

The Crystal Structure of Potassium and Rubidium Oxalate Monoperhydrates, $K_2C_2O_4 \cdot H_2O_2$ and $Rb_2C_2O_4 \cdot H_2O_2$

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The crystal structures of potassium oxalate monoperhydrate, $K_2C_2O_4 \cdot H_2O_2$, and the isotopic rubidium salt, $Rb_2C_2O_4 \cdot H_2O_2$, have been determined from three-dimensional X-ray diffraction data.

The structure of the two compounds is closely related to the structure of the corresponding monohydrates.

The hydrogen peroxide molecule possesses the skew conformation with dihedral angles of $101.6 \pm 0.6^\circ$ and $103.4 \pm 0.7^\circ$ in the potassium and rubidium compounds, respectively. The O—O distance is $1.441 \pm 0.009 \text{ \AA}$ and $1.443 \pm 0.012 \text{ \AA}$, and the O...O—O angle is $102.5 \pm 0.6^\circ$ and $102.0 \pm 0.7^\circ$.

The oxalate ion is centrosymmetric and planar. The distances compare well with earlier investigations, and the same deviations from the regular ion are found: long C—C distances of $1.563 \pm 0.013 \text{ \AA}$ and $1.572 \pm 0.016 \text{ \AA}$, and O—C—O angles greater than 120° : $125.2 \pm 0.6^\circ$ and $123.4 \pm 0.7^\circ$.

The hydrogen peroxide molecules are engaged in relatively short hydrogen bonds of $2.591 \pm 0.009 \text{ \AA}$ and $2.635 \pm 0.012 \text{ \AA}$ to oxalate oxygens in both directions, thus building a three-dimensional network, constituting a relatively open, but fairly stable structure.

The potassium and rubidium ions are eight-coordinated by oxalate and hydrogen peroxide oxygens. The mean K—O distance is 2.907 \AA and the mean Rb—O distance is 3.036 \AA , both $\pm 0.007 \text{ \AA}$.

Investigations carried out at our institute have shown that all the alkali metal oxalates form monoperhydrates, a fact which seems to have escaped attention earlier.

Originally we thought that only the metal oxalates that do not form stable hydrates, such as lithium and sodium, might form perhydrates, but surprisingly enough experiments show that also the remaining alkalimetal oxalates form stable perhydrates by crystallization from a saturated perhydrol solution at room temperature. The stability of the potassium and rubidium compounds are even better than for the lithium and sodium salts.

In this paper we will present the crystal structure of two of these monoperhydrates, the potassium oxalate monoperhydrate, $K_2C_2O_4 \cdot H_2O_2$, and the isotopic rubidium salt, $Rb_2C_2O_4 \cdot H_2O_2$. By comparison with the known struc-

ture of other perhydrates,^{1,2} we will show that the conformation of the hydrogen peroxide molecule varies from one compound to another, and discuss in some detail the factors determining this conformation.

EXPERIMENTAL

Potassium oxalate monohydrate (*p.a.* E. Merck) was dissolved in perhydrol (30 % H_2O_2 in water). By slow evaporation at room temperature crystals in the form of diamond shaped plates separated out. The composition was determined analytically, and the results very closely correspond to $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$. Several batches of crystals were grown, and the composition invariably was the same when potassium oxalate monohydrate was allowed to crystallize from a saturated perhydrol solution.

The rubidium oxalate monoperhydrate crystals were synthesized and analysed by the same methods. The rubidium oxalate monohydrate was made by evaporation of a water solution of stoichiometric amounts of Rb_2CO_3 (*purum*, Fluka AG.) and oxalic acid dihydrate (*p.a.* Merck).

The crystals are relatively stable, and can be kept for several days in air. However, some decomposition seems to occur by exposure to X-rays, and hence several crystals had to be used to get a complete set of intensity data.

The intensity data consisted of multiple film zero-fifth layer Weissenberg equi-inclination diagrams taken rotating about the *b*-axis and zero layer Weissenberg diagrams rotating about the *a*-axis, using Ni-filtered $\text{CuK}\alpha$ radiation for both compounds, giving a total of about 400 independent reflections for each compound. The intensities were estimated visually and corrected in the usual way for Lorentz and polarization effects. No absorption correction was applied, however, partly because of the irregular shape of the crystals and difficulties in grinding them to a more symmetrical form. The appearance of the spots on the higher level Weissenberg diagrams were allowed for using a method described by Philips.³

The unit cell dimensions were determined from oscillation and Weissenberg diagrams, and refined by Guinier powder patterns using $\text{CuK}\alpha_1$ radiation. The values are:

	<i>a</i>	<i>b</i>	<i>c</i>	β
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	8.969 Å	6.532 Å	10.955 Å	108.40°
$\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	9.251 Å	6.808 Å	11.199 Å	107.45°

With four formula units in the cell a density of 2.18 g/cm³ and 2.90 g/cm³ is derived for the two compounds, whereas the density determined by the floatation method is 2.18 g/cm³ and 2.91 g/cm³, respectively.

The scattering factors used throughout the calculation were taken from the *International Tables for X-ray Crystallography*.⁴

STRUCTURE DETERMINATION

As judged from systematic absences two space groups are possible *C2/c* and *Cc*. The similarity in cell dimensions and Weissenberg-film intensity distribution between these two salts and the corresponding hydrates,^{5,6} however, made us choose the highest symmetric space group *C2/c*, in which the hydrates crystallize. The choice was supported by the subsequently successful determination of structure based upon the centrosymmetric space group.

