

The Crystal Structure of Sodium Percarbonate: An Unusual Layered Solid

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The structure of sodium percarbonate, $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$, has been solved from film-scanned data and refined to $R = 0.114$. [$Aba2$, $a = 9.224$ (4), $b = 15.805$ (4), $c = 6.747$ (2) Å, $Z = 8$, $d_m = 2.05$, $d_c = 2.12$ g cm⁻³, $\lambda_1(\text{Cu } K\alpha_1) = 1.54051$ Å.] The CO_3 ions and H_2O_2 molecules lie in planes about 3.5 Å apart, although the H_2O_2 molecules are inclined somewhat with respect to the CO_3 ions. The Na ions are midway between these molecular sheets. One of the H_2O_2 molecules is disordered between two possible orientations.

Introduction

Sodium percarbonate is the most stable common perhydrate (*i.e.* a solid containing H_2O_2 of crystallization) and is used extensively in industry as a bleach. All previous work on the alkali-metal percarbonates was summarized and extended by Partington & Fathallah (1950) who showed that compounds previously formulated as $M_2\text{CO}_4 \cdot x\text{H}_2\text{O}$ are identical to those formulated $M_2\text{CO}_3 \cdot (x-1)\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$. This conclusion was further confirmed by De Celis & Masaguer (1955) for the title compound. Connor & Richards (1958) showed by NMR that sodium percarbonate gave a narrow proton resonance line consistent with the view that all the H is present as H_2O_2 . Despite this preponderance of evidence to show that sodium percarbonate is a true perhydrate and not a peroxy salt the structural study was undertaken, bearing in mind the quotation 'speculation about the structure of these compounds is less profitable than X-ray crystallographic examination' (Wells, 1975).

Experimental

Many perhydrates can be grown by slow evaporation from H_2O_2 solution, *e.g.* Pedersen & Pedersen (1964). However, single crystals of sodium percarbonate cannot be grown from an $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}/\text{H}_2\text{O}_2$ system because any percarbonate formed is immediately decomposed by water. Commercial samples are produced from a slurry of Na_2CO_3 and H_2O_2 solution in CCl_4 but this procedure does not give suitable single crystals. Since it is known that H_2O_2 is stabilized in solution at high pH, it was decided to study crystal growth from the $\text{Na}_2\text{CO}_3/\text{NaOH}/\text{H}_2\text{O}/\text{H}_2\text{O}_2$ system. Two products could be obtained that were definitely *not* sodium percarbonate. These were (i) $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, which was made by adding 50% (w/w) H_2O_2 solutions to concentrated NaOH and (ii) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. Both these products were identified from Guinier

photographs. The following method was finally developed and was found to give consistent products. 10 g NaOH were dissolved in 10 cm³ water, and 10 g Na_2CO_3 were dissolved in 30 cm³ water with a little warming. 10 cm³ of 50% (w/w) H_2O_2 solution were placed in a 250 cm³ beaker and cooled in an ice bath. When this solution was at 0°C, 2 cm³ of the NaOH solution were added with constant stirring. 1 cm³ of the Na_2CO_3 solution was then added, the stirrer was switched off and the solution left overnight. Fine, clear needle-shaped crystals were produced which gave an X-ray powder diffraction pattern identical to that given by a commercial material. Analysis of the crystals by $\text{I}_2/\text{S}_2\text{O}_3^{2-}$ titrations gave the formula $\text{Na}_2\text{CO}_3 \cdot 1.54\text{H}_2\text{O}_2$.

Photographs were used to determine the cell dimensions, and systematic absences were consistent with space groups $Aba2$ or (with change of axis) $Cmca$. Two different crystals, both $\sim 0.1 \times 0.1 \times 0.4$ mm, were used to collect data sets (levels 0–4 about *c* and 0–1 about *b*) with a Stoe Weissenberg camera. The films were scanned by the SRC Microdensitometer Service with an Optronics P1000 microdensitometer. No correction was made for absorption. Crystal data are given in the abstract.

