for O2 ··· O4 agree well with those found in $Na_2CO_3 \cdot 1.5\,H_2O_2$.[4] The hydrogen peroxocarbonate anions are linked by the hydrogen bonds into zigzag-shaped ${}^1_\infty[H(O_2)CO_2]$ chains, which run along the [100] direction. A similar structural feature is found for sodium hydrogen carbonate[10] and ammonium hydrogen carbonate,[11] which are characterized by stacks of ${}^1_\infty[HCO_3]$ chains. Thus the hydrogen peroxocarbonate structural unit fits readily into the system developed for hydrogen carbonates.[7] In contrast to the hydrate-free $NaHCO_3$, the ${}^1_\infty[H(O_2)CO_2]$ chains found in $KH(O_2)CO_2 \cdot H_2O_2$ are linked by H_2O_2 molecules to form ${}^2_\infty\{[H(O_2)CO_2](H_2O_2)\}$ layers, which run parallel to the *ac* plane (Figure 2). The potassium ions are embedded between these layers and exhibit a 7 + 2 coordination by nine oxygen atoms (seven O atoms at distances ranging between 274.7(2) and 283.1(2) pm, and two O atoms at 306.2(2) and 312.7(2) pm), which belong to three H_2O_2 molecules and four hydrogen peroxocarbonate anions.

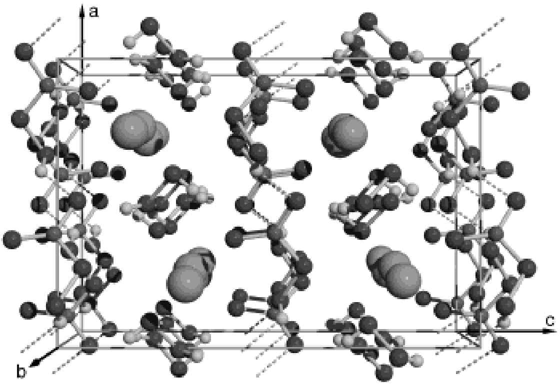

Figure 1. Crystal structure of $KH(O_2)CO_2 \cdot H_2O_2$ with unit cell, shown along [010]. The hydrogen bonds between the $[H(O_2)CO_2]^-$ ions and the H_2O_2 molecules have been omitted for clarity.[18]

Table 1. Atomic coordinates and equivalent isotropic displacement parameters for $KH(O_2)CO_2 \cdot H_2O_2$.

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}[a]
K	0.23463(4)	0.09434(9)	0.81255(3)	171(3)
C	0.3971(2)	0.1733(3)	0.5126(1)	133(7)
O1	0.3788(2)	0.1624(2)	0.4187(1)	178(5)
O2	0.5066(1)	0.2248(2)	0.5621(1)	206(5)
O3	0.2857(2)	0.1245(2)	0.5793(1)	254(6)
O4	0.1649(2)	0.0443(3)	0.5251(1)	293(6)
O5	0.5980(2)	0.3499(2)	0.7768(1)	197(6)
O6	0.4963(2)	0.4425(2)	0.7119(1)	196(6)
H1	0.108(9)	0.139(9)	0.529(7)	29(5)
H2	0.544(4)	0.341(4)	0.823(2)	4(1)
H3	0.481(5)	0.367(5)	0.668(3)	6(1)

[a] [pm^2]; H atoms: 10^2 [pm^2]. U_{eq} is in the form $\exp\{-8\pi^2 U_{ij}{}^2(\sin^2\theta/\lambda)^2\}$.