From the Weissenberg data three-dimensional Patterson syntheses were calculated. From the peaks in the resulting maps it was evident that there was a close relationship between this structure and that of the corresponding hydrates.

The heavy atom coordinates were determined and Fourier maps evaluated, and from subsequent three-dimensional Fourier maps the light atom coordinates were determined. It turned out that the metal and the oxalate ion in the perhydrates and in the hydrates have the same spatial arrangement, and the hydrogen peroxide molecule is located with the oxygen-oxygen bond vertical to the very same twofold axis as the water oxygen in the hydrates sits on. The hydrogen peroxide molecule in the perhydrates is hydrogen bonded to the same pair of oxalate oxygens as the water molecule in the hydrates.

The atomic positional parameters were refined by the three-dimensional least squares method using a programme written by Sparks and Trueblood,⁷ modified for use on Univac 1107, and also by three-dimensional partial difference syntheses where the contributions from the heavy atoms had been subtracted.

In the first cycles of refinement isotropic temperature-factors were used, but during the refinement procedure the heavy atom thermal parameters were changed to anisotropic — a change which seemed to be well founded as the agreement between observed and calculated structurefactors improved, and the difference Fourier maps smoothed.

In the last cycles of refinement anisotropic temperature-factors also for the light atoms were introduced, but the anisotropy of these atoms have less significance than that of the heavier atoms.

Attempts to locate the hydrogen atom from the difference maps were tried, but failed. Even in the partial difference syntheses there was no single

Table 1. Final positional parameters and their standard deviations in parentheses, as fractions of the cell edges.

	<i>x</i>	<i>y</i>	<i>z</i>
K ⁺	0.3614 (0.0002)	0.3414 (0.0004)	0.3647 (0.0002)
O ₁	0.3042 (0.0007)	0.4745 (0.0011)	0.0906 (0.0006)
O _p	0.4551 (0.0007)	—0.0032 (0.0012)	0.1826 (0.0006)
O ₂	0.1152 (0.0007)	0.2520 (0.0011)	0.0856 (0.0006)
C	0.2285 (0.0010)	0.3186 (0.0018)	0.0499 (0.0008)

Table 2.

Rb ⁺	0.3612 (0.0001)	0.3363 (0.0003)	0.3645 (0.0001)
O ₁	0.3054 (0.0010)	0.4635 (0.0016)	0.0905 (0.0008)
O _p	0.4571 (0.0010)	—0.0111 (0.0016)	0.1845 (0.0009)
O ₂	0.1232 (0.0010)	0.2598 (0.0015)	0.0875 (0.0008)
C	0.2287 (0.0013)	0.3179 (0.0023)	0.0490 (0.0012)

Table 3. Anisotropic thermal parameters β_{ij} and their standard deviations in parentheses. The expression used is: $\exp-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K ⁺	0.0105 (0.0002)	0.0165 (0.0009)	0.0075 (0.0002)	0.0057 (0.0009)	0.0057 (0.0003)	0.0000 (0.0007)
O ₁	0.0129 (0.0010)	0.0137 (0.0025)	0.0083 (0.0007)	-0.0107 (0.0033)	0.0089 (0.0014)	-0.0046 (0.0024)
O _p	0.0136 (0.0011)	0.0242 (0.0031)	0.0078 (0.0007)	0.0075 (0.0035)	0.0070 (0.0015)	0.0053 (0.0024)
O ₂	0.0115 (0.0009)	0.0145 (0.0027)	0.0068 (0.0005)	-0.0123 (0.0029)	0.0098 (0.0012)	-0.0105 (0.0022)
C	0.0099 (0.0011)	0.0229 (0.0049)	0.0051 (0.0007)	-0.0012 (0.0046)	0.0046 (0.0015)	0.0050 (0.0032)

Table 4.

Rb ⁺	0.0087 (0.0001)	0.0367 (0.0009)	0.0073 (0.0001)	0.0035 (0.0005)	0.0040 (0.0002)	-0.0025 (0.0005)
O ₁	0.0128 (0.0016)	0.0329 (0.0057)	0.0088 (0.0011)	-0.0086 (0.0049)	0.0065 (0.0022)	-0.0091 (0.0039)
O _p	0.0130 (0.0014)	0.0380 (0.0058)	0.0098 (0.0010)	0.0027 (0.0048)	0.0081 (0.0020)	0.0059 (0.0035)
O ₂	0.0099 (0.0012)	0.0329 (0.0048)	0.0060 (0.0008)	-0.0053 (0.0039)	0.0079 (0.0017)	0.0038 (0.0032)
C	0.0099 (0.0019)	0.0516 (0.0099)	0.0059 (0.0012)	-0.0012 (0.0072)	0.0045 (0.0025)	-0.0022 (0.0057)

sharp peak attributable to the hydrogen atom. The maximum height of the residual peaks being 0.6 el./Å³. The final reliability indexes for the two compounds, all reflections included, are 7.6 % for the potassium compound and 8.2 % for the rubidium compound.

