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The crystal structure of potassium bicarbonate, $KHCO_3$.

By Isamu Nitta, Yujiro Tomiie and Chung Hoe Koo, *Department of Chemistry, Osaka University, Nakanoshima, Osaka, Japan*

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Among acid carbonates, the crystal structures of sodium bicarbonate, $NaHCO_3$ (Zachariasen, 1933), ammonium bicarbonate, NH_4HCO_3 (Brooks & Alcock, 1950), and sodium sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$ (Brown, Peiser & Turner-Jones, 1949), have been examined by X-ray methods. In these crystals, the modes of atomic arrangement were found to be largely governed by the hydrogen-bond formation. Potassium bicarbonate, $KHCO_3$, was investigated by Dahr (1937), who gave the cell dimensions, the number of formula units and the space group, without giving any further account about the atomic arrangement. We have determined the structure of this substance to obtain some further information about the role of the hydrogen bond in the structures of acid salts.

Useful X-ray data were obtained from oscillation photographs taken with Cu $K\alpha$ radiation. The unit cell containing four formula units has the dimensions

$$a = 15{\cdot}11,\ b = 5{\cdot}67,\ c = 3{\cdot}71\ \text{Å},\ \beta = 103°\ 45',$$

which agree with Dahr's data approximately. The space group is C_{2h}^5–$P2_1/a$. The intensities of reflexions were visually estimated. Ordinary Patterson projections on (001) and (010), a refined Patterson projection with sharpened peaks on (001), a Harker section $H(x, \frac{1}{2}, z)$, and electron-density maps projected on (001), (010) and (100) were obtained. By successive approximation, we obtained the final values of the atomic coordinates, of which the x and y parameters were corrected for termination error. They are given in Table 1. In calculating the structure factors, the value of B in the temperature factor was taken as 1·77 Å^2. The values of $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ are 0·19, 0·16, 0·29 for ($hk0$), ($h0l$) and ($0kl$) zones respectively.

Table 1. *Final atomic parameters*

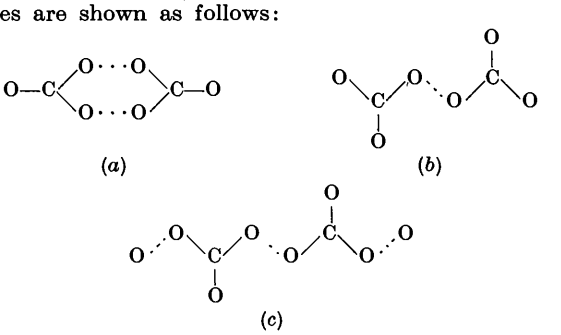
	x	y	z
K	$0{\cdot}163_3$	0·021	0·301
O_I	$0{\cdot}196_0$	0·541	0·078
O_{II}	$0{\cdot}081_3$	0·725	−0·317
O_{III}	$0{\cdot}078_9$	0·320	−0·233
C	$0{\cdot}117_7$	0·529	−0·150

Table 2. *Interatomic distances and bond angles*

C–O	1·28, 1·32, 1·33 Å
O–H · · · O	2·61
K · · · O	2·68, 2·69, 2·74, 2·82, 2·88, 2·92, 2·92, 3·13
K · · · K	3·71, 3·90
∠ O–C–O	118·5°, 119·5°, 122°
∠ C–O · · · O	116°, 122°

The interatomic distances and bond angles are given in Table 2. The CO_3 group has a planar configuration with the C–O distances 1·28, 1·32 and 1·33 Å, while the reported values of the C–O distances are 1·313 Å in calcite (Elliott, 1937), 1·27 Å in sodium bicarbonate, 1·23 and 1·26 Å in sodium sesquicarbonate, and 1·22 and 1·25 Å in sodium carbonate monohydrate (Harper, 1936). The two oxygen atoms with the longer C–O distances are hydrogen bonded in pairs to another CO_3 group with an O–H · · · O distance 2·61 Å, thus linking two CO_3 groups so as to form a complex anion $[H_2C_2O_6]^{--}$. This type of approximately co-planar conjugation of two bicarbonate ions is a new one found in acid carbonates and resembles that of a dimeric carboxylic acid such as formic acid in vapour.

Thus three types of the 'acid-salt' hydrogen bonding have so far been found: (*a*) the carboxylic acid or two-hydrogen-bond dimer type in $KHCO_3$, (*b*) the one-hydrogen-bond dimer type in $Na_2CO_3.NaHCO_3.2H_2O$, and (*c*) the chain type in $NaHCO_3$ and NH_4HCO_3. These types are shown as follows:



All these hydrogen bonds are very strong, the bond distances being 2·52, 2·55 and 2·61 Å for sodium sesquicarbonate, sodium bicarbonate and potassium bicarbonate respectively, and are approximately co-planar with the CO_3 groups.

Each potassium ion has eight oxygen neighbours with the K · · · O distances 2·68–3·13 Å.

(According to a recent private communication from Prof. T. Watanabé, now in the U.S.A., to whom our thanks are due, Couture-Mathieu (1950) has proposed a structure of potassium bicarbonate from a study of Raman spectra of single crystals. Her x and y parameters agree surprisingly well with ours when the origin is transferred to $(0, \frac{1}{4}, 0)$, but her z parameters differ entirely from ours. Although details of her investigation are not yet available to us, it is to be remarked that, if it is concerned with the same crystal modification, her structure does not account for the observed X-ray data.)

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