

Rutile-Type Compounds. IV. SiO₂, GeO₂ and a Comparison with other Rutile-Type Structures

BY WERNER H. BAUR AND AJAZ A. KHAN

Department of Geological Sciences, University of Illinois at Chicago, Chicago, Illinois 60680, U.S.A.

(Received 5 October 1970)

Single crystal X-ray diffraction data on rutile-type GeO₂, collected on an automatic four-circle diffractometer, have been refined anisotropically to $R=0.020$ (306 F_{obs}). Result: $x=0.3059$ (2), $(\text{Ge-O})_1=1.872$ Å and $(\text{Ge-O})_2=1.902$ Å (with $a=4.3975$ (2) and $c=2.8625$ (4) Å). Powder data from a sample of natural stishovite (SiO₂) obtained on a diffractometer have been refined anisotropically to $R=0.047$ (29 F_{obs}). Result: $x=0.3062$ (13), $(\text{Si-O})_1=1.757$ Å and $(\text{Si-O})_2=1.810$ Å (with $a=4.1790$ (4) and $c=2.6649$ (4) Å). In both these oxides, as in TiO₂, the four coplanar $(A-B)_1$ bonds located in the plane (110) are slightly shorter than the two axial $(A-B)_2$ bonds normal to the plane (110). However, three other rutile-type oxides, CrO₂, RuO₂ and OsO₂, for which crystal data have been reported recently, do not follow this pattern. Previously reported lattice energy calculations based on a simple Born model fail to account for these differences in geometry. A plot of V vs. c/a vs. x of all accurately determined rutile-type structures shows that the four main-group oxides of Si, Ge, Sn and Pb fall on a smooth curve. The other oxides depart from this simple pattern thus indicating that asymmetries in their d -electron distribution cause deviations from the 'normal' geometry of the main-group elements. The importance of the electronic configuration is also shown by the mixed oxide $(\text{V}_{0.5}\text{Nb}_{0.5})\text{O}_2$, which is isoelectronic with GeO₂, has a very similar c/a ratio to GeO₂, and a unit-cell volume which is exactly as much greater than the volume of GeO₂, as is required by the larger size of the V⁴⁺ and Nb⁴⁺ ions.

Introduction

The rutile-type structure is geometrically simple: two parameters, the axial ratio c/a and the free parameter x of the anion position define the geometry. Many physical properties of rutile-type compounds have been measured (see the review papers by Grant, 1959, and by Rogers, Shannon, Sleight & Gillson, 1969). Nevertheless there is still much discussion going on regarding the question of the nature of the chemical bonds in compounds crystallizing in this structure-type. A comprehensive theory, correlating all of the properties of rutile-type compounds is still not available.

Accurate determinations of both c/a and x are only available for TiO₂, SnO₂, MgF₂ (Baur, 1956a), MnF₂, FeF₂, CoF₂, NiF₂, ZnF₂ (Baur, 1958), RuO₂ (Boman, 1970a), OsO₂ (Boman, 1970b); less accurate values are available for CrO₂ (Cloud, Schreiber & Babcock, 1962) and PbO₂ (Leciejewicz & Padlo, 1962). A refinement of the crystal structure of stishovite, SiO₂, was reported by Stishov & Belov (1962) who claim that the free parameter x of the oxygen atom is 0.317. Therefore, it would seem that the coordination octahedron around Si is more distorted than in any other known rutile-type compound. Preisinger (1962) on the other hand determined x to be 0.301 which would mean that all the Si-O distances within the coordination octahedron are of equal length. The two determinations are not only at variance with each other but are also not compatible with our present knowledge of the crystal chemistry of other rutile-type compounds (Baur, 1961). Since the crystal chemistry of octahedrally six-coordinated Si⁴⁺ is currently of interest in connection with

experimental high-pressure studies of silicates (as models for the behavior of matter in the earth's mantle) it was decided to re-refine the crystal structure of stishovite and compare it with other rutile-type compounds. In order to base this comparison on as reliable data as possible the old determinations were re-evaluated. The original refinement of rutile-type GeO₂ (Baur, 1956a) was done with powder data and was not very accurate. Single crystals of rutile-type GeO₂ became available recently (Harvill, 1966) and therefore a new refinement of its crystal structure was undertaken. The original data on TiO₂, SnO₂, MgF₂, MnF₂, FeF₂, CoF₂, NiF₂, and ZnF₂ (Baur, 1956a, 1958) were re-evaluated using modern least-squares techniques and more accurate unit cell data which became available meanwhile (Naidu, 1966).

Experimental

Rutile-type crystals have the space-group $P\frac{4_2}{m}\frac{2_1}{n}\frac{2}{m}$ with $Z=2$, the cations occupy equivalent position $2(a)$ at $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ with site symmetry mmm , the anions reside in $4(f)$ at $\pm(x, x, 0; \frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2})$ with site symmetry mm (Vegard, 1916). Unless otherwise noted below the atomic scattering curves used for the calculations of the F_c are from Doyle & Turner (1968) and a Hughes-type weighting scheme was applied in the least-squares calculation. The computer programs used in the course of the work are the same as those listed in Baur & Khan (1970). In addition ORFFE2, the IBM 360 computer-compatible version of ORFFE (Busing, Martin & Levy, 1964) was used. The main data are presented in Table 1. The definition of R is

$\sum||F_o| - |F_c|| / \sum|F_o|$. The crystallographic data for CrO_2 , RuO_2 , OsO_2 and PbO_2 available in the literature are summarized in Table 4.