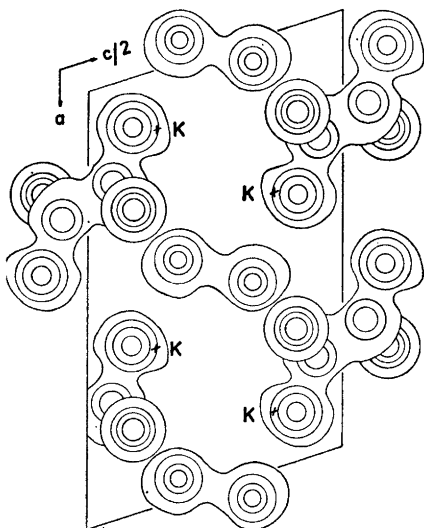


Fig. 1. Composite Fourier map of K₂C₂O₄·H₂O₂. The heavy atoms are subtracted, and their positions marked by crosses in the map.

The final positional and thermal parameter values for the two compounds are given in Tables 1—4. The anisotropy of the atoms were analysed,⁸ and the directions of the principle axes of the thermal ellipsoids relative to the crystallographic axes were determined together with the root mean square atomic displacement along these axes. The result of this analysis is given in Table 5. Tables 6 and 7 give the observed and calculated structure-factors for the two compounds. The final composite Fourier map with the potassium ion subtracted for clarity is shown in Fig. 1. Interatomic distances and angles calculated from the final parameter values are given in Table 8 for the potassium compound, and in Table 9 for the rubidium compound. The packing relations in the compounds viewed along [010] is shown in Fig. 2.

DISCUSSION

The commonly observed conformation of the oxalate ion is centrosymmetric and planar. In only one compound, (NH₄)₂C₂O₄·H₂O,⁹ the ion is found to be non planar. The bond lengths and angles observed in the oxalate ion in a series of alkalimetal oxalates are given in Table 10 together with the results of this

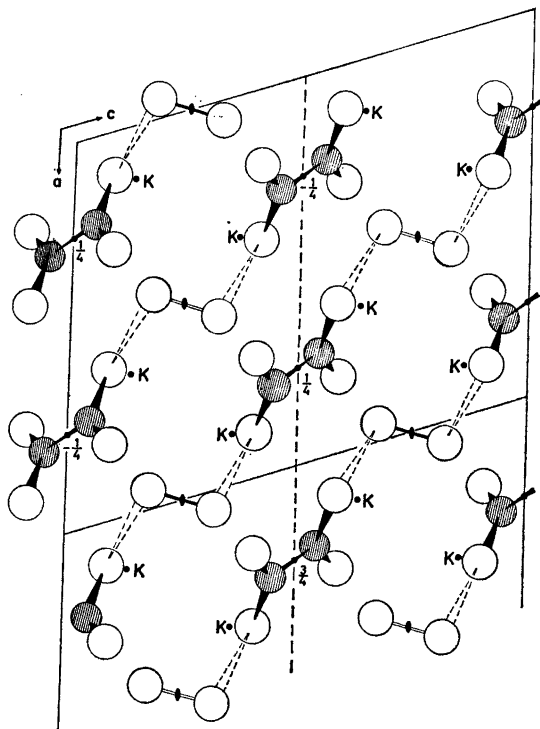


Fig. 2. Packing relations in K₂C₂O₄·H₂O₂ and Rb₂C₂O₄·H₂O₂ viewed along [010].

Table 5. Root mean square vibrational displacement (\AA) along the principal axis of the thermal ellipsoids, and components of the displacement along the direct cell edges.

Atom	Principal axes	$\sqrt{u^2}$	u_x	u_y	u_z
K	1	0.168	0.110	-0.128	0.001
	2	0.213	0.160	0.138	-0.007
	3	0.202	0.071	0.005	0.213
O ₁	1	0.145	0.075	0.126	0.026
	2	0.241	0.206	-0.112	0.151
	3	0.199	0.066	-0.032	-0.165
O _p	1	0.191	0.092	-0.110	0.159
	2	0.250	0.163	0.189	0.107
	3	0.211	0.142	-0.068	-0.103
O ₂	1	0.124	0.045	0.099	0.076
	2	0.250	0.182	-0.144	0.166
	3	0.163	0.109	0.032	-0.087
C	1	0.156	0.009	-0.055	0.149
	2	0.231	0.028	-0.215	-0.073
	3	0.190	0.198	0.027	0.060
Rb	1	0.184	0.192	-0.018	0.062
	2	0.296	0.031	0.291	-0.034
	3	0.207	0.002	-0.031	-0.204
O ₁	1	0.203	0.133	0.094	0.168
	2	0.295	0.100	-0.262	0.128
	3	0.225	0.161	-0.001	-0.115
O _p	1	0.220	0.175	0.018	-0.089
	2	0.305	0.039	0.291	0.093
	3	0.233	0.156	-0.066	0.214
O ₂	1	0.150	0.077	0.034	-0.103
	2	0.283	0.047	-0.276	-0.033
	3	0.207	0.186	0.011	0.162
C	1	0.184	0.043	0.008	0.192
	2	0.348	0.008	-0.348	0.017
	3	0.198	0.202	0.002	0.017

investigation. From Table 10 it can be seen that the distances and angles found in $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ and $\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ compare well with earlier investigations; the same deviations from the regular ion are found, *i.e.* long C—C distances of 1.563 \AA and 1.572 \AA , and O—C—O angles greater than 120°, 125.2°, and 123.4°, respectively. The oxalate ion is found to be centrosymmetric and planar within the experimental uncertainty. The equation to the plane through the symmetry-centre ($\bar{1}$), O₁ and O₂ is:

$$\begin{aligned} \text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2 : & -0.6276 X + 0.5551 Y - Z + 0.01813 = 0 \\ \text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2 : & -0.7355 X + 0.5910 Y - Z + 0.01336 = 0 \end{aligned}$$

and the carbon atom is, respectively, 0.02 \AA and 0.04 \AA out of these planes. The C—O distances and O—C—C angles listed in Tables 8 and 9 are of normal size.

