tanium ester solutions is consistent with the existence of two equilibrium constants

$$K_1 = X_{\mathrm{TPT\cdot EtNH_2}}/X_{\mathrm{TPT}}\gamma_{\mathrm{EtNH_2}}X_{\mathrm{EtNH_2}}$$
$$K_2 = X_{\mathrm{TPT\cdot EtNH_2}}/X_{\mathrm{TPT\cdot EtNH_2}}\gamma_{\mathrm{EtNH_2}}X_{\mathrm{EtNH_2}}$$

The solid curves on Fig. 2 represent that variation of $p_{\mathrm{EtNH_2}}/\gamma_{\mathrm{EtNH_2}}X^{t}_{\mathrm{EtNH_2}}P^{0}_{\mathrm{EtNH_2}}$ with $EtNH_2$ concentration to be expected from (1) and (2) for the case where $K_1 = 3.7$ and $K_2 = 2.5$. Behavior observed at 35° can again be accounted for by (1) and (2), with the best fit of the data being given by $K_1 \sim 3.4$, $K_2 \sim 2.3$. Less satisfactory fits of the data are obtained by assuming that the complexing of $EtNH_2$ is accomplished solely by (1) or (2).

The magnitudes of the constants K_1 and K_2 indicate that the coördination compounds $TPT\cdot EtNH_2$ and $TPT\cdot 2EtNH_2$, if indeed they exist in solution, have only a low stability. Application of the van't Hoff equation to these K's at 25 and 35° indicates that the enthalpy change for (1) and (2) is < -2 kcal.

The weakness of the TPT–ethylamine interaction was unexpected in view of the relatively high stability of the reported $TiCl_4$–amine compounds. The comparative stabilities of the TPT and $TiCl_4$ complexes possibly reflect the relative abilities of the isopropoxide and the chloride groups to supply electrons to the Ti(IV) atoms to which they are bonded. Alkoxide groups, being less electronegative than chlorides, should behave as more effective electron donors to the vacant orbitals of the Ti(IV) atoms and accordingly Ti(IV) alkoxides might be anticipated to act as weaker Lewis acids than $TiCl_4$.

Although isopropoxy groups are more bulky than are chlorides, the formation of TPT–ethylamine complexes is not precluded by steric effects. This can be demonstrated by construction of a Fisher–Hirschfelder scale model of octahedral $TPT\cdot 2EtNH_2$. $EtNH_2$ groups are observed to fit into such a structure without strain.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL AND METALLURGICAL DIVISION, SYLVANIA ELECTRIC PRODUCTS, INC.]

Preparation, Properties and Structure of Cadmium Peroxide

BY C. W. W. HOFFMAN, R. C. ROPP AND R. W. MOONEY

RECEIVED DECEMBER 15, 1958

A compound shown to be CdO_2 has been prepared and some of its properties are given. The crystal structure of this material has been studied by powder diffraction methods. Patterns were indexed on the basis of a cubic pyrites-type lattice with the cadmium atoms occupying the fcc positions. A value for a_0 of 5.313 ± 0.003 Å. and an oxygen–oxygen peroxide distance of 1.49 ± 0.04 Å. were found.

Introduction

True peroxides, containing the –O–O– linkage, of the type M_2O_2 and MO_2, of the alkali and alkaline earth elements, respectively, are comparatively well-known and their crystal structures have been established. Extensive references easily may be found in standard inorganic reference books such as Mellor's treatise.[1] Recently Föppl[2] has published a comprehensive paper on the preparation and structure of the alkali, or Group Ia, peroxides. Föppl discusses the –O–O– linkage and includes a survey of the currently known structures of inorganic peroxides. Significantly, his summary includes only the alkali peroxides, hydrogen peroxide, the peroxides of Ca, Sr and Ba, and the octahydrates of these Group IIa peroxides.

Group Ib and IIb peroxides (along with the peroxides of Be and Mg), on the other hand, do not form easily defined chemical species. The difficulty in preparation and the instability of these peroxides is attributed to the lower electropositive nature of the Group IIb metals as compared to Ia and IIa. No structural studies on the Group Ib or IIb peroxides have been made.