A powder pattern of a sample of natural stishovite from Meteor Crater, Arizona (Bohn & Stöber, 1966) was prepared on a diffractometer (Cu $K\alpha$ with Ni filter). The intensities were measured by planimetry of the area under the peaks. Overlapping reflections (222 and 330, 132 and 240, 402 and 510) were calculated apart on the basis of the ratios of the calculated intensities. The F_o and F_c are listed in Table 2.

A single crystal of GeO_2 , prepared by Harvill (1966), was ground to a sphere of a diameter of 0.039 cm. Three-dimensional X-ray data were collected on an automatic four-circle diffractometer using Ag $K\alpha$ radiation with Pd filter (up to $\sin \theta/\lambda = 1.37 \text{ \AA}^{-1}$). Procedures for measuring the data were as described previously (Baur & Khan, 1970). Data were collected within a complete sphere of reflection. The 2800 measured F_{hkl} yielded 350 unique F_{hkl} of which 44 were of zero intensity (smaller than 1σ). The data were corrected for absorption [$\mu(\text{Ag } K\alpha) = 149.9 \text{ cm}^{-1}$]. The refinement proceeded readily to an R of 0.08. At this point it became clear that the data were severely affected by extinction. An extinction correction (Zachariasen, 1963) allowed R to be reduced to 0.020 ($C = 0.0025$). The F_o and F_c are listed in Table 3. When the 44 unobserved reflexions are included R equals 0.029.

The original F_o data on TiO_2 , SnO_2 , MgF_2 , MnF_2 , FeF_2 , CoF_2 , NiF_2 and ZnF_2 (Baur, 1956a, 1958) were re-refined by the least-squares method. Since the old data included only F_{hko} the β_{33} could not be determined. The values listed in Table 1 under β_{33} are converted from the isotropic β from a preceding least-squares refinement with isotropic temperature factors. The new refinement resulted in values of x which are within one-half the estimated standard deviation (e.s.d.) of the original refinement. The new values are reported nevertheless since the new e.s.d.'s are, with one exception, appreciably lower than the confidence limits achieved in 1956 and 1958 by refinement with difference syntheses. For the refinement of SnO_2 the atomic scattering factors of Pauling & Sherman (1932) were used. As has been shown previously (Baur, 1956b) this curve approximates the experimental scattering curve of Sn very well. Using the Doyle & Turner (1968) Sn atomic scattering factors the R value for SnO_2 is only 0.068, while using Pauling & Sherman's f_{Sn} the R value equals 0.036.

Results

The positional parameter x of the oxygen atom in SiO_2 has a significantly different value from the values reported previously by Stishov & Belov (1962) and by Preisinger (1962). This is due to the fact that these authors did not refine their data. A least-squares refinement performed by us on Stishov & Belov's data

Table 1. Crystal data and refinement results for ten rutile-type compounds

Number of F_{hkl}	R (%)	a	c	c/a	x	x_m	Anion			Cation		
							β_{11}	β_{33}	β_{12}	β_{11}	β_{33}	β_{12}
SiO_2	29	4.1790 (4)	2.6649 (4)	0.63769	0.3062 (13)	0.3008	112 (29)	347 (84)	5 (45)	78 (21)	287 (55)	2 (20)
TiO_2	51	4.5941 (1)	2.9589 (1)	0.64407	0.3057 (7)	0.3019	75 (5)	[176]	-1 (9)	68 (3)	[175]	-1 (3)
GeO_2	306	4.3975 (2)	2.8625 (4)	0.65094	0.3059 (2)	0.3030	38 (1)	56 (5)	-14 (2)	21 (1)	28 (1)	0 (1)
SnO_2	46	4.7380 (1)	3.1865 (2)	0.67254	0.3071 (13)	0.3065	26 (10)	[41]	-22 (12)	13 (1)	[15]	-5 (3)
MgF_2	49	4.6213 (1)	3.0159 (1)	0.66040	0.3028 (6)	0.3045	119 (7)	[239]	-26 (8)	78 (5)	[163]	-6 (5)
MnF_2	46	4.8738 (1)	3.3107 (1)	0.67929	0.3053 (12)	0.3077	131 (10)	[250]	-11 (14)	93 (3)	[182]	-11 (8)
FeF_2	44	4.6945 (4)	3.3097 (1)	0.70502	0.3010 (8)	0.3121	124 (9)	[211]	-62 (12)	65 (2)	[110]	-8 (4)
CoF_2	45	4.6954 (4)	3.1774 (4)	0.67670	0.3052 (8)	0.3072	98 (7)	[204]	-34 (9)	51 (2)	[100]	0 (5)
NiF_2	43	4.6498 (3)	3.0838 (1)	0.66321	0.3012 (13)	0.3050	77 (13)	[147]	-48 (17)	32 (3)	[48]	10 (7)
ZnF_2	41	4.7048 (1)	3.1338 (2)	0.66609	0.3024 (16)	0.3055	106 (13)	[210]	-23 (18)	74 (4)	[157]	-6 (7)

The value of x refers to the positional parameter of the anion as determined experimentally, while x_m refers to the calculated value of this parameter assuming that the six cation-anion distances are of equal length, that is $x = \frac{1}{2} + (c^2/8a^2)$. All unit cell parameters are from Naidu (1966), except those for SiO_2 which are from Chao, Fahey, Littler & Milton (1962). Listed are the β_{11} , β_{33} , β_{12} and β_{11} , β_{33} , β_{12} where the temperature factor is $\exp[-(\beta_{11}(h^2 + k^2) + \beta_{33}l^2 + 2\beta_{12}hk)]$.