Determination of the structure

The most distinctive feature of a Wilson plot performed on the data (279 unique reflexions) was its oscillating nature. The overall temperature factor was also very low at 0.4 Å². $N(z)$ tests for centrosymmetry fell between the theoretical values for 1 and $\bar{1}$ but were closer to the latter. Determination of the structure was originally attempted with *MULTAN* (Germain, Main & Woolfson, 1971) in $Cmca$. When this failed, the axes and indices of the reflexions were transformed to $Aba2$ and a solution again attempted with *MULTAN*. An *E* map computed from the set of phases with the highest combined figure of merit gave chemically reasonable

peak positions for all the nonhydrogen atoms ($R = 0.32$). Isotropic refinement reduced R to 0.13, at which stage a difference synthesis showed that too much electron density had been placed at the $\frac{1}{2}\text{H}_2\text{O}_2$ position; there was also a region close to this group where insufficient electron density had been placed. Two different models were tried (Fig. 1): (i) Random substitution in some unit cells of H_2O for H_2O_2 . This refined to give site occupancies for H_2O_2 of 0.7 and for H_2O of 0.3. The peroxide O—O distance was 1.20 Å and R was 0.121. (ii) H_2O_2 molecules randomly disposed between two orientations. The site occupancy for each was set at 0.5 and the final R was 0.114.* The peroxide O—O distance was 1.49 Å. An anisotropic refinement gave problems with thermal parameters going non-positive definite and, although R improved, the e.s.d.'s of the positional parameters remained approximately constant. Refinement was therefore terminated and values for the isotropic refinement are reported.†

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32754 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† Since it was considered possible that the true space group was $Cmca$, a new refinement was undertaken in $Cmca$. It did not prove possible to reduce R below 0.20. The noncentrosymmetric structure therefore appears to be correct.

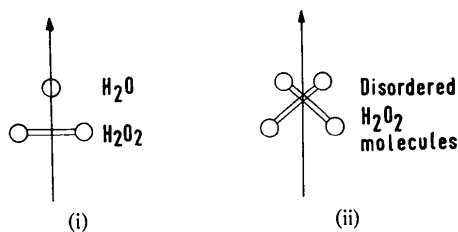


Fig. 1. The two models for the ' $\frac{1}{2}\text{H}_2\text{O}_2$ ' group. (i) Some of the hydrogen peroxide randomly replaced by water molecules and (ii) hydrogen peroxide disordered between two orientations.

Table 1. Fractional atomic coordinates and isotropic temperature factors with their standard deviations

	The site occupancy of O(4) and O(7) is 0.5.			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
Na(1)	0.2474 (18)	0.9886 (4)	0.274 (7)	0.018 (2)
Na(2)	0.9994 (17)	0.2502 (9)	0.281 (7)	0.013 (2)
C(1)	0.2481 (20)	0.1620 (9)	0.030 (fixed)	0.009 (3)
O(1)	0.1846 (14)	0.0902 (6)	0.019 (7)	0.007 (3)
O(2)	0.3915 (13)	0.1652 (7)	0.023 (8)	0.008 (3)
O(3)	0.1771 (13)	0.2317 (7)	0.010 (7)	0.010 (3)
O(4)	0.5445 (28)	0.0327 (14)	0.984 (8)	0.005 (6)
O(5)	0.9082 (23)	0.1130 (14)	0.923 (8)	0.041 (6)
O(6)	0.8438 (23)	0.1381 (13)	0.120 (7)	0.042 (6)
O(7)	0.5075 (47)	0.0254 (19)	0.142 (9)	0.034 (10)

Table 2. Bond lengths (Å)

C(1)—O(1)	1.28 (2)	Na(1)—O(6 ^{vi})	2.40 (4)
C(1)—O(2)	1.32 (2)	Na(1)—O(7 ^{vi})	2.42 (5)
C(1)—O(3)	1.29 (2)	Na(1)—O(7 ⁱⁱ)	2.60 (5)
O(4)—O(7 ⁱ)	1.49 (7)	Na(2)—O(2 ^{vii})	2.40 (6)
O(5)—O(6)	1.51 (6)	Na(2)—O(2 ^{viii})	2.34 (5)
Na(1)—O(1 ⁱⁱ)	2.42 (5)	Na(2)—O(3 ^{ix})	2.47 (5)
Na(1)—O(1 ⁱⁱⁱ)	2.38 (5)	Na(2)—O(3 ^x)	2.25 (5)
Na(1)—O(4 ^{iv})	2.36 (5)	Na(2)—O(5 ^{xi})	2.50 (4)
Na(1)—O(4 ^v)	2.75 (6)	Na(2)—O(6)	2.51 (4)
Na(1)—O(5 ^{iv})	2.39 (4)		