The potassium- and rubidium ions are surrounded by eight nearest neighbors, six oxalate oxygens and two peroxide oxygens in a deformed dodeca-

Table 6. Observed and calculated structure factors for K₂C₂O₄·H₂O₂.

M	K	L	KFOB	FCAL	M	K	L	KFOB	FCAL	M	K	L	KFOB	FCAL
0	0	2	27.82	25.24	3	1	8	13.34	-10.86	4	2	-11	15.88	14.20
0	0	4	134.22	-143.70	3	1	9	27.95	-25.33	4	2	-10	16.12	15.75
0	0	6	6.60	-7.46	3	1	11	14.42	-16.08	4	2	-9	36.19	32.31
0	0	8	8.08	6.96	3	1	13	8.71	-7.98	4	2	-7	39.05	-33.02
0	0	10	9.88	-9.54	3	1	15	26.29	27.44	4	2	-6	31.01	-28.73
0	0	12	5.48	-6.84	3	1	17	32.01	32.91	4	2	-5	55.90	-58.17
0	0	14	10.09	-13.25	3	1	19	17.54	-17.16	4	2	-4	13.51	-11.81
0	0	16	28.83	36.24	3	1	21	26.80	-26.84	4	2	-3	38.31	40.99
0	0	18	7.82	7.46	3	1	23	8.45	7.67	4	2	-2	15.58	13.57
0	0	20	24.01	-31.37	3	1	25	7.39	-6.25	4	2	-1	34.15	36.55
0	0	22	16.12	-16.26	3	1	27	20.01	-19.84	4	2	0	57.50	61.33
0	0	24	6.00	5.86	3	1	29	7.39	-6.25	4	2	1	48.54	-54.48
0	0	26	43.96	-45.96	3	1	31	28.26	28.44	4	2	2	25.20	-15.77
0	0	28	17.82	-16.44	3	1	33	7.38	-6.32	4	2	3	10.11	-9.50
0	0	30	4.93	6.93	3	1	35	18.86	-35.28	4	2	4	44.95	-53.12
0	0	32	69.08	76.50	3	1	37	25.72	24.39	4	2	5	34.71	38.41
0	0	34	21.28	-21.23	3	1	39	32.35	30.17	4	2	6	8.13	7.71
0	0	36	7.48	9.86	3	1	41	11.57	10.52	4	2	7	7.42	6.99
0	0	38	77.92	-81.44	3	1	43	21.31	16.99	4	2	8	11.00	-14.00
0	0	40	6.33	-5.43	3	1	45	32.68	-28.13	4	2	9	18.04	14.50
0	0	42	145.17	146.79	3	1	47	26.21	-24.85	4	2	10	20.58	-19.70
0	0	44	76.71	-77.95	3	1	49	9.73	-9.88	4	2	11	12.99	-13.71
0	0	46	23.45	23.28	3	1	51	18.52	20.25	4	2	12	21.48	-19.66
0	0	48	33.63	29.44	3	1	53	7.84	-8.52	4	2	13	44.42	-41.24
0	0	50	10.13	-11.63	3	1	55	6.64	-5.70	4	2	14	16.03	15.84
0	0	52	7.65	8.93	3	1	57	19.80	-19.07	4	2	15	31.43	29.79
0	0	54	4.87	-2.81	3	1	59	35.82	-33.91	4	2	16	17.42	16.66
0	0	56	31.79	33.58	3	1	61	10.73	10.61	4	2	17	39.34	-39.21
0	0	58	35.06	53.04	3	1	63	16.17	-15.82	4	2	18	7.37	-9.36
0	0	60	23.11	-20.32	3	1	65	35.72	36.13	4	2	19	8.03	6.35
0	0	62	96.77	-103.35	3	1	67	18.94	19.32	4	2	20	32.76	34.54
0	0	64	19.69	17.71	3	1	69	33.13	-32.40	4	2	21	5.06	-4.44
0	0	66	65.39	61.21	3	1	71	14.64	-12.99	4	2	22	6.47	-6.57
0	0	68	29.17	-29.63	3	1	73	12.94	-10.91	4	2	23	10.04	-11.30
0	0	70	17.18	-18.72	3	1	75	24.52	22.73	4	2	24	11.14	-12.65
0	0	72	9.42	11.73	3	1	77	36.73	35.17	4	2	25	5.38	-6.67
0	0	74	23.85	23.72	3	1	79	20.63	21.36	4	2	26	20.86	21.35
0	0	76	31.47	-28.75	3	1	81	19.37	-17.47	4	2	27	17.96	18.60
0	0	78	35.34	-32.27	3	1	83	7.69	-6.96	4	2	28	12.82	12.53
0	0	80	16.62	16.46	3	1	85	15.80	-16.71	4	2	29	36.55	-34.84
0	0	82	25.84	24.98	3	1	87	7.52	6.59	4	2	30	9.86	-10.34
0	0	84	8.30	-6.96	3	1	89	21.88	20.83	4	2	31	11.41	-10.02