Table 2. SiO₂, observed and calculated structure factors

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>
1	0	0	22.2	23.2	4	0	0	13.1	12.7
1	0	1	10.2	11.0	1	4	0	7.2	7.3
1	1	1	17.1	15.9	2	2	2	15.5	14.7
1	2	0	13.7	12.1	3	3	0	16.8	16.5
1	2	1	19.9	18.4	1	4	1	9.6	9.8
2	2	0	22.8	22.4	1	5	2	7.7	7.7
0	3	2	23.8	24.3	2	4	0	9.0	9.2
1	3	0	19.0	19.2	3	2	1	4.3	4.1
2	2	1	4.9	4.7	1	0	3	6.7	6.1
3	0	1	22.7	22.0	4	1	3	5.9	5.6
1	1	2	13.0	13.6	4	3	2	9.9	9.1
1	3	1	4.1	4.5	5	1	0	10.8	10.5
2	0	2	5.6	5.0	1	4	2	4.2	5.1
1	2	2	5.0	5.1	1	2	3	8.2	9.0
2	3	1	3.3	3.9					

Table 3. GeO₂, observed and calculated structure factors (×10) and σ's used in the least-squares procedure

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>				
1	0	0	165	165	3	18	12	2	83	93	7	2	77	78	4	3	0	2	0				
2	56	361	14	6	23	25	13	H=	2, K=	2	3	2	5	0	H=	4, K=	4	4	51	87			
4	260	245	11	7	117	118	7	0	148	134	14	4	74	75	6	0	217	211	9	5	0	2	0
8	175	167	9	H=	2, K=	11	1	2	4	52	52	11	1	2	4	11	H=	5, K=	8	5	8	8	8
H=	3, K=	1	0	279	274	11	2	298	299	12	0	16	14	14	2	189	189	8	0	0	5	0	0
1	279	284	11	1	52	52	5	3	31	28	6	1	109	110	7	3	45	50	6	1	151	148	8
7	230	233	10	2	243	243	10	4	207	209	9	2	15	14	15	4	144	142	7	2	0	5	0
5	140	145	8	3	12	31	6	5	25	19	8	H=	3, K=	3	5	34	39	9	3	134	133	7	
7	105	100	7	4	166	165	6	1	140	146	8	0	312	299	12	6	107	108	7	4	0	4	0
H=	0, K=	2	5	27	21	9	7	0	14	9	1	22	19	7	H=	4, K=	5	H=	5, K=	9	9	9	9
0	231	251	10	6	114	113	7	H=	2, K=	3	2	269	265	11	0	12	9	12	0	105	106	7	
2	231	235	10	7	20	15	12	0	35	36	5	3	14	13	14	1	180	177	8	1	0	6	0
4	156	156	8	H=	1, K=	4	1	235	234	11	4	134	155	9	3	145	144	8	2	102	101	7	
6	102	100	7	0	83	85	5	2	28	26	6	5	13	10	14	4	0	7	0	3	0	5	0
H=	0, K=	3	1	245	257	10	3	176	174	8	6	143	142	8	5	115	112	7	4	90	91	6	6
1	133	143	13	2	67	67	5	4	18	17	10	7	0	7	0	6	0	5	H=	5, K=	10	10	10
3	258	264	11	3	155	156	9	5	113	115	7	H=	3, K=	4	H=	4, K=	6	0	0	25	20	0	0
5	178	192	9	4	40	58	6	6	17	17	16	0	35	36	5	0	176	171	6	1	73	72	7
7	132	133	7	5	124	135	7	7	87	85	6	1	242	230	10	1	43	42	6	2	0	2	0
H=	0, K=	4	6	36	35	3	H=	2, K=	4	2	31	31	6	2	155	156	8	H=	6, K=	5	6	5	6
2	271	285	11	7	150	151	7	0	252	248	10	3	189	187	8	2	37	37	7	0	146	142	8
2	242	246	10	H=	1, K=	5	1	51	50	6	4	25	23	9	4	129	128	7	1	30	32	8	
4	173	175	6	0	247	251	12	2	219	217	9	5	138	136	8	5	27	29	11	2	135	134	7
6	125	125	5	1	14	12	9	3	36	37	6	6	21	17	11	6	101	102	7	3	30	27	5
H=	0, K=	5	2	219	220	9	4	156	156	8	7	103	104	7	H=	4, K=	7	4	114	114	7	7	7
1	175	178	8	3	13	9	11	6	11	11	9	1	0	0	0	32	34	7	5	24	21	10	
3	135	134	7	4	162	165	8	6	114	112	7	0	168	164	8	1	145	144	7	H=	6, K=	7	7
5	96	93	7	5	13	7	10	7	20	20	11	1	11	7	12	2	31	32	8	0	28	27	9
7	71	72	6	6	144	122	7	H=	2, K=	5	2	147	145	7	3	128	126	7	1	138	135	7	
H=	0, K=	6	7	0	5	0	0	11	6	10	3	0	6	0	4	27	27	10	2	26	25	10	10
0	220	226	9	H=	1, K=	6	1	249	250	10	4	106	106	7	5	102	104	7	3	123	121	7	
2	197	203	5	0	46	48	6	2	0	5	0	5	0	0	H=	4, K=	8	4	23	21	11	6	6
4	155	157	8	1	185	186	6	3	204	203	9	6	83	81	6	0	121	121	7	5	103	103	6
6	121	121	7	2	42	43	6	4	20	20	4	0	H=	3, K=	6	1	14	13	15	H=	6, K=	8	8
H=	0, K=	7	3	151	151	8	5	153	153	8	H=	0	19	22	11	2	116	116	6	1	100	94	7
1	190	193	9	4	34	35	7	6	0	3	0	1	194	192	9	2	15	12	15	1	0	7	0
3	162	165	8	5	114	115	7	7	114	117	7	2	21	20	8	4	98	98	7	2	94	92	7
5	129	131	7	6	79	26	9	H=	2, K=	6	3	163	162	8	5	14	5	16	3	8	6	0	0
H=	0, K=	8	H=	1, K=	7	0	174	173	8	4	19	16	12	H=	4, K=	9	4	83	83	6	6	6	6
7	110	108	7	0	158	159	8	1	31	32	7	5	128	128	7	0	34	34	8	H=	8, K=	9	9
2	101	99	7	1	36	37	7	2	154	153	7	6	15	12	17	1	117	116	7	0	27	26	10
4	84	93	7	2	142	145	7	3	26	27	8	H=	3, K=	7	2	34	32	8	1	97	97	7	
H=	0, K=	9	3	13	32	8	11	7	0	179	178	8	3	105	105	7	2	106	107	6	6	25	9
1	125	126	7	116	117	7	5	2	21	12	1	15	19	10	4	26	28	10	3	89	90	9	
3	109	113	7	5	26	25	10	6	91	92	7	2	165	164	8	H=	4, K=	10	H=	10, K=	10	10	
5	54	46	6	6	92	93	6	H=	2, K=	7	3	16	17	11	0	105	105	7	0	103	105	7	
H=	0, K=	10	H=	1, K=	8	0	24	24	8	4	137	137	8	1	0	10	0	1	0	1	0	10	10
7	139	140	8	0	14	13	12	1	141	141	7	5	17	13	13	2	101	101	7	H=	7, K=	7	7
2	133	132	7	1	153	154	6	2	23	22	8	6	109	110	7	3	0	9	0	0	123	123	8
4	114	117	7	2	13	12	14	3	118	118	7	H=	3, K=	8	H=	4, K=	11	1	20	19	11	11	
H=	0, K=	11	3	136	136	7	4	18	18	13	0	0	0	0	0	22	20	10	2	119	116	7	
1	77	80	7	4	0	10	0	5	95	96	7	1	104	107	7	1	65	66	6	3	16	17	15
3	72	75	7	5	109	112	7	6	15	14	16	2	0	4	0	H=	5, K=	5	4	102	103	7	
H=	0, K=	12	H=	1, K=	9	H=	2, K=	8	3	90	91	7	0	213	208	9	H=	7, K=	8	7, K=	8	8	
0	76	77	7	0	126	127	7	0	167	168	8	4	0	3	0	1	0	0	0	0	11	0	0
H=	1, K=	1	1	35	36	8	1	0	10	0	5	7	7	2	194	191	9	1	83	84	7	7	
0	324	307	8	2	117	120	7	2	155	157	8	H=	3, K=	9	4	142	157	8	2	14	10	16	
1	151	154	7	3	31	32	9	3	13	9	17	0	119	119	7	5	0	1	0	3	79	78	6
2	295	301	12	4	101	103	7	4	132	133	7	1	17	18	14	6	126	125	7	H=	7, K=	9	9
3	71	70	5	5	23	26	11	5	0	0	2	112	112	14	H=	5, K=	6	0	97	99	7	7	
4	201	204	9	H=	1, K=	12	H=	2, K=	9	3	18	16	14	0	12	9	14	1	24	21	13	13	
5	41	44	7	0	15	12	15	0	28	25	9	4	56	48	7	1	125	126	7	2	94	95	6
6	136	135	8	1	102	99	7	1	119	120	7	H=	3, K=	10	2	0	9	H=	8, K=	8	8	8	
7	30	31	10	2	0	11	0	2	10	10	0	0	0	0	0	3	112	109	7	0	118	117	7
H=	1, K=	2	3	90	91																		