Symmetry code

(i)	$1 - x, -y, 1 + z$	(x)	$1 - x, \frac{1}{2} - y, \frac{1}{2} + z$
(ii)	$x, 1 + y, z$	(xi)	$2 - x, \frac{1}{2} - y, -\frac{1}{2} + z$
(iii)	$\frac{1}{2} - x, 1 + y, \frac{1}{2} + z$	(xii)	$1 + x, y, 1 + z$
(iv)	$-\frac{1}{2} + x, 1 - y, -\frac{1}{2} + z$	(xiii)	$x, y, 1 + z$
(v)	$1 - x, 1 - y, -1 + z$	(xiv)	$1\frac{1}{2} - x, y, -\frac{1}{2} + z$
(vi)	$1 - x, 1 - y, z$	(xv)	$-\frac{1}{2} + x, -y, -\frac{1}{2} + z$
(vii)	$\frac{1}{2} + x, \frac{1}{2} - y, z$	(xvi)	$x, 1 + y, -1 + z$
(viii)	$1\frac{1}{2} - x, y, \frac{1}{2} + z$	(xvii)	$-\frac{1}{2} + x, 1 - y, \frac{1}{2} + z$
(ix)	$1 + x, y, z$	(xviii)	$\frac{1}{2} - x, 1 + y, -\frac{1}{2} + z$

Table 3. Bond angles (°)

O(1)—C(1)—O(2)	119 (1)	O(4 ^{iv})—Na(1)—O(4 ^v)	163 (1)	O(2 ^{vii})—Na(2)—O(2 ^{viii})	178 (2)
O(1)—C(1)—O(3)	121 (1)	O(4 ^{iv})—Na(1)—O(5 ^{iv})	98 (2)	O(2 ^{vii})—Na(2)—O(3 ^{ix})	78 (2)
O(2)—C(1)—O(3)	118 (1)	O(4 ^{iv})—Na(1)—O(6 ^{vi})	82 (1)	O(2 ^{vii})—Na(2)—O(3 ^x)	98 (1)
O(1 ⁱⁱ)—Na(1)—O(1 ⁱⁱⁱ)	97 (1)	O(4 ^{iv})—Na(1)—O(7 ^{vi})	160 (2)	O(2 ^{vii})—Na(2)—O(5 ^{xi})	87 (1)
O(1 ⁱⁱ)—Na(1)—O(4 ^{iv})	109 (1)	O(4 ^{iv})—Na(1)—O(7 ⁱⁱ)	163 (3)	O(2 ^{vii})—Na(2)—O(6)	81 (1)
O(1 ⁱⁱ)—Na(1)—O(4 ^v)	75 (1)	O(4 ^v)—Na(1)—O(5 ^{iv})	78 (1)	O(2 ^{viii})—Na(2)—O(3 ^{ix})	100 (1)
O(1 ⁱⁱⁱ)—Na(1)—O(5 ^{iv})	153 (2)	O(4 ^v)—Na(1)—O(6 ^{vi})	80 (1)	O(2 ^{viii})—Na(2)—O(3 ^x)	84 (2)
O(1 ⁱⁱⁱ)—Na(1)—O(6 ^{vi})	99 (2)	O(4 ^v)—Na(1)—O(7 ^{vi})	24 (2)	O(2 ^{viii})—Na(2)—O(5 ^{xi})	94 (2)
O(1 ⁱⁱⁱ)—Na(1)—O(7 ^{vi})	91 (2)	O(4 ^v)—Na(1)—O(7 ⁱⁱ)	32 (1)	O(2 ^{viii})—Na(2)—O(6)	99 (1)
O(1 ⁱⁱ)—Na(1)—O(7 ⁱⁱ)	80 (1)	O(5 ^{iv})—Na(1)—O(6 ^{vi})	81 (1)	O(3 ^{ix})—Na(2)—O(3 ^x)	175 (2)
O(1 ⁱⁱⁱ)—Na(1)—O(4 ^{iv})	83 (2)	O(5 ^{iv})—Na(1)—O(7 ^{vi})	62 (2)	O(3 ^{ix})—Na(2)—O(5 ^{xi})	99 (1)
O(1 ⁱⁱⁱ)—Na(1)—O(4 ^v)	113 (1)	O(5 ^{iv})—Na(1)—O(7 ⁱⁱ)	75 (1)	O(3 ^{ix})—Na(2)—O(6)	88 (2)
O(1 ⁱⁱⁱ)—Na(1)—O(5 ^{iv})	90 (2)	O(6 ^{vi})—Na(1)—O(7 ^{vi})	95 (2)	O(3 ^x)—Na(2)—O(5 ^{xi})	82 (1)
O(1 ⁱⁱⁱ)—Na(1)—O(6 ^{vi})	162 (2)	O(6 ^{vi})—Na(1)—O(7 ⁱⁱ)	111 (2)	O(3 ^x)—Na(2)—O(6)	89 (1)
O(1 ⁱⁱⁱ)—Na(1)—O(7 ^{vi})	94 (1)	O(7 ^{vi})—Na(1)—O(7 ⁱⁱ)	18 (1)	O(5 ^{xi})—Na(2)—O(6)	164 (1)
O(1 ⁱⁱⁱ)—Na(1)—O(7 ⁱⁱ)	82 (1)				