0	0	86	11.37	-10.86	3	1	91	10.10	-9.02	4	2	32	46.98	-29.15
0	0	88	12.98	17.23	3	1	93	6.91	-5.73	4	2	33	11.14	-13.48
0	0	90	6.20	-8.20	3	1	95	8.47	-7.72	4	2	34	7.83	11.60
0	0	92	26.12	-29.95	3	1	97	20.28	19.01	4	2	35	8.00	9.79
0	0	94	19.53	19.91	3	1	99	21.58	18.38	4	2	36	6.94	6.88
0	0	96	31.48	30.28	3	1	101	9.32	6.58	4	2	37	14.62	-19.34
0	0	98	5.49	-13.58	3	1	103	26.75	-22.26	4	2	38	6.98	40.06
0	0	100	7.96	-10.47	3	1	105	25.32	-22.21	4	2	39	7.48	-7.27
1	1	-13	11.10	11.99	11	1	-7	4.68	-4.68	10	2	-1	16.54	21.51
1	1	-12	12.44	-10.40	11	1	-5	70.89	-10.96	10	2	-1	11.57	11.87
1	1	-11	82.71	-20.94	11	1	-3	6.38	5.74	1	3	-12	8.99	-8.96
1	1	-9	21.37	-18.74	11	1	-1	7.19	7.17	1	3	-10	17.06	-13.03
1	1	-8	55.07	53.18	11	1	1	3.15	3.36	1	3	-9	11.01	10.86
1	1	-7	59.70	60.83	11	1	3	80.15	-20.70	1	3	-7	29.79	24.03
1	1	-6	41.35	-53.89	11	1	5	42.08	-40.91	1	3	-5	13.34	-11.38
1	1	-5	48.63	53.08	11	1	7	68.57	76.74	1	3	-3	51.00	48.24
1	1	-4	103.52	-97.45	11	1	9	24.02	23.07	1	3	-1	31.53	-30.34
1	1	-3	72.03	-70.74	11	1	11	15.91	13.16	1	3	1	33.58	-38.05
1	1	-2	36.69	39.62	11	1	13	43.21	-44.19	1	3	3	74.06	-71.95
1	1	-1	53.92	-46.68	11	1	15	12.52	-9.31	1	3	5	36.68	36.68
1	1	0	6.38	4.15	11	1	17	19.99	-19.03	1	3	7	104.23	99.96
1	1	1	13.37	12.74	11	1	19	28.76	29.26	1	3	9	27.03	27.75
1	1	2	21.87	24.41	11	1	21	37.15	34.16	1	3	11	82.55	-78.76
1	1	3	64.71	-66.76	11	1	23	17.73	15.68	1	3	13	10.39	-10.92
1	1	4	19.96	16.90	11	1	25	13.83	8.28	1	3	15	14.97	-14.60
1	1	5	43.87	-46.75	11	1	27	17.67	-15.68	1	3	17	7.90	-7.34
1	1	6	6.78	6.62	11	1	29	31.91	-26.89	1	3	19	19.18	15.66
1	1	7	42.53	43.97	11	1	31	11.53	6.55	1	3	21	42.43	-37.15
1	1	8	37.25	39.09	11	1	33	52.18	44.77	1	3	23	28.52	24.27
1	1	9	21.00	-18.18	11	1	35	55.81	55.34	1	3	25	17.36	-18.11
1	1	10	12.98	-10.07	11	1	37	21.31	-18.03	1	3	27	42.60	43.20
1	1	11	16.81	-19.92	11	1	39	39.90	-36.57	1	3	29	23.75	-21.52
1	1	12	21.02	-20.65	11	1	41	140.53	-139.42	1	3	31	53.71	-51.68
1	1	13	30.49	28.71	11	1	43	82.60	80.29	1	3	33	20.90	19.47
1	1	14	16.99	18.13	11	1	45	21.63	22.85	1	3	35	26.89	-26.74
1	1	15	10.93	-11.52	11	1	47	36.17	36.81	1	3	37	41.15	46.12
1	1	16	51.40	-57.74	11	1	49	19.95	22.24	1	3	39	19.95	22.24
1	1	17	46.12	53.88	11	1	51	75.58	76.33	1	3	41	7.51	6.50
1	1	18	6.22	-4.28	11	1	53	71.22	-75.69	1	3	43	32.51	-34.49
1	1	19	93.46	86.99	11	1	55	22.72	23.41	1	3	45	26.90	-30.34
1	1	20	65.53	-63.12	11	1	57	24.58	-21.64	1	3	47	13.72	-16.25
1	1	21	108.80	-102.34	11	1	59	9.25	8.61	1	3	49	37.91	39.72
1	1	22	20.09	-20.62	11	1	61	12.97	32.84	1	3	51	13.34	-12.88
1	1	23	48.66	-50.51	11	1	63	12.97	-13.82	1	3	53	9.82	10.08
1	1	24	31.04	-31.59	11	1	65	7.02	-9.28	1	3	55	6.56	-6.13
1	1													

Table 7. Continued.