There are several general methods employed to prepare peroxides. Often the direct reaction of oxygen with the metal in air (or oxygen) and in liquid ammonia may be employed. Another common method is the reaction of a metal salt, usually in basic solution, with hydrogen peroxide. In addition to these preparations, thermal decomposition of the superoxides may yield the peroxides and a recent paper[3] describes the reactions of various metal salts with alkali superoxides in liquid ammonia to obtain certain peroxides.

Cadmium peroxide of doubtful purity has been reportedly prepared by all of these methods except by the decomposition of a definitely established superoxide of cadmium. Manchot[4] reported that the low-temperature oxidation of cadmium produced some CdO_2. Teletof,[5] and later Perkins,[6] utilized hydrogen peroxide to prepare materials which probably were fairly pure CdO_2. Perkins, in addition, also tried to prepare this peroxide from cadmium dimethyl in ethereal solution with hydrogen peroxide. Perkins' work is the most recent and authoritative discussion of this method. He gives, in addition, references to earlier inconclusive CdO_2 preparations. However, Perkins, largely because he depended upon chemical evidence alone, was unable to establish definitely the presence of CdO_2. Recently, Schechter and Kleinberg[3] claimed a reaction product rich in the corresponding peroxide upon treating cadmium salts in liquid ammonia with alkali superoxides.

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(1) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1922.

(2) H. Föppl, *Z. anorg. allgem. Chem.*, **291**, 12 (1957).

(3) D. L. Schechter and J. Kleinberg, THIS JOURNAL, **74**, 3297 (1954).

(4) W. Manchot, *Ber.*, **42**, 3942 (1909).

(5) I. S. Teletof, *J. Russ. Phys. Chem. Soc.*, **43**, 131 (1911).

(6) T. R. Perkins, *J. Chem. Soc.*, 1687 (1929).

In this Laboratory, while attempting to prepare cadmium oxide of high purity, the preparation of CdO_2 was attempted. The precipitation method using hydrogen peroxide was selected as the most feasible. Ammoniacal cadmium salt solutions were found to be satisfactory as long as chloride (and presumably halide and cyanide) ion concentration was low. Chemical analyses of the products indicate the formula to be CdO_2. Spectroscopic analyses show very minor metallic contamination.

Initial X-ray diffraction patterns of these materials indicated a strikingly simple crystal structure. Accordingly, a structure has been proposed which accounts very well for the pattern and is compatible with the formula CdO_2. Föppl[2] has proposed a value of about 1.49 Å. for the peroxide –O–O– linkage and our value derived for CdO_2 is 1.49 ± 0.04 Å., in agreement with that figure.

It seems likely that Perkins,[6] and perhaps some other early workers, also obtained CdO_2. However, because of limited analytical techniques the formula, CdO_2, was never definite. By means of improved analyses, thermogravimetric data, and particularly the X-ray diffraction results, the existence and crystal structure of CdO_2 have now been established.

Experimental

A. Preparation and Chemical Analyses of CdO_2.—The method of preparation was very similar to that used by Teletof[5] in his preparations of cadmium peroxides of uncertain composition. A cadmium salt, such as cadmium acetate, nitrate or sulfate, was dissolved by the addition of a large excess of NH_4OH, thus ensuring the formation of $Cd(NH_3)_4^{++}$. Addition of a commercial grade 30% H_2O_2 solution produced a cream-colored amorphous precipitate. On standing in contact with the mother liquor for several hours, the crystallinity improved greatly and the solution temperature increased from room temperature to about 80° or even higher, sometimes resulting in boiling. This heating effect, as well as the accompanying evolution of gas, probably is due to the decomposition of H_2O_2. The final CdO_2 precipitate was washed, filtered and dried at 120° for several hours.

