that the slow change in R going toward pure hydrogen iodide is due to an energy dependence of the type proposed above. These considerations indicate that the simple moderation equations proposed do not adequately describe the details of the processes involved, but the experimental data do not justify further refinements.

In the case of deuterium iodide (Fig. 4) the data do not justify an attempt to extrapolate for values of R_∞. It is apparent that all quantities, R_0, R_∞ and $E_1 - E_2$, are larger than for hydrogen iodide.

In the photolysis of hydrogen bromide (Fig. 5), the value of R_0 (0.66) stands in contrast to the value of k_6/k_7 = 8.6 obtained in the bromination of hydrogen.[9] In the latter case, no hot atom effect is to be expected, and we conclude that our value of the retardation constant in pure hydrogen bromide refers to the ratio of rate constants of the hot atom reactions

$$\mathrm{H} + \mathrm{HBr} \longrightarrow \mathrm{H_2} + \mathrm{Br} \quad k_8$$
$$\mathrm{H} + \mathrm{Br_2} \longrightarrow \mathrm{HBr} + \mathrm{Br} \quad k_9$$

A linear extrapolation of the points obtained with added hydrogen (the more elaborate treatment is not justified) indicates that $R_\infty = 9.5 \pm 1$. This value which we take as a proper measure of k_6/k_7 is in satisfactory agreement with previous results.[9] This transition from a hot atom value for the retardation constant to a previously observed thermal value seems to be an excellent confirmation of the hypothesis.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Participation of f Orbitals in Bonding in Uranium and the Transuranium Elements[1]

BY ROBERT E. CONNICK AND Z Z. HUGUS, JR.

RECEIVED MAY 19, 1952

On the basis of chemical and X-ray evidence it is suggested that f orbitals participate in the metal–oxygen bonding in the oxygenated ions MO_2^{++} and MO_2^+ of the uranides. The electronic structures and the small coördination number are discussed. The uranium–oxygen bonding in the infinite chains of . . . U—O—U—O . . . in UO_3 is compared with that in uranyl ion. It is shown that the entropy of uranyl ion can be accounted for by a charge distribution of +4 on the uranium and −1 on each oxygen. The conclusion is drawn that plutonyl ion should hydrolyze less readily than uranyl ion in spite of the actinide contraction.

Recently Glueckauf and McKay[2] have suggested that f orbitals are involved in the bonding of uranyl ion to other groups such as nitrate ion, water or ether molecules. Katzin[3] has given convincing evidence that the experimental data do not support this conclusion. We might add that the comparison which Glueckauf and McKay made between UO_2^{++} and such doubly charged ions as Mn^{++}, Co^{++} and Cu^{++}, can at best be only qualitative, as shown by the more negative entropy of uranyl ion. As is discussed below the charge on each of the oxygens may approximate −1 and that on the uranium +4. It is not surprising that such a divalent ion behaves differently from Co^{++}, etc.

More recently Street and Seaborg, and Diamond[4] have interpreted some aspects of the complexing behavior of the +3 ions of uranium and the transuranium elements as being due to the participation of f orbitals in the bonding. The observed effects are small but apparently real. We believe that much more striking evidence of f-orbital bonding is to be found in the metal–oxygen bonds of the ions of the +5 and +6 oxidation states of the actinide elements (except protactinium).

Chemical Evidence.—The oxide of uranium(VI), UO_3, readily dissolves in acidic solutions to form uranyl ion, UO_2^{++}. This is in sharp contrast to the behavior of MoO_3 and WO_3 which are the antecedents of uranium in the sixth group. These substances show little tendency to dissolve in acids unless strong complexing anions are also present. However it is to be expected that UO_3 would be more basic than MoO_3 and WO_3 because of the greater ionic size. Therefore it is not possible to conclude that the difference in basicity does in fact arise from a change in the type of bonding.

Kraus and Dam[5] have pointed out that in the case of the oxides and ions of the +5 oxidation states an even greater difference in behavior is found. Niobium, tantalum and protactinium oxides are all chemically inert and only very slightly soluble in strongly acidic solutions which do not contain complexing anions. In contrast the ions UO_2^+, NpO_2^+ and PuO_2^+ are easily obtained in aqueous solution. They show very little tendency to hydrolyze; for example the equilibrium constant for the reaction

$$PuO_2^+ + H_2O = PuO_2OH + H^+$$

is 2×10^{-10} or smaller.[5] As far as coulombic effects are concerned, the +5 oxidation states of uranium, neptunium and plutonium should have hydrolytic properties between those of protactinium and tantalum since their radii lie between those of the latter two elements. Kraus and Dam concluded that there must be a difference in electronic structure responsible for this change and that these actinide elements are "characterized by greater

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 121st Meeting of the American Chemical Society, Buffalo, New York, March, 1952.