and OsO_2 do not, which means that for these oxides $(A-B)_1$ is longer than $(A-B)_2$ and thus the situation is more complicated than it was before. A simple Born model has been applied previously (Baur, 1961) to some rutile-type compounds. The lattice energy U_E was evaluated according to $U_E = E - R_{AB} - R_{BB}$, where E is the electrostatic part of the lattice energy, R_{AB} is the non-electrostatic repulsion term between cations and anions, while R_{BB} is the non-electrostatic repulsion term between the anions. Van der Waals terms, zero-point energy and non-electrostatic repulsion terms between the cations were neglected in the calculation, because their contribution was believed to be very small. The value of E was evaluated using Ewald's (1921) method, while the repulsion terms were calculated using Lennard-Jones's (1925) potentials (inverse 10th-power terms). The computations were performed as a function of both c/a and x (for TiO_2 , GeO_2 , SnO_2 , MgF_2 , MnF_2 , FeF_2 , CoF_2 , NiF_2 , and ZnF_2) and the minimum value of U_E was taken to be the calculated lattice energy. The values of x and c/a at the minimum lattice energy (the theoretical equilibrium values) when

compared with the experimentally determined values are systematically displaced: all theoretical values (see Fig. 2) are in an area of the plot where the distance $(A-B)_1$ is greater than the distance $(A-B)_2$. This means that according to the simple Born model the distortions in all rutile-type compounds should be of the same kind as is experimentally found for all rutile-type fluorides and different from the kind of distortion found in some rutile-type oxides. Accordingly it was concluded that the bonding in the rutile-type oxides, TiO_2 , GeO_2 and SnO_2 , could not be completely ionic, but must be, at least partly, covalent. An additional more detailed comparison of theoretical and experimental c/a and x values showed that only MgF_2 , ZnF_2 and MnF_2 could conceivably have dominantly ionic bonding character, while FeF_2 , and probably CoF_2 and NiF_2 , had to be at least partly non-ionic.