1	3	2	122.39	147.45	5	3	4	6.10	-8.91	0	4	8	37.86	-34.64	4	4	5	50.29	-57.11
1	3	3	21.92	26.36	5	3	5	9.76	7.77	0	4	9	41.30	-31.01	4	4	6	24.90	27.50
1	3	4	47.76	53.33	5	3	6	45.53	45.63	0	4	10	22.19	22.80	4	4	7	6.74	-4.71
1	3	5	3.48	1.96	5	3	7	3.94	-1.22	0	4	11	5.39	-1.67	4	4	8	14.39	14.74
1	3	6	103.31	-118.28	5	3	8	15.29	-11.50	0	4	12	8.03	14.24	4	4	9	20.67	22.59
1	3	7	7.35	-8.91	7	3	-11	3.18	1.06	2	4	-12	9.21	9.73	4	4	10	7.90	-10.73
1	3	8	17.55	-14.73	7	3	-10	31.63	31.68	2	4	-11	23.70	23.16	4	4	11	16.76	-17.41
1	3	9	8.32	-7.91	7	3	-9	8.02	-4.7	2	4	-10	19.16	-19.13	4	4	12	35.25	37.22
1	3	10	40.70	43.41	7	3	-8	36.00	-34.66	2	4	-9	23.08	-22.79	4	4	13	27.51	27.89
3	3	-13	5.05	7.07	7	3	-7	7.60	2.97	2	4	-8	26.60	-24.13	4	4	14	16.02	14.34
3	3	-12	8.91	-6.15	7	3	-6	27.67	-25.97	2	4	-7	37.31	-30.61	4	4	15	30.48	29.40
3	3	-11	3.95	2.37	7	3	-5	23.02	18.51	2	4	-6	50.81	46.29	4	4	16	41.27	-36.08
3	3	-10	56.09	-60.18	7	3	-4	54.27	52.00	2	4	-5	33.28	47.96	4	4	17	57.95	-47.64
3	3	-9	13.21	-5.62	7	3	-3	4.38	1.49	2	4	-4	66.62	65.00	4	4	18	7.40	-2.26
3	3	-8	46.23	36.76	7	3	-2	15.18	13.47	2	4	-3	45.56	-65.44	4	4	19	35.96	-28.49
3	3	-7	10.03	-12.61	7	3	-1	22.45	-19.70	2	4	-2	84.86	-83.02	4	4	20	23.14	19.31
3	3	-6	80.41	80.00	7	3	0	85.01	-79.92	2	4	-1	12.99	12.61	4	4	21	46.52	42.42
3	3	-5	21.90	-14.16	7	3	1	10.79	-9.90	2	4	0	39.07	-35.18	4	4	22	16.47	-13.22
3	3	-4	90.08	-90.51	7	3	2	6.80	-7.07	2	4	1	40.63	37.53	4	4	23	10.83	5.98
3	3	-3	18.96	15.37	7	3	3	4.24	5.94	2	4	2	64.55	64.76	4	4	24	18.84	-12.38
3	3	-2	60.54	-61.43	7	3	4	62.01	62.62	2	4	3	27.95	-27.56	4	4	25	37.16	-37.72
3	3	-1	46.75	47.87	7	3	5	3.63	6.26	2	4	4	27.87	27.96	4	4	26	18.50	20.85
3	3	0	76.05	80.92	7	3	6	6.95	-5.92	2	4	5	19.56	-16.69	4	4	27	11.23	6.06
3	3	1	3.14	-3.10	0	3	-10	26.44	-27.62	2	4	6	38.64	-31.74	4	4	28	17.32	26.96
3	3	2	39.87	31.16	0	3	-9	3.05	1.03	2	4	7	17.41	19.87	4	4	29	9.19	9.10
3	3	3	33.23	-32.34	0	3	-8	27.66	-27.07	2	4	8	6.41	-1.28	4	4	30	10.58	-20.94
3	3	4	81.62	-82.45	0	3	-7	3.68	3.35	2	4	9	10.74	11.40	4	4	31	31.91	-33.66
3	3	5	-12.46	-11.19	0	3	-6	44.88	45.53	2	4	10	12.33	18.60	4	4	32	6.71	-6.30
3	3	6	8.70	-3.72	0	3	-5	7.96	-8.72	2	4	11	10.29	-17.22	4	4	33	15.77	-11.97
3	3	7	4.32	2.70	0	3	-4	16.13	13.78	4	4	-11	13.07	-14.63	4	4	34	24.79	29.61
3	3	8	69.52	47.85	0	3	-3	13.28	-12.14	4	4	-10	11.56	-13.34	4	4	35	48.59	47.74
5	5	-12	21.60	-29.81	0	3	-2	43.28	43.81	4	4	-9	26.94	-26.19	4	4	36	7.00	-7.98
5	5	-11	3.79	-5.24	0	3	-1	3.90	1.91	4	4	-8	26.75	23.73	4	4	37	6.92	10.32
5	5	-10	20.05	20.39	0	3	0	11.17	8.17	4	4	-7	37.47	37.21	4	4	38	21.17	-21.38
5	5	-9	4.34	1.40	0	3	1	12.19	12.33	4	4	-6	16.10	16.19	4	4	39	34.10	-35.14
5	5	-8	44.47	52.97	0	3	2	35.74	36.07	4	4	-5	44.13	35.10	4	4	40	16.96	16.90
5	5	-7	4.32	-2.04	0	3	3	2.79	1.73	4	4	-4	28.24	-24.11	4	4	41	5.38	2.07
5	5	-6	61.28	-59.94	0	3	4	8.62	-9.93	4	4	-3	58.18	-55.64	4	4	42	7.91	7.73
5	5	-5	4.04	3.12	1	3	-5	3.96	-4.67	4	4	-2	4.32	-4.79	4	4	43	8.03	11.64
5	5	-4	63.90	-67.03	1	3	-4	27.64	-36.46	4	4	-1	24.90	-25.21	10	4	44	15.91	24.02
5	5	-3	8.61	8.81	0	4	1	48.68	-59.03	4	4	0	49.18	41.12	10	4	45	4.44	-2.84
5	5	-2	119.90	120.12	0	4	2	10.16	11.62	4	4	1	61.47	76.22	10	4	46	8.43	-2.39
5	5	-1	3.79	1.85	0	4	3	38.22	-44.18	4	4	2	29.80	-25.30	10	4	47	18.27	-27.29
5	5	0	55.45	46.06	0	4	4	32.04	34.93	4	4	3	16.01	13.22	10	4	48	8.51	-11.26
5	5	1	11.95	-12.52	0	4	5	80.42	54.14	4	4	4	40.80	-37.76	10	4	49	7.15	10.34
5	5	2	94.44	-92.57	0	4	6	29.42	-29.80										
5	5	3	4.23	-4.21	0	4	7	16.26	12.76										