[2] E. Glueckauf and H. A. C. McKay, *Nature*, **165**, 594 (1950).

[3] L. I. Katzin, *ibid.*, **166**, 605 (1950).

[4] K. Street, Jr., and G. T. Seaborg, THIS JOURNAL, **72**, 2790 (1950); R. M. Diamond, U. S. Atomic Energy Commission Report, UCRL-1434, August 1951.

[5] K. A. Kraus and J. R. Dam, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Volume 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 478.

availability of d electron orbitals for covalent bond formation." We believe that the participation of f orbitals in the bonding is responsible for these effects.

Kraus and Dam in proposing the d orbital explanation pointed out that the abrupt change in hydrolytic properties in going from protactinium(V) to uranium(V) is paralleled by a similar change in going from niobium(V) to molybdenum(V) and from tantalum(V) to tungsten(V). The ready availability of the d orbitals in the latter two cases is shown by the strong covalent complexes formed by molybdenum and tungsten in the +3 and +4 oxidation states. However, such covalent complexes of uranium(III) and -(IV) do not exist, and, therefore, it appears that the d orbitals are not readily available for bond formation in this case. Therefore, it may be concluded that the break in hydrolytic properties in going from protactinium to uranium is not due to the use of d orbitals in the latter. In addition, it may be pointed out that the scanty data in the literature indicate a marked difference in properties between the +5 uranides[6] and molybdenum(V) and tungsten(V) in aqueous solution. Thus compounds such as pyridinium molybdenum(V) thiocyanate, $(C_5H_6N)_2MoO_2(CNS)_3$, are strongly hydrolyzed in water, probably to the neutral species $MoO_2OH \cdot xH_2O$.[7] From this fact one calculates that the hydrolysis constant of molybdenum(V) is at least 10^7 times greater than those of the +5 uranides.

X-Ray Evidence.—Strong confirmation of the uniqueness of the UO_2^{++} type of structure for the uranides is obtained from X-ray structural studies. In uranyl compounds two oxygens lie on opposite sides of the uranium at a distance of approximately 1.9 Å. from the uranium.[8] The great stability of this grouping is proved by the fact that it persists in UO_3[9a] and the uranates, such as $CaUO_4$.[9b] In the former compound the uranium atoms lie in chains with oxygen atoms separating the uraniums and lying 2.08 Å. from the uraniums. In addition each uranium has six oxygens surrounding it at a distance of 2.39 Å. and arranged in staggered positions about the equator of the uranyl group. In calcium and strontium uranate each uranium has the identical environment of oxygens, with the uranyl oxygens at 1.91 ± 0.10 Å. and the other six at 2.29 Å.

Apparently no X-ray determinations have been made of salts of molybdenum VI and tungsten VI which according to their formulas might contain the groups MoO_2^{++} and WO_2^{++}. The X-ray study of MoO_3[10,11] indicates the molybdenum is surrounded by a distorted octahedron of oxygens. There is no evidence of significant shortening of two of the metal–oxygen bond distances as is found in UO_3. In WO_3[10] the octahedral arrangement of oxygens around the tungsten is only slightly distorted with the metal–oxygen distances ranging from 1.80 to 1.86 Å.

Magneli[12] has made an extensive X-ray study of the crystals of oxides of molybdenum and tungsten whose compositions lie between MO_2 and MO_3. All but one of the five compounds consist of octahedra of oxygens around the metal ion, sharing edges and corners. The one exception, Mo_4O_{11}, contains tetrahedra as well as octahedra. Although there are variations in metal–oxygen bond distances of several tenths of ångströms, caused by distortion of the octahedra, there is no significant shortening of the metal–oxygen bond distances over that normally expected, as judged by, for example, the distance found in the cubic tungsten bronzes[13] where the octahedron of oxygens is symmetrical. Presumably an easily detectable shortening would have occurred if covalent bond formation similar to that in UO_3 had taken place.