Another comparison was made (Baur, 1961) between the calculated lattice energy and the experimental (U_C) one, derived from the Born-Haber cycle: The agreement between U_E and U_C was found to be very good for the fluorides (especially when a reasonable

Table 5. Bond lengths, bond angle and unit-cell volume V for 14 rutile-type compounds

For source of data see text. The numbers in brackets refer to Fig. 1. $(A-A)_2$ is the cation distance from 0,0,0 to $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. $(A-B)_m$ is the mean $A-B$ distance calculated with x_m (Tables 1 and 4) as parameter. The multiplicities refer to one coordination octahedron.

	$(A-B)_1$ 4 × [1]	$(A-B)_2$ 2 × [2]	$(A-B)_m$	$(B-B)_1$ 8 × [3]	$(B-B)_2$ 2 × [4]	$(A-A)_1[5]$ = $(B-B)_3[6]$ = c 2 ×	$(A-A)_2$ 8 ×	$(B-A-B)_1$ 2 × [7]	V
SiO_2	1.757 (5) Å	1.810 (8) Å	1.778 Å	2.522 (4) Å	2.291 (16) Å	2.6649 (4) Å	3.242 (1) Å	81.4 (4)°	46.54 Å ³
TiO_2	1.945 (3)	1.986 (5)	1.961	2.780 (3)	2.525 (9)	2.9589 (1)	3.570 (1)	80.9 (2)	63.45
CrO_2	1.92 (3)	1.88 (4)	1.903	2.69 (3)	2.49 (6)	2.917	3.450	80.9 (20)	57.01
GeO_2	1.872 (1)	1.902 (1)	1.884	2.669 (1)	2.414 (2)	2.8625 (4)	3.423 (1)	80.3 (1)	55.36
RuO_2	1.984 (6)	1.942 (10)	1.968	2.776 (7)	2.468 (16)	3.1066 (7)	3.536 (1)	76.9 (4)	62.68
SnO_2	2.052 (5)	2.057 (9)	2.054	2.906 (5)	2.586 (17)	3.1865 (2)	3.710 (1)	78.1 (4)	71.53
OsO_2	2.006 (8)	1.962 (13)	1.990	2.806 (13)	2.441 (20)	3.1839 (4)	3.558 (1)	75.0 (5)	64.48
PbO_2	2.17 (3)	2.16 (4)	2.161	3.06 (3)	2.68 (6)	3.3866 (2)	3.893 (1)	76.4 (20)	83.21
MgF_2	1.998 (3)	1.979 (4)	1.990	2.812 (2)	2.578 (8)	3.0519 (1)	3.606 (1)	80.4 (2)	65.18
MnF_2	2.131 (6)	2.104 (9)	2.121	2.995 (5)	2.684 (17)	3.3107 (1)	3.823 (1)	78.1 (4)	78.64
FeF_2	2.118 (4)	1.998 (6)	2.072	2.912 (3)	2.643 (10)	3.3097 (1)	3.709 (1)	77.2 (2)	72.94
CoF_2	2.049 (3)	2.027 (5)	2.040	2.882 (3)	2.587 (10)	3.1774 (4)	3.681 (1)	78.3 (2)	70.05
NiF_2	2.022 (6)	1.981 (9)	2.006	2.830 (4)	2.615 (17)	3.0838 (1)	3.631 (1)	80.6 (4)	66.67
ZnF_2	2.046 (7)	2.012 (10)	2.033	2.869 (5)	2.630 (20)	3.1338 (2)	3.677 (1)	80.0 (5)	69.37

Table 6. Dimensions and orientations of the ellipsoids of thermal vibration of the atoms in rutile-type SiO_2 and GeO_2

Compound	Atom	Principal axis	R.m.s. component (Å)	Angle (°) between principal axis and vectors a, b, c			$(A-B)_1$	$(A-B)_2$
				a	b	c		
SiO_2	Si	1	0.08 (1)	45.0	135.0	90.0	—	—
		2	0.08 (1)	135.0	135.0	90.0	—	—
		3	0.10 (1)	90.0	90.0	0.0	—	—
	O	1	0.10 (2)	45.0	135.0	90.0	90.0	90.0
		2	0.10 (2)	135.0	135.0	90.0	49.3	180.0
		3	0.11 (1)	90.0	90.0	0.0	139.3	90.0
GeO_2	Ge	1	0.034 (1)	90.0	90.0	0.0	—	—
		2	0.045 (1)	135.0	45.0	90.0	—	—
		3	0.045 (1)	45.0	45.0	90.0	—	—
	O	1	0.048 (2)	90.0	90.0	0.0	139.8	90.0
		2	0.048 (2)	135.0	135.0	90.0	49.8	180.0
		3	0.072 (2)	45.0	135.0	90.0	90.0	90.0

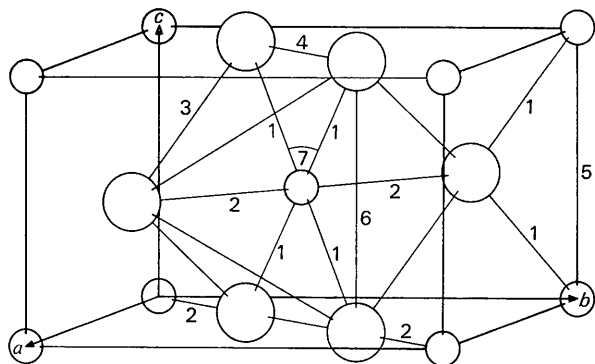


Fig. 1. Unit cell of a rutile-type structure. Large circles correspond to anions, small circles to cations. The bonds and angles are numbered in the same way as in Table 5.