Table 8. Interatomic distances and valence angles \pm standard deviations.

Distances in the oxalate ion:

$$\begin{aligned} \text{C}-\text{O}_1 &= 1.274 \pm 0.009 \text{ \AA} & \angle \text{C}-\text{C}-\text{O}_1 &= 114.7 \pm 0.6^\circ \\ \text{C}-\text{O}_2 &= 1.227 \pm 0.009 \text{ \AA} & \angle \text{C}-\text{C}-\text{O}_2 &= 120.1 \pm 0.6^\circ \\ \text{C}-\text{C} &= 1.563 \pm 0.013 \text{ \AA} & \angle \text{O}-\text{C}-\text{O} &= 125.2 \pm 0.6^\circ \end{aligned}$$

Hydrogen bond distance: 2.591 \pm 0.009 \AA Distances in the H₂O₂ molecule:

$$\begin{aligned} \text{O}-\text{O} &= 1.441 \pm 0.009 \text{ \AA} & \varphi &= 101.6 \pm 0.6^\circ \\ & & \angle \text{O}\dots\text{O}-\text{O} &= 102.5 \pm 0.6^\circ \end{aligned}$$

Interionic distances:

$$\begin{aligned} \text{K}-\text{O}_p &= 2.903 \pm 0.007 \text{ \AA} & \text{K}-\text{O}_a &= 2.938 \pm 0.007 \text{ \AA} \\ \text{K}-\text{O}_b &= 2.930 \pm 0.007 \text{ \AA} & \text{K}-\text{O}_c &= 2.917 \pm 0.007 \text{ \AA} \\ \text{K}-\text{O}_2 &= 3.010 \pm 0.007 \text{ \AA} & \text{K}-\text{O}_1 &= 2.734 \pm 0.007 \text{ \AA} \\ \text{K}-\text{O}_3 &= 3.010 \pm 0.007 \text{ \AA} & \text{K}-\text{O}_1 &= 2.817 \pm 0.007 \text{ \AA} \end{aligned}$$

building a three-dimensional network, constituting a relatively open, but fairly stable structure.

Perhaps the most interesting feature of these compounds is connected to the conformation of the hydrogen peroxide molecule. The conformation is determined by four parameters, the O—H and O—O distances and the H—O—O and the dihedral angles. Table 11 gives the last three of these dimen-

Table 9. Interatomic distances and valence angles \pm standard deviations.

$\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$

Distances in the oxalate ion:

$$\begin{array}{ll} \text{C}-\text{O}_1 = 1.244 \pm 0.012 \text{ \AA} & \angle \text{C}-\text{C}-\text{O}_1 = 116.4 \pm 0.7^\circ \\ \text{C}-\text{O}_2 = 1.228 \pm 0.012 \text{ \AA} & \angle \text{C}-\text{C}-\text{O}_2 = 120.2 \pm 0.7^\circ \\ \text{C}-\text{C} = 1.572 \pm 0.016 \text{ \AA} & \angle \text{O}-\text{C}-\text{O} = 123.4 \pm 0.7^\circ \end{array}$$

Hydrogen bond distance: $2.635 \pm 0.012 \text{ \AA}$

Distances in the H_2O_2 molecule:

$$\text{O}-\text{O} = 1.443 \pm 0.012 \text{ \AA} \quad \angle \text{O} \cdots \overset{\varphi}{\text{O}}-\text{O} = 103.4 \pm 0.7^\circ$$

Interionic distances:

$$\begin{array}{ll} \text{Rb}-\text{O}_p = 3.013 \pm 0.007 \text{ \AA} & \text{Rb}-\text{O}_3 = 3.052 \pm 0.007 \text{ \AA} \\ \text{Rb}-\text{O}_p = 3.045 \pm 0.007 \text{ \AA} & \text{Rb}-\text{O}_2 = 3.088 \pm 0.007 \text{ \AA} \\ \text{Rb}-\text{O}_2 = 3.080 \pm 0.007 \text{ \AA} & \text{Rb}-\text{O}_1 = 2.984 \pm 0.007 \text{ \AA} \\ \text{Rb}-\text{O}_2 = 3.095 \pm 0.007 \text{ \AA} & \text{Rb}-\text{O}_1 = 2.929 \pm 0.007 \text{ \AA} \end{array}$$
Table 10. Observed bond lengths (\AA) and angles ($^\circ$) in the oxalate ion.