The high content of releasable oxygen is remarkable. According to the decomposition reaction of $KH(O_2)CO_2 \cdot H_2O_2$ in Equation (a), this released oxygen constitutes

$$KH(O_2)CO_2 \cdot H_2O_2 \longrightarrow KHCO_3 + H_2O + O_2\uparrow \qquad (a)$$

21.3% by mass, which is substantially higher than the values found for commercially used peroxo species such as $(H_2N)_2CO \cdot H_2O_2$ (17.0 wt%),[12] $Na[BO_2(OH)_2]$ (16.0 wt%),[13] and $Na_2CO_3 \cdot 1.5\,H_2O_2$ (theory: 15.2 wt%, practice: 14.5 wt%). While $KH(O_2)CO_2 \cdot H_2O_2$ is not stable at room temperature, further experiments[14] have shown that

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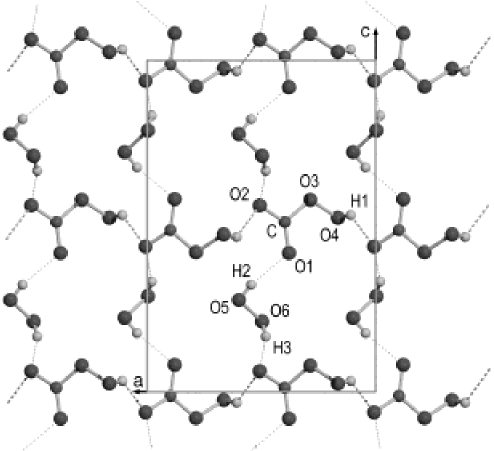

Figure 2. Section of the crystal structure of $KH(O_2)CO_2 \cdot H_2O_2$ along [010], showing the linkage of the $[H(O_2)CO_2]^-$ ions and the H_2O_2 molecules through hydrogen bonds to give $^2_\infty\{[H(O_2)CO_2](H_2O_2)\}$ layers.[18]

varying the cation leads to increased thermal stability. Therefore, a temperature-dependent decomposition might be feasible that can be adjusted for various applications.

This is of great importance for the large industrial demand for readily accessible and easily manageable compounds with a high content of releasable oxygen. In this context, peroxo compounds such as hydrogen peroxide, perborates, persulfates, organic hydrogen peroxide derivatives as well as hydrogen peroxide adducts are employed on large scales, for example, as bleaching and oxidizing agents, components of detergents, antiseptic agents and disinfectants, oxygen reservoirs, radical initiators for polymerizations, catalysts. The growing market for water, sewage, and exhaust treatment systems is also of increasing importance.[15]

Experimental Section

$KH(O_2)CO_2 \cdot H_2O_2$: H_2O_2 (ca. 30% solution) was cooled to -10 to $-15\,^\circ C$ and saturated with solid $KHCO_3$. The resulting solution was layered with ethanol (approximately half the volume of the solution) and stored at -15 to $-20\,^\circ C$. After a few days the desired product formed in the aqueous phase in the form of crystalline needles. Initial studies indicated that with increased reaction time, potassium carbonate (tris)peroxohydrate[16] was also obtained.

Crystal structure data for $KH(O_2)CO_2 \cdot H_2O_2$: orthorhombic, space group *Pbca* (no. 61), $a = 891.3(2)$, $b = 857.4(1)$, $c = 1293.7(2)$ pm, $V = 988.6(3) \times 10^6\,pm^3$, $\rho_{calcd} = 2.017\,g\,cm^{-3}$, $Z = 8$, crystal dimensions $0.1 \times 0.15 \times 0.35\,mm^3$, $T = 173(2)$ K, $F(000) = 608$, $\mu(Mo_{K\alpha}) = 1.018\,mm^{-1}$, $\lambda = 71.073$ pm, Enraf-Nonius-CAD4-diffractometer, graphite monochromator, $\omega/2\theta$ scan, 1797 measured, 918 symmetry-independent reflections, 732 reflections with $F_o > 4\sigma|F_o|$, 85 refined parameters; structure solution with direct methods and successive Fourier- and difference Fourier syntheses.[17] All atomic positions were refined anisotropically (K,C,O) or isotropically (H) against $|F^2|$ to yield $R = 0.036$ and $wR2 = 0.082$; largest residual electron densities $-0.574 \leq \delta \leq 0.990$ near the potassium atom ($GooF = S = 1.061$ for all data). Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407779.

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