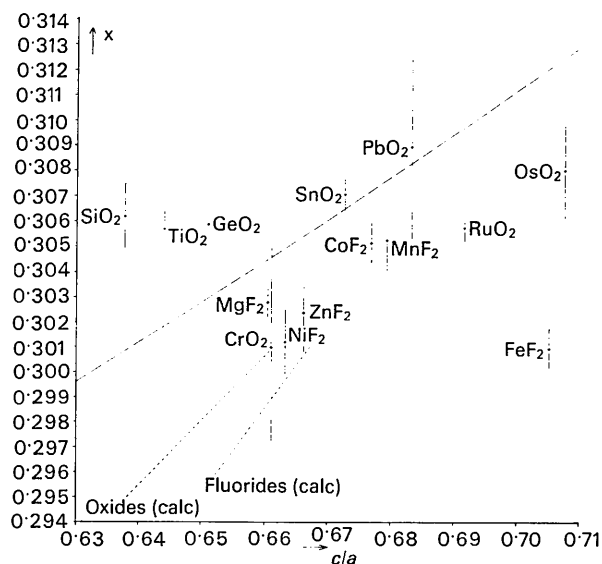


Fig. 2. Axial ratio c/a and positional parameter x of anion for the rutile-type compounds listed in Table 5. The long-dashed line corresponds to those $x, c/a$ -pairs for which $(A-B)_1 = (A-B)_2$ [i.e. $x = \frac{1}{4} + (c^2/8a^2)$]. The short-dashed lines marked Fluorides (calc) and Oxides (calc) show the values calculated to have minimum lattice energies, see also text (Baur, 1961).

estimate of the van der Waals term is added), but it was found to be poor for the oxides (U_C is about 20% larger than U_E). This adds further weight to the opinion that the rutile-type oxides do not have purely ionic bonds. The results of Wackman, Hirthe & Frounferker, (1967) and Ladd (1969) seem to contradict this conclusion. In both these papers values of U_E for TiO₂ are calculated in good agreement with U_C . However the authors did not attempt to prove that the lattice energy calculated by them corresponds to a minimum. In other words, they did not show that the Born model as applied by them is physically reasonable. The previous calculations (Baur, 1961) showed that a minimum of the lattice energy for the oxides can only be found

using the simple Born model if and when the nonelectrostatic repulsion terms become so large that the resulting calculated lattice energy U_E is appreciably smaller than U_C . The obvious conclusion from this is that the Born model as applied by Baur (1961) is insufficient for describing the rutile-type oxides. An advance beyond these calculations may be conceivable by using a more refined Born model (along the lines followed by Busing, 1970) but this has not been attempted by either Wackman *et al.* (1967) or by Ladd (1969).

In Fig. 3 we have plotted the unit-cell volume V vs. c/a vs. x for all rutile-type compounds listed in Table 5 and added NbO₂, MnO₂, VO₂, RhO₂, IrO₂, and TaO₂ from Table II of Rogers *et al.* (1969). NbO₂ crystallizes in a distorted rutile-type; the c/a value is calculated for a cell equivalent to the rutile cell. For the other five compounds no x values are available. The plot is a graphic representation of the complete geometrical relationships between the different compounds. The values of c/a and x are only ratios, and just by themselves do not give an impression of the size relations (see Fig. 2), which however are added into the plot by introducing the unit-cell volume V . The four main-group oxides of Si, Ge, Sn and Pb fall on an almost smooth curve. With increasing volume (from Si to Pb) c/a increases distinctly and x seems to increase also (that is if the x value of PbO₂ is actually more reliable than its stated precision would indicate). This is the same type of relationship which was found in the theoretical calculations for both the oxides and the fluorides (Fig. 2). It is due to the fact that with increasing $A-X$ separation the relative contribution of the repulsive terms decreases and the crystal structure approaches the geometry favored by the electrostatic lattice energy contribution: x about 0.315, c/a about 0.72 (Baur, 1961). The oxides of the transition metals Ti, V, Cr, Mn, Nb, Ru, Rh, Ta, Os, and Ir are situated in a seemingly erratic way to the left and right of this curve. The only slight indication of a systematic distribution is the fact that the compounds with no or with one d electron (VO₂, TiO₂, NbO₂, TaO₂) are to the left of the curve, while all other ones are to the right of it. There are less data points for the fluorides but the arrangement is somewhat similar. The line from MgF₂ to ZnF₂ is parallel to the GeO₂-SnO₂ line, the other fluorides deviate from this pattern. If the geometry of the rutile-type compounds were governed by the sizes of the ions and by spherically symmetric forces alone (as we use them in the simple Born model) we would expect the points for all the oxides to fall on one smooth curve, the points for the fluorides on another. If we accept the SiO₂-PbO₂ curve of Fig. 3 as a 'normal' curve, since the compounds of cations with closed d shells fall on it, the deviations of the other oxide compounds from it can be taken as indications of the asymmetric distribution of the d electrons over their orbitals. The slightly different geometries caused by differently populated orbitals in this simple structure should be a fruitful field of study.