	C-C	C-O ₂	C-O ₁	O-C-O	C-C-O ₁	C-C-O ₂
$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}^a$	1.569	1.252	1.263	126.0	116.5	117.5
$\text{Li}_2\text{C}_2\text{O}_4^a$	1.561	1.264	1.252	127.3	116.3	116.4
$\text{Na}_2\text{C}_2\text{O}_4^b$	1.54	1.23	1.23	124	115	121
$\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2^1$	1.570	1.259	1.270	126.7	115.1	118.2
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}^b$	1.585	1.238	1.247	126.4	116.4	117.1
$\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}^6$	1.58	1.271	1.272	125.2	116.6	118.2
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	1.563	1.227	1.274	125.2	114.7	120.1
$\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	1.572	1.228	1.244	123.4	116.4	120.2

^a) Beagley, B. and Small, R. W. H. *Acta Cryst.* **17** (1964) 183.

^b) Jeffrey, G. A. and Parry, G. S. *J. Am. Chem. Soc.* **76** (1954) 5283.

Table 11. Observed parameters for the hydrogen peroxide molecule.

		O-O	$\angle \text{H}-\text{O}-\text{O}$ ($\text{O} \cdots \text{O}-\text{O}$)	φ
H_2O_2 (gas) ¹²	IR	1.475	94.8	111.5
H_2O_2 (solid) ¹¹	ND	1.453	102.7	90.2
$\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}^{13}$	XR	1.481	97.7	139
$\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}_2^{14}$	XR	1.46	101.5	106.7
$\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2^1$	XR	1.466	97.3	180.0
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	XR	1.441	102.5	101.6
$\text{Rb}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$	XR	1.443	102.0	103.4

sions in compounds where the structure has been determined. It should, however, be pointed out that the hydrogen atoms are not located in the K- and Rb-compounds, and the value of the dihedral angle is therefore derived assuming linear hydrogen bonds, an assumption which probably holds fairly well as judged from the only two existing examples where both angles are known. In solid H₂O₂^{11,16} the difference between these two angles is 3°, and in urea-perhydrate^{14,15} (hyperol) the two angles are equal, with an experimental uncertainty of ± 2.1°.

The O—O distance in the H₂O₂ molecule is 1.441 ± 0.009 Å and 1.443 ± 0.012 Å in these two compounds, and do not deviate significantly from O—O distances found from earlier investigations, 1.453 Å—1.475 Å.¹¹⁻¹⁴ The H—O—O or rather the O...O—O angle also seems to be fairly constant from one compound to another, and values from 95° to 103° have been found for this angle.

From Table 11 it can be seen that the dihedral angle must be very sensitive to the environment of the molecule, and values from 90° to 180° have been observed from this angle.

The value of the dihedral angle is connected to a more general problem, namely how the potential energy varies as the two hydroxyl groups of the molecule are rotated relative to each other. Many investigations, both experimental and theoretical, have been performed to elucidate this problem during the last thirty years. It was pointed out by Penney and Sutherland¹⁷ that the potential energy to a great extent would depend on repulsion between the unshared electron pairs on the oxygen atoms, and calculations based on pure *p*-orbitals led to an equilibrium value of 90° for this angle. Theoretical and experimental work carried out later on has given somewhat differing results. However, there is generally agreed on that the potential energy has two maxima, one for the *cis*- and one for the *trans*-conformation, with dihedral angles of 0° and 180°, respectively.

In a recent thorough infrared-investigation in the gas phase by Hunt, Leacock, Peters, and Hecht¹⁸ a three parameter potential energy function is derived from the far infrared spectrum. The *cis*- and *trans*-barriers are determined to 7 and 1 kcal/mole, respectively, and the potential function minimum is located 111.5° from the *cis*-configuration. This latter work further confirms the parameter values of the H₂O₂ molecule earlier determined by Redington, Olson, and Cross,¹² also from a high resolution infrared investigation.

In solids the hydrogen peroxide molecule will be influenced by intercrystalline forces, and hence the potential energy function will be a sum of two terms, one *intra*- and one *inter*-molecular term, where the *intra*-molecular term will be approximately as for a free H₂O₂ molecule, whereas the *inter*-molecular term will vary from one compound to another. The *inter*-molecular term is mainly determined by the hydrogen bonds formed by the H₂O₂-molecule, and as the energy associated with hydrogen-bond formation is approximately 3 kcal/mole, this term is of the same magnitude as the *intra*-molecular term.

A crystalline structure is the result of a compromise between different effects, all of which can not be optimized at the same time. The dihedral angle adopted by the hydrogen peroxide molecule in a given compound is therefore a measure of the ease with which the conformation of the hydrogen peroxide

molecule has adjusted itself to fit into the particular local surroundings in that compound.

The stability of the potassium- and the rubidium salt is markedly better than that of the sodium salt which loses its hydrogen peroxide rapidly in air. This change in stability might be due to the fact that the hydrogen peroxide molecules in the former salts have a conformation closer to the gas configuration with dihedral angles of 101.6° and 103.4° , respectively.

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