The use of concentrated ammonia solutions had the added advantage that it permitted a purification of the soluble cadmium complex with respect to insoluble hydroxides. Furthermore, a nearly neutral or preferably basic solution (pH >5.5) was necessary for the precipitation of the peroxide. However, the use of strong bases such as NaOH is not recommended because of the possible formation of the cadmate ion. Na_2O_2 may be substituted for H_2O_2, but $CdCl_2$ solutions cannot be used since they lead to the formation of basic cadmium chlorides.

Per cent. cadmium was determined by electrodeposition and/or gravimetrically as the sulfate.

Anal. Calcd. for CdO_2: Cd, 77.8. Found: Cd, 75.1 ± 0.6, based on 13 different samples having an average water content of 2–3%.

Oxygen was determined in two different ways, neither of which was entirely satisfactory. In the first method, CdO_2 was decomposed in a closed system and the resulting oxygen collected over water. After decomposition, the powder that remained was identified as CdO by X-ray diffraction. Materials partially converted from CdO_2 to CdO were obtained and their X-ray patterns examined. Only the lines due to unconverted CdO_2 or CdO could be found. Unfortunately, CdO_2 decomposes violently and therefore the conversion to CdO is difficult to control.

Anal. Calcd. for CdO_2: O_2, 22.16. Found: O_2, 21.0 ± 0.3.

The second method involved the determination of "active" oxygen by titration with potassium permanganate after dissolution in sulfuric acid.

Anal. Calcd. for CdO_2: O_2, 22.16. Found: O_2, 18.4 ± 0.2, based on 5 different samples.

These results were believed to be low since an appreciable evolution of gas was always observed when dissolving the CdO_2 in acid before titration. This evolution of gas persisted at temperatures down to 0°.

B. Differential Thermal and Thermogravimetric Analyses.—The decomposition of CdO_2 to CdO and O_2 was studied by differential thermal and thermogravimetric means. However, since CdO_2 made from cadmium nitrate or cadmium acetate exploded violently on heating due to its high purity, a less pure product made from cadmium sulfate and containing about 1% $CdSO_4$ had to be used except to fix the decomposition temperatures.

The differential thermal analyses were performed on equipment that was similar to that described by Stone,[7] using a heating rate of 10° per minute. All runs gave a sharp exothermic peak between 180 and 200°.

The thermogravimetric analyses were performed on a Stanton thermogravimetric balance. In order to determine the adsorbed water and to fix more accurately the decomposition temperature, the balance was maintained at various constant temperatures for considerable lengths of time, often several hours. Several runs of materials heated at 10° per minute also were made. The weight loss occurring below 180° indicated about 2% adsorbed water in agreement with prolonged drying experiments at 110°. The weight loss corresponding to the decomposition to CdO gave these results.

Anal. Calcd. for the reaction $CdO_2 \rightarrow CdO + {}^1/_2\, O_2$: weight loss, 11.1. Found: weight loss, 11.5.

C. X-Ray Methods.—The X-ray diffraction patterns were taken on a Philips Norelco unit using Ni-filtered Cu $K\alpha$ radiation of 1.5418 Å. Debye–Scherrer powder photographs were obtained with large diameter (114.6 mm.) cameras giving 2θ values and relative intensities. G.M. counter diffractometer tracings taken at a scanning speed of ${}^1/_4$° per minute were also obtained giving 2θ values in good agreement with the powder photographs as well as more accurate relative intensity values. The experimental arrangement used in the latter method eliminated the need for any absorption correction. The observed intensities were measured on the diffractometer tracings by graphical integration. The resulting values were corrected for changes in slit width giving the arbitrary I_0 values listed in Table I. High-purity tungsten was used as an internal standard for the 2θ measurements. Values calculated for the cell dimension of tungsten agreed closely with published values.[8] The samples did not deteriorate during exposures, which normally varied from 3 to 5 hr. Several long exposures of 12 to 20 hr. also were taken to detect and measure the weaker reflections. The lines at d = 1.77 and 1.47 were taken from these films and given an arbitrary intensity of five since they could not be measured accurately from the diffractometer traces.