Unit weights were used. Scattering factors for Na^+ , C, O (for the H_2O_2 molecules) and $\text{O}^{2/3-}$ (for the carbonate groups) were taken from *International Tables for X-ray Crystallography* (1974). All calculations except the structure solution were made with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Fractional atomic coordinates and isotropic temperature factors are given in Table 1, bond lengths and angles in Tables 2 and 3.

Discussion

The structure (Figs. 2 and 3) is made up of layers of hydrogen-bonded CO_3 ions and H_2O_2 molecules with Na ions midway between these layers. The main

features of the structure are therefore clear and the possibility of sodium percarbonate containing CO_4^{2-} groups can be discounted; the ideal formula for this compound is $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$. The most interesting part of the structure is the $\frac{1}{2}\text{H}_2\text{O}_2$ group. Model (i) in which some of this H_2O_2 was randomly replaced by water, a characteristic sometimes seen in perhydrates (Pedersen, 1972*b*), had certain anomalous features. The O—O distance refined to 1.2 Å which is too short to be a peroxide O—O and is only consistent with an O_2 molecule. This possibility was investigated by Raman spectroscopy and was discounted; the compound was also shown to be diamagnetic which confirmed the absence of triplet O_2 . Model (ii), however, fitted experimental data in that the Raman spectra showed the O—O stretch at 870 cm^{-1} characteristic of H_2O_2 (Pedersen, 1967); iodine/thiosulphate titrimetry also

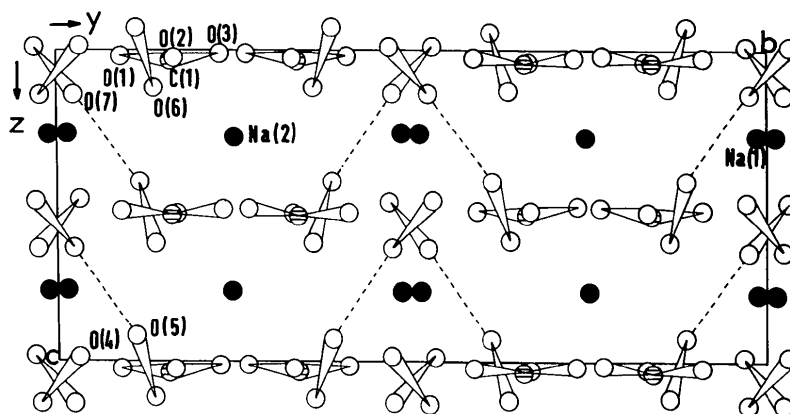


Fig. 2. Projection of the structure onto (100). The hydrogen bonding between sheets is shown.