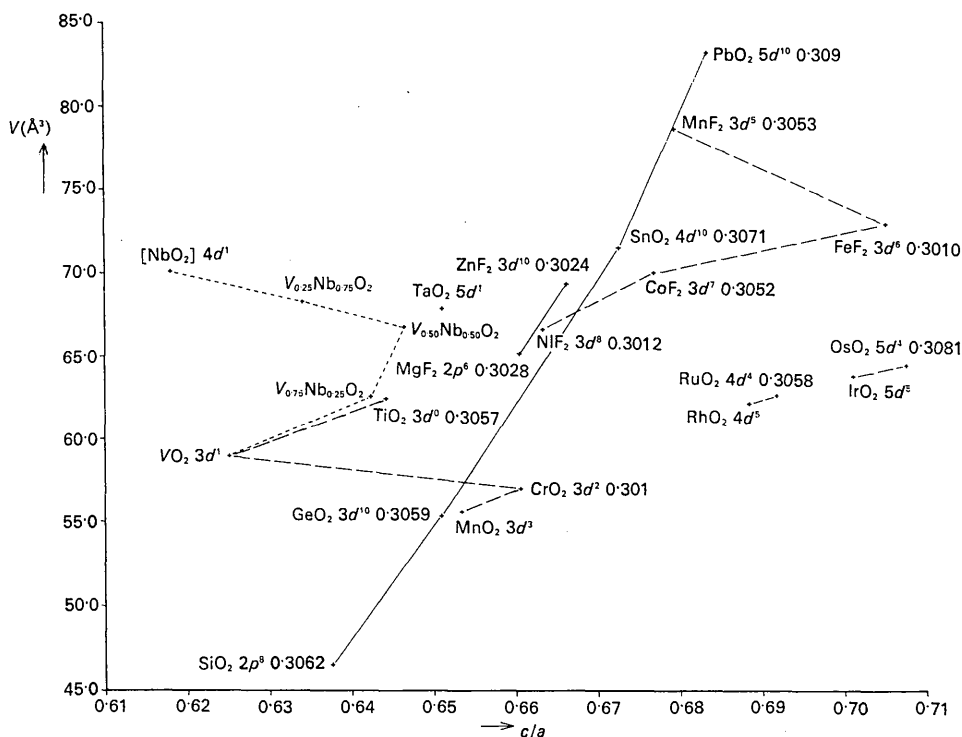


Fig. 3. Unit-cell volume V versus c/a for the rutile-type compounds listed in Table 5 and for 6 additional compounds (Rogers *et al.*, 1969) for which no x values are known. The electron configurations and the x values are indicated. The solid line is the 'normal' curve connecting the main group oxides. The long-dashed lines join for every subshell compounds of elements with neighboring atomic numbers. The short-dashed lines connect the points of VO_2 with those of NbO_2 via their intermediate solid solutions.

Marinder & Magnéli (1957) suggested that the short metal-metal distances in the pairs of metal atoms present in distorted rutile-type structures of the MoO_2 type are caused by bonds between these metal atoms. Their plot of metal-metal separation *versus* the number of free valence electrons available for metal-metal bonding is very convincing. By analogy they interpreted low c/a ratios in undistorted rutile-phases as indications of metal-metal bonding, because the lower the c/a ratio, the shorter the metal-metal distance. Marinder & Magnéli's approach is not sufficient to explain the details of our plot (Fig. 3). Conceivably a further development of the ideas of Rogers *et al.* (1969) could lead to a deeper understanding of these distortions.

Of particular interest for an understanding of the bonding in these compounds could be the study of the mixed oxides of rutile-type (see Marinder & Magnéli, 1958; Marinder, Dorma & Seleborg, 1962). The points for one series of these compounds, for rutile-type $(\text{V}, \text{Nb})\text{O}_2$, are shown in Fig. 3. The intermediate compositions are not even nearly on a straight line between VO_2 and NbO_2 . The composition $\text{V}_{0.5}\text{Nb}_{0.5}\text{O}_2$, which is (on the average) isoelectronic with GeO_2 has a very similar c/a ratio to GeO_2 , and a unit-cell volume which is exactly as much greater than the volume of GeO_2 , as required by the larger size of the V^{4+} and

Nb^{4+} ions. The compound $\text{V}_{0.5}\text{Nb}_{0.5}\text{O}_2$ appears to be a pseudo- GeO_2 .

We thank Drs Harvill and R. Roy for the single crystal of GeO_2 , Mr Bohn and Dr Stöber for the powder sample of stishovite and the NSF for supporting this investigation in part through grants GP-7275 (computer) and GA-314 (X-ray equipment). We are grateful to Drs Robert D. Shannon and Charles T. Prewitt for a critical reading of the manuscript.

References

- BAUR, W. H. (1956a). *Acta Cryst.* **9**, 515.
 BAUR, W. H. (1956b). *Acta Cryst.* **9**, 538.
 BAUR, W. H. (1958). *Acta Cryst.* **11**, 488.
 BAUR, W. H. (1961). *Acta Cryst.* **14**, 209.
 BAUR, W. H. & KHAN, A. A. (1970). *Acta Cryst.* **B26**, 1584.
 BOHN, E. & STÖBER, W. (1966). *Neues Jb. Miner. Mh.* p. 89.
 BOMAN, C.-E. (1970a). *Acta Chem. Scand.* **24**, 116.
 BOMAN, C.-E. (1970b). *Acta Chem. Scand.* **24**, 123.
 BUSING, W. R. (1970). *Trans. Amer. Cryst. Assoc.* **6**, 57.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
 CHAO, E. C. T., FAHEY, J. J., LITTLER, J. & MILTON, D. J. (1962). *J. Geophys. Res.* **67**, 419.
 CLOUD, W. H., SCHREIBER, D. S. & BABCOCK, K. R. (1962). *J. Appl. Phys.* **33**, 1193.

- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A **24**, 390.
 EWALD, P. P. (1921). *Ann. Phys. Lpz.* **64**, [4], 253.
 GRANT, F. A. (1959). *Rev. Mod. Phys.* **31**, 646.
 HARVILL, M. L. (1966). *Hydrothermal Crystal Growth of the Rutile Structure Oxides TiO₂, GeO₂ and SnO₂*. Ph.D. Thesis, Pennsylvania State Univ.
 LADD, M. F. C. (1969). *Acta Cryst.* A **25**, 486.
 LECIEJEWICZ, J. & PADLO, I. (1962). *Naturwissenschaften*, **49**, 373.
 LENNARD-JONES, J. E. (1925). *Proc. Roy. Soc.* A **109**, 584.
 MARINDER, B.-O., DORM, E. & SELEBORG, M. (1962). *Acta Chem. Scand.* **16**, 293.
 MARINDER, B.-O. & MAGNÉLI, A. (1957). *Acta Chem. Scand.* **11**, 1635.
 MARINDER, B.-O. & MAGNÉLI, A. (1958). *Acta Chem. Scand.* **12**, 1345.
 NAIDU, S. V. N. (1966). *X-ray Studies on Rutile-Type Compounds*. Ph.D. Thesis, Osmania Univ.
 PAULING, L. & SHERMAN, J. (1932). *Z. Kristallogr.* **81**, 1.
 PREISINGER, A. (1962). *Naturwissenschaften*, **49**, 345.
 ROGERS, D. B., SHANNON, R. D., SLEIGHT, A. W. & GILLSON, J. L. (1969). *Inorg. Chem.* **8**, 841.
 SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B **25**, 925.
 STISHOV, S. M. & BELOV, N. V. (1962). *Dokl. Akad. Nauk SSSR*, **143**, 951.
 VEGARD, L. (1916). *Phil. Mag.* **32**, [6], 65.
 WACKMAN, P. H., HIRTHE, W. M. & FROUNFELKER, R. E. (1967). *J. Phys. Chem. Sol.* **28**, 1525.
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.
 ZUEV, V. V. (1969). *J. Struct. Chem.* **10**, 152.

Acta Cryst. (1971) B **27**, 2139

The Structure of the Catecholamines. III. Crystal Structure of Adrenalone Hydrochloride Monohydrate

BY ROLF BERGIN

Department of Medical Physics, Karolinska Institutet, S-104 01 Stockholm 60, Sweden

(Received 23 November 1970)

The crystals of adrenalone hydrochloride monohydrate, C₉H₁₁O₃N·HCl·H₂O, are monoclinic, space group *P*2₁/*c*, four formula units in a cell with *a* = 7·13, *b* = 10·14, *c* = 17·61 Å, β = 119·0°. The structure was determined by minimum functions and Fourier synthesis and was refined by least-squares methods to a final *R* value of 0·048 with 2271 observed reflexions. Estimated standard deviations for bond lengths and angles involving non-hydrogen atoms are in the range of 0·003–0·004 Å and around 0·2°, respectively. The molecule is approximately planar, and the structure is held together by six hydrogen bonds involving all hydrogen atoms on the nitrogen and oxygen atoms.

Introduction

Adrenalone is a catecholamine, structurally resembling the biologically important hormone adrenaline (epinephrine); a carbonyl radical has replaced the alcoholic hydroxyl group on the β-carbon atom. The physiological effect of adrenalone is that of a sympathomimetic amine (Loewi & Meyer, 1905). Despite its resemblance to adrenaline, its action is more like that of noradrenaline. This could be explained by the probable indirect action of adrenalone with an activity about $\frac{1}{10}$ that of noradrenaline (Wennmalm, 1970). It was considered valuable to determine the structure of adrenalone in order to compare it with other catecholamines and related phenethylamines in our research programme.

Experimental

Well developed, water-clear crystals of suitable size were obtained by slow evaporation of an aqueous solution of pure adrenalone hydrochloride (Fluka,

Switzerland). The monoclinic crystals were six-sided prisms bounded by {011} (predominant) and {001}, and terminated by {100} (predominant) and {102}. Twinning was frequently observed; composition plane (010) and twinning axis = *a*. According to Faber (1929), adrenalone hydrochloride monohydrate is dimorphous and crystallizes in an orthorhombic and a monoclinic form, the latter being the stable one at room temperature. Optical properties were also investigated by Faber. In a detailed re-investigation Faber (1930) found that the principal refractive indices differed from crystal to crystal, and he concluded that these differences were caused by crystal imperfections. The crystals are highly birefringent ($\gamma_D - \alpha_D = 0\cdot242$).

A suitable crystal was trimmed to an almost spherical shape (0·42 × 0·45 × 0·46 mm). The calculated value of the linear absorption coefficient for Mo *K*α equals 3·39 cm⁻¹ which is low enough for absorption corrections to be neglected. Unit-cell dimensions were determined in a linear diffractometer. Density was measured by flotation in an xylene-chloroform mixture.