Structure Determination

Initial Debye–Scherrer patterns were readily indexed as cubic (Table I) with the systematic absence of hkl reflections with $h + k, k + l, l + h = 2n + 1$ indicating face-centered symmetry. However, longer exposures showed five additional weak reflections consistent with simple symmetry having $h^2 + k^2 + l^2$ = 5, 6, 9, 13 and 14. The isometric unit cell has an a_0 value of 5.313 ± 0.003 Å. obtained as an average of the 16 most intense reflections listed in Table I. The systematic absence of $hk0$ reflections with $h = 2n + 1$, especially the absence of the low angle reflections from the 100, 110 and 310 planes indicated that the space group was T_h^6-Pa3. Following the notation of the International Tables,[9] it was apparent that the pyrites-type arrangement of dumbbell-shaped anion pairs around the special positions of (4b) with metal atoms in the

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(7) R. L. Stone, Ohio State Univ. Engineering Series, Bulletin No. 146, 1951.

(8) H. E. Swanson and E. Tatge, Natl. Bur. Standards (U. S.) Circ. No. 539, Vol. 1, 1953, p. 28.

(9) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, 1952.

TABLE I

hkl	*d*	a_0	I_0	I_c
111	3.067	5.312	690	701
200	2.657	5.314	720	741
210	2.379	5.320	11	10
211	2.167	5.308	8	11
220	1.879	5.315	407	398
221	1.77	5.316	<5	2
311	1.602	5.314	358	367
222	1.534	5.314	104	112
230	1.47	5.30	<5	5
321	1.418	5.306	7	12
400	1.328	5.312	25	35
410 322			..	2
411			..	1
331	1.219	5.314	128	118
420	1.188	5.313	101	98
421			..	0
332			..	0
422	1.085	5.315	73	73
430			..	1
431			..	0
511 333	1.023	5.316	120	102
250 432			..	1
521			..	1
440	0.9386	5.310	31	29
522 441			..	0
433			..	0
531	0.8981	5.313	135	107
600 442	0.8857	5.314	81	68
610			..	0
611 532			..	1
620	0.8401	5.313	45	48
621 450 443			..	1
541			..	1
533	0.8098	5.310	53	69
622	0.8010	5.313	68	69

special positions of (4a) would: (1) be consistent with a peroxide structure having –O–O– bonds, and (2) explain the strong reflections for $h + k$, $k + l$, $l + h = 2n$ since Cd atoms occupying the fcc positions would make these reflections especially strong compared to the reflections obtained from O atoms only.

The density determined by ordinary pycnometer techniques was 5.93 g. cm.$^{-3}$ as compared to a calculated value of 4.77 g. cm.$^{-3}$ for $3CdO_2$ per unit cell and 6.36 g. cm.$^{-3}$ for $4CdO_2$ per unit cell. Space group symmetry and the final structure analysis both demand four rather than three molecules in the unit cube. Apparently the experimentally determined value of density is low by about 7%. All of the data are therefore compatible with the assumption that the space group is T_h^6–Pa3 with the Cd atoms in special positions (4a) with coördinates

$$0, 0, 0;\ 0, \tfrac{1}{2}, \tfrac{1}{2};\ \tfrac{1}{2}, 0, \tfrac{1}{2};\ \tfrac{1}{2}, \tfrac{1}{2}, 0$$

and the O atoms in special positions (8c) with coordinates

$$\pm (x, x, x;\ \tfrac{1}{2} + x, \tfrac{1}{2} - \bar{x}, \bar{x};\ x, \tfrac{1}{2} + x, \tfrac{1}{2} - x;\ \tfrac{1}{2} - x, \bar{x}, \tfrac{1}{2} + x)$$