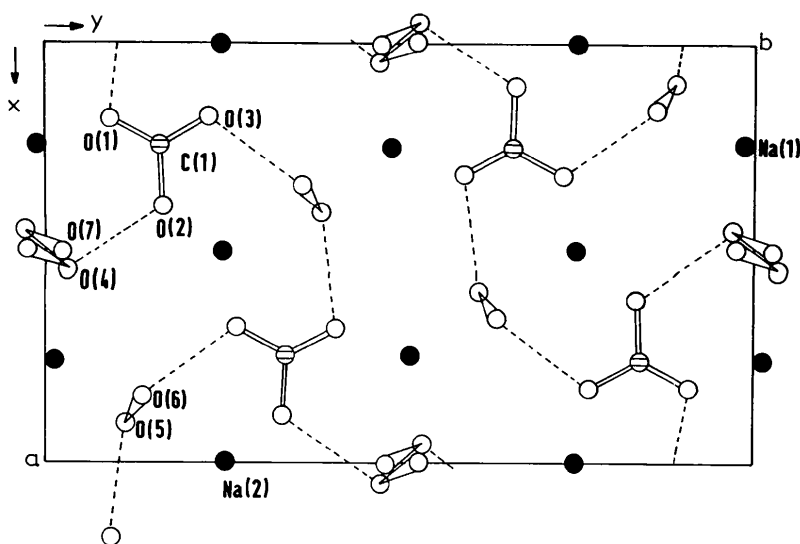


Fig. 3. Projection of the structure onto (001), from $z = -0.2$ to $z = +0.3$. The hydrogen bonds in this layer are shown.

gave a value very close to 1.5 H₂O₂ molecules/formula. It would seem, therefore, that the disordered H₂O₂ model (ii) is to be preferred.

The sheets of the structure consist of symmetrical CO₃ ions and H₂O₂ molecules held together by hydrogen bonds (Table 4) which are all fairly short, ranging from 2.52–2.66 Å. One hydrogen bond [O(7)–O(5^{xiv})] links each layer to the next (Fig. 2) and is short at 2.48 Å. Infrared evidence on the hydrogen-bonding distances (Pimentel & Sederholm, 1956) is in good agreement with these values and gives an average O...O distance of 2.60 Å. Any idea that the relatively high stability of sodium percarbonate would be reflected in the short (and therefore strong) hydrogen bonds is shown to be unconvincing since the distances found are similar to those found in other simple perhydrates of much lower stability (Adams & Pritchard, 1976; Pedersen, 1969, 1972a; Pedersen & Pedersen, 1964) where they are 2.59–2.69 Å.

The Na ions are held midway between the sheets; their coordination shells are made up of O atoms from CO₃ ions and H₂O₂ molecules. The environment about

Na(2) is not too irregular with Na–O ranging from 2.35 to 2.51 Å and adjacent ∠O–Na–O angles between 78 and 100°. Na(1), however, has a more complicated environment due to the disordered H₂O₂ groups. Four of the O atoms surround Na(1) in every unit cell: O(1ⁱⁱ), O(1ⁱⁱⁱ), O(5^{iv}) and O(6^{vi}). Four other O atoms can come within the normal coordination distance: O(4^{iv}), O(4^v), O(7^{vi}) and O(7ⁱⁱ) (Fig. 4). If the substitution in each cell is truly random then it would be possible to have several combinations of these O atoms about a particular Na(1): O(4^{iv}) and O(7^{vi}), or O(7^{vi}), or O(4^{iv}) and O(4^v) and O(7ⁱⁱ), or O(4^v) and O(7ⁱⁱ). Under these circumstances Na(1) could have a coordination number of 6, 5, 7 or 6 respectively.

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Table 4. *Hydrogen-bonding geometry*

O(5)···O(1 ⁱⁱⁱ)	2.63 (3) Å	O(4)···O(2 ⁱⁱⁱ)	2.52 (3) Å
O(6)···O(3 ^{vii})	2.66 (3)	O(7)···O(5 ^{xiv})	2.48 (7)

Other close contacts made by the O(4)–O(7) peroxide molecule

O(4)···O(1 ⁱ)	3.15 (3)	O(4)···O(6 ^{viii})	3.14 (6)
O(4)···O(2 ⁱ)	3.17 (3)	O(7)···O(5 ^{xv})	3.03 (6)

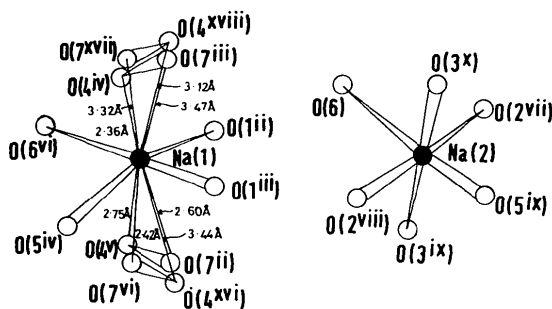


Fig. 4. Coordination environment about the sodium cations Na(1) and Na(2).