The only undetermined atomic parameter in the structure was therefore x. As a first approximation, a value of 0.40 was chosen and relative intensities calculated from the well-known relation

$$I_c = kp|F_{hkl}|^2 \frac{(1 + \cos^2 2\theta)}{(\sin^2 \theta \cos \theta)}$$

where p is the multiplicity; F_{hkl}, the structure amplitude; $f(\theta)$ the usual Lorentz polarization term; and k, a factor for scaling I_c to I_0 by setting $\Sigma I_c = \Sigma I_0$. Values of atomic scattering factors were taken from James and Brindley.[10] The reliability index, $R = \Sigma(I_0 - I_c)/\Sigma I_0$, obtained for $x = 0.40$ was 0.29. A temperature factor, $B = 1.5$ Å.$^{-2}$, was next applied, decreasing R to 0.136. The variable parameter x then was refined by the method of least squares[11] to minimize $\Sigma w(I_0 - I_c)^2$ and determine the probable error in x. The weighting factor w was assigned a value of unity throughout. The final refinement gave a value for Δx of 0.0002 yielding 0.4192 for x. In terms of the O–O distance, this value of x corresponds to a separation of 1.49 Å. The least squares treatment[11] gave a probable error for x which corresponded to a value slightly less than 0.02 Å. In terms of the O–O separation, the probable error is thus 0.04 Å. The final value of R for $x = 0.4192$ was 0.057 when all intensities were considered. The final values for the calculated and observed intensities are shown in Table I. I_c values less than 0.5 are listed as zero.

Discussion

Stoichiometry.—Only the results of the permanganate titrations are in poor agreement with the formula CdO_2. The low per cent. oxygen is very likely due to a loss of oxygen since a considerable evolution of gas occurs when the CdO_2 is dissolved in acid before the permanganate reaction. This may be attributed to the decomposition of the H_2O_2 produced and catalytically decomposed by CdO_2. It is well known that certain copper and silver salts catalyze the decomposition of H_2O_2; it may well be that CdO_2 acts in this manner too. Perhaps the heating and gas evolution during the preparation of CdO_2 is partially due to the decomposition of H_2O_2 catalyzed by CdO_2; however, the well-known decomposition of H_2O_2 in alkaline media is almost certainly responsible for this.

The other analytical results strongly support the formula CdO_2. Weight losses at 180–200° are in close agreement with the reaction $CdO_2 \rightarrow CdO + {}^1/_2O_2$. Thermal experiments indicating a few per cent. of adsorbed water are quite consistent with the analytical data. This amount of water is almost impossible to avoid due to the method of preparation, the small particle size and the instability of the material. When a correction is made for this adsorbed water, the % Cd is in excellent agreement with calculated amounts based upon CdO_2.

It is likely that Teletof,[5] Perkins[6] and perhaps other early workers succeeded in preparing fairly

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[10] R. W. James and G. W. Brindley, *Z. Krist.*, **78**, 470 (1931).

[11] D. P. Shoemaker, J. Donohue, V. Schomaker and R. B. Corey, THIS JOURNAL, **72**, 2328 (1950).

pure CdO_2. In discussing CdO_2, Emeléus and Anderson[12] mention the reported peroxides, Cd_3O_5, Cd_4O_7 and Cd_5O_8, but remark that "there can be no doubt that these are merely mixtures of CdO with varying amounts of CdO_2. Better defined products, having the composition $Cd(OH)_2 \cdot 1\text{–}4\text{-}CdO_2$ are obtained by the action of hydrogen peroxide on cadmium hydroxide." Except that our findings indicate that the methods of Teletof and Perkins gave fairly pure CdO_2 plus varying amounts of adsorbed water, this seems correct. $Cd(OH)_2$ was considered as a starting material, but due to its insolubility, it was rejected in favor of the direct dissolution of cadmium salts in NH_4OH.

The exothermal behavior of CdO_2 is not surprising, although Vol'nov[13] among others has noted that some alkali and alkaline earth peroxides decompose endothermally. However, hydrogen peroxide decomposes with the evolution of considerable heat. Vol'nov also investigated the thermal behavior of a material of gross composition $CdO_2 \cdot 2H_2O$. Vol'nov reports the material underwent an endothermal dehydration at 110° and a strongly exothermal reaction at 195–220°, which he regards as being due to the successive formation Cd(OH)(OOH) and $Cd(OH)_2$. No preparations or references thereto are given, nor are the means of positive identification of the pyrolysis products given. If CdO were the final product, it would seem surprising that it could be confused with $Cd(OH)_2$, since the latter is usually white, whereas CdO is a deep brown. Apparently Vol'nov's original material was not CdO_2, although both decompose at nearly the same temperature in a strongly exothermic reaction.

Structure.—The structure of CdO_2 is entirely analogous to FeS_2, pyrites, recently examined by Gordon[14] although Wyckoff[15] lists no similar peroxides. Each O–O dumbbell is surrounded by six Cd atoms forming a symmetrical octahedron. Each oxygen has three nearest Cd neighbors at 2.30 Å. and another three at 3.14 Å. The centers of the O–O dumbbells form a regular octahedron about the Cd atoms. Cd has then six nearest neighbors at 2.30 Å., one from each O–O dumbbell. This type of coördination is common for AX_2 substances.

Abrahams and Kalnajs[16] in a recent paper illustrate the surroundings of the O–O dumbbell in barium peroxide, BaO_2. The structure of CdO_2 is similar to that of BaO_2 although there are definite differences. The structures of CaO_2[17] and SrO_2[18] are believed to have the BaO_2 arrangement of atoms although the O–O distance appears questionable.

From considerations of cation size, it might appear that CdO_2 should conform to the BaO_2 (*i.e.*, CaC_2)-type structure, since the ionic radius of Cd is similar to that of Ca although the covalent radius of Cd is considerably lower than that of Ca. It seems that the small differences in their peroxide structure are due to the lower electropositive nature of Cd and its known tendency to form covalent bonds, relative to Ca. Carrying this reasoning further, ZnO_2 and perhaps even HgO_2 might be expected to form the cubic pyrites structure. At least for ZnO_2 that appears to be the case. Powder diffraction data on ZnO_2 reported by the New Jersey Zinc Company[19] may be indexed on the basis of a face-centered cubic structure with an a_0 of about 4.86 Å. In our laboratories we have succeeded in preparing a material believed to be ZnO_2. Preliminary diffraction patterns definitely indicate that ZnO_2 crystallizes in the pyrites structure. Weak lines due to the oxygen atoms are more numerous and more intense than those found on CdO_2 patterns. Complete data will be reported at a later date.

Table II lists some pertinent information on Group Ia and IIa peroxides. Unless otherwise referenced, values listed in the various columns are taken from the reference given after the compound. The structures of Group Ia peroxides vary considerably depending upon the element considered. The variety in structure undoubtedly is a consequence of the considerable cation size differences. The case of H_2O_2, which has recently been reinvestigated,[20] is somewhat special since considerable hydrogen and covalent bonding occur. Covalent bonding, between the cation and the peroxide group, is probably not so important in the other Group Ia peroxides. Further references to Group Ia peroxides may be found in Föppl's paper.[2] The tabulation of densities is included to show that in the case of the peroxides, at least, considerable difficulty is encountered in obtaining a pure peroxide and in measuring its density by pycnometer. In the case of CdO_2, the extremely fine particle size and the absorbed water contribute to the discrepancy between the calculated and observed density.

TABLE II

	Form	Space group	O–O Distance, Å.	Density	
				X-Ray	Exptl.
H_2O_2	Tetr.	D_4^4	1.49 ± 0.02[20]	1.70	1.69
Li_2O_2	Hex.	D^4_{6h}	$1.49 \pm .03$[2,21]	2.33	2.30
Na_2O_2	Hex.	D^3_{3h}	$1.49 \pm .03$[2]	2.62	2.60
K_2O_2	Rhomb.	D^{18}_{2h}	$1.49 \pm .03$[2]	2.40	2.40
Rb_2O_2	Rhomb.	D^{25}_{2h}	$1.49 \pm .03$[2]	3.80	3.60
Cs_2O_2	Rhomb.	D^{25}_{2h}	$1.49 \pm .03$[2]	4.76	4.47
CaO_2	Tetr.	D^{17}_{4h}	1.30[17]	3.19	2.92
SrO_2	Tetr.	D^{17}_{4h}	1.35[18]	4.77	4.45
BaO_2	Tetr.	D^{17}_{4h}	1.29[18]	5.67	5.43
			1.49 ± 0.04[16]		
CdO_2	Cubic	T^6_h	1.49 ± 0.04	6.36	5.93

This table draws attention to the low values proposed by early workers for the O–O distance in the alkaline earth peroxides. The O–O distance in BaO_2 has been recalculated by Butuzov[22] giving a

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[12] H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

[13] I. I. Vol'nov, *Doklady Akad. Nauk S.S.S.R.*, **94**, 477 (1954).

[14] R. B. Gordon, *Am. Mineral.*, **36**, 918 (1951).

[15] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948.

[16] S. C. Abrahams and J. Kalnajs, *Acta Cryst.*, **7**, 838 (1954).

[17] V. Kotov and S. J. Raikhshtein, *J. Phys. Chem. (USSR)*, **15**, 1057 (1941).

[18] J. D. Bernal, E. Djatlowa, I. Kazarnovskii, S. Raikhshtein and A. G. Ward, *Z. Krist.*, **A92**, 344 (1935).

[19] X-Ray Powder Data File, Card No. 1-1150, American Society for Testing Materials, X-Ray Department, Philadelphia, 1957.

[20] S. C. Abrahams, R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, **4**, 15 (1951).

[21] H. Föppl, private communication.

[22] V. P. Butuzov, *Doklady Akad. Nauk S.S.S.R.*, **58**, 1411 (1947).

value of 1.47 Å. which has been confirmed by Abrahams and Kalnajs.[16] It is probable that the O–O distance in all these compounds is in the neighborhood of 1.49 Å.

The constancy of the O–O peroxide type bond is illustrated by several other determinations. Harr[23] obtained 1.48, 1.49 and 1.48 Å. for this distance in $CaO_2 \cdot 8H_2O$, $SrO_2 \cdot 8H_2O$ and $BaO_2 \cdot 8H_2O$, respectively. Recently, Harvey and Bauer[24] have found the O–O distance in F_5SOOSF_5 to be 1.47 ± 0.03 Å. The value found for CdO_2 is in line with all of these determinations and lends credence to the proposed structure.

One further structural relationship remains to be discussed, the effective radius of the Cd and O atoms. The well-known Pauling and Goldschmidt ionic radii for Cd are conveniently summarized in a paper by Goldschmidt[25] and in many inorganic texts. They are 0.97 and 1.03 Å., respectively, both values being for the coördination number of 6. Föppl[2] deduces that the effective radius of O in the peroxide group is between 1.23 and 1.35 depending upon whether the evaluation is made at right angles to the O–O bond or projects a distance beyond one of the O in the group. Föppl's values were found by assuming Goldschmidt's ionic radii of the Group Ia elements. As remarked before, the distance of closest approach of the Cd and O atoms is 2.30 Å. Assuming Pauling's value for Cd, the effective radius of the O is 1.33 Å. whilst if Goldschmidt's radius for Cd is assumed, the value 1.27 Å. results. Both these values appear to confirm Föppl's figures.

Acknowledgments.—The authors are indebted to G. J. Meisenhelter, J. E. Mathers and G. V. Potter for chemical analyses and density determinations and to J. E. Webster for many preparations of CdO_2.

TOWANDA, PENNA.

[23] T. E. Harr, Thesis, Syracuse University, 1952.

[24] R. B. Harvey and S. H. Bauer, THIS JOURNAL, **76**, 859 (1954).

[25] V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**, 253 (1929).

[CONTRIBUTION FROM THE REFRACTORY METALS LABORATORY, GENERAL ELECTRIC CO.]

The Tungstic Acids

BY MEYER L. FREEDMAN

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A chemical and X-ray investigation was made of the solid phases precipitated from W(VI) solutions by strong acids at concentrations of 0.2 to 9.0 *N* and temperatures of 25, 50 and 100°. Of the four phases obtained by direct precipitation two phases, $WO_3 \cdot 2H_2O$ and $WO_3 \cdot H_2O$, were identified as hydrates by comparison with the isomorphous Mo compounds. A new phase was discovered in studying the reactions of the hydrates with Na_2WO_4 solution. This new compound, a cation exchanger, has a composition of $Na_2O \cdot (WO_3 \cdot H_2O)_n$ where n can vary from approximately 4 to 10. The unique phases were studied by potentiometric titration to determine acid properties and to relate their structures to those of the soluble isopoly tungstates. The tungstic acids were compared to similar compounds of Mo(VI) and U(VI) and in, particular, the relative stabilities of the oxy-anions of these elements as a function of *p*H were compared.

Introduction

Tungstic acid is the ambiguous term applied to various solids precipitated from W(VI) solutions by strong acids. Despite an extensive literature there is evident uncertainty as to the identity and chemical nature of these substances. Two compounds, H_2WO_4 and $H_2WO_4 \cdot H_2O$, have been characterized by X-ray diffraction and described as acids[1,2] while similar precipitates have been identified as WO_3 by electron diffraction.[3] A third compound, $WO_3 \cdot {}^1/_2H_2O$ or $H_2W_2O_7$, was obtained by treating H_2WO_4 with alkaline solutions.[4–6] Other compounds have been claimed.[7] Limiting conditions for the precipitation of specific compounds were not determined and the designation as acids was based only on thermal stability. Of the soluble W(VI) anions[8] only the metatungstate anion is sufficiently stable at low *p*H to be isolated as the free acid.[6,9] Acid behavior of the precipitated tungstic acids should thus be observed as a surface phenomenon, similar to silica,[10] or by cation exchange, similar to the polyuranates.[11]

This investigation was undertaken to clarify the state of knowledge of the tungstic acids. Fifty precipitations were made with HCl or HNO_3 at concentrations of 0.2 to 9.0 *N* and at temperatures of 25, 50 and 100°. The precipitates were characterized by chemical analysis, X-ray diffraction and potentiometric titration at high ionic strength. The ranges of homogeneity of the unique phases were estimated and their reactions were studied. A series of molybdic acids were prepared for comparison. The chemistry of the tungstic acids then was related to the chemistry of W(VI) compounds in aqueous solution and compared with that of Cr(VI), Mo(VI) and U(VI) compounds.

Structural Considerations.—The compounds previously written as $H_2WO_4 \cdot H_2O$ and H_2WO_4 are tungstic oxide hydrates rather than acids because they are isomorphous with the yellow $MoO_3 \cdot 2H_2O$ and $MoO_3 \cdot H_2O$ compounds which have been shown to be hydrates.[12] Also, the known structure of $MoO_3 \cdot 2H_2O$[13,14] defines that of $WO_3 \cdot 2H_2O$.

[1] A. Morley, *J. Chem. Soc.*, 1987 (1930).

[2] P. Kerr and F. Young, *Amer. Mineral.*, **29**, 192 (1944).

[3] S. N. Chatterjee, *J. Colloid Sci.*, **13**, 61 (1958).

[4] A. Chretien and G. Biehler, *Compt. rend.*, **224**, 934 (1947).

[5] G. Schott and G. Harzdorf, *Z. anorg. Chem.*, **288**, 15 (1956).

[6] E. Nikitina, *Sbornik Statei Obshchei Chim. Akad. Nauk SSSR*, **1**, 44(1953).

[7] "Gmelin's Handbuch der anorganishen Chemie, Wolfram," Verlag Chemie, Weinheim, 1933, p. 130, Vol. 54.

[8] D. Bettinger and S. Y. Tyree, THIS JOURNAL, **79**, 3355 (1957).

[9] E. Buchholz, *Z. anorg. Chem.*, **244**, 149 (1940).

[10] G. Sears, *Anal. Chem.*, **28**, 1981 (1956).

[11] J. Maly and V. Vesely, *J. Inorg. Nucl. Chem.*, **7**, 119 (1958).

[12] S. Maricic and J. Smith, *J. Chem. Soc.*, 889 (1958).

[13] I. Lindqvist, *Acta Chem. Scand.*, **4**, 650 (1950).

[14] I. Lindqvist, *ibid.*, **10**, 1362 (1956).