The molybdate and tungstate ions consist of tetrahedra of oxygens surrounding the metal atoms. Of the many structures investigated[14] a number are known from symmetry to have constant metal–oxygen distances, while in the others the distortion appears to be small.

In summary, the X-ray evidence indicates that the MO_2^{++} and MO_2^{+} structures in solids exist only in the case of the uranide elements. The chemical evidence, based on a comparison of the hydrolytic properties of the uranides and their antecedents in the periodic table, is in accord with this idea of uniqueness, but in itself is not conclusive. The stability of the MO_2^{++} and MO_2^{+} structures is not plausibly accounted for by d orbital bonding.

Electronic Structure.—On the basis of the foregoing crystallographic and chemical evidence it would appear that there is a special stability associated with the metal–oxygen bonds in the UO_2^{++} and UO_2^{+} types of ions. The most striking difference between the electronic structures of the uranides and the elements lying above them in the periodic table is the presence of relatively stable 5f orbitals in the former. It is tempting to associate the enhanced stability of the metal–oxygen bonds with the presence of these orbitals.

In general when a molecule is formed by bringing certain atoms up to a given atom, the atomic orbitals on the given atom are highly perturbed and the original designation of such orbitals as s, p, d and f, is no longer valid. One therefore has difficulty in specifying the contribution of the various atomic orbitals to the resulting molecular orbital. However, from a knowledge of the properties of the atomic orbital it is possible to deduce qualitatively the general nature of the molecular orbital to which the

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(6) The term "uranides" will be used to denote uranium and the transuranium elements.

(7) R. G. James and W. Wardlaw, *J. Chem. Soc.*, 2726 (1928).

(8) For UO_2F_2 W. H. Zachariasen (*Acta Cryst.*, **1**, 277 (1948)) gave the uranium–oxygen distance as 1.91 Å. We have estimated the corresponding distance to be 1.84 Å. in $RbUO_2(NO_3)_3$ by subtracting Pauling's ionic radii for oxygen and rubidium from the measured uranium–rubidium distance (Hoard and Stroupe, National Nuclear Energy Series, Division III, Vol. 2, McGraw–Hill Book Co., Inc., New York, N. Y., 1949, p. 15 ff). The oxygens are believed to lie on a line connecting the uranium and rubidium atoms.

(9) (a) W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948); (b) *ibid.*, 1, 281 (1948).

(10) H. Braekken, *Z. Krist.*, **78**, 484 (1931).

(11) N. Wooster, *ibid.*, **80**, 504 (1931).

(12) A. Magneli, *Acta Chem. Scand.*, **2**, 501 (1948); *ibid.*, **2**, 861 (1948); *Arkiv Kemi*, **1**, no. 25, 223 (1949); *ibid.*, **1**, no. 59, 513 (1950).

(13) A. Magneli, *Nova Acta Regiae Soc. Sci. Upsaliensis*, Ser. IV, **14**, no. 8 (1950).

(14) R. W. G. Wyckoff, "Crystal Structures," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1951.

atomic orbital will make an appreciable contribution.

An attempt[15] has been made to explain certain features of the chemistry of the elements preceding the rare earth series by bonding involving the imminently stable 4f orbitals. It should be noted that the conditions for possible participation of f orbitals in bonding (*i.e.*, high kernel charge, small radius, and appreciable stability of the f orbitals) obtain in the uranide (V), and (VI) oxidation states. In fact, in the uranide ions it would appear that the optimum possibility of f-orbital bonding exists. The non-existence of the V and VI oxidation states of the rare earths precludes the above conditions for f-orbital bonding in the lanthanides.

Protactinium(V) does not appear to form the UO_2^+ type of ion. The 5f orbitals begin to become stable with respect to 6d orbitals in the neighborhood of thorium and protactinium.[16] According to our explanation of f bonding it must be assumed that the 5f orbitals are not sufficiently stabilized in protactinium to participate in bonding.

Before concluding that there can be a real contribution to the bonding by the 5f orbitals in, say, UO_2^{++}, certain known facts must be explained. In particular, the low coördination number of two in UO_2^{++} seems anomalous if we are to use additional orbitals (5f) in bonding, since one would expect an increased coördination number on increasing the number of available atomic orbitals over those available in, say, tungsten(VI). Further, the non-exchange of uranyl oxygen with water oxygen, observed by Crandall[17] indicates rather definitely that the metal–oxygen bonds are quite strong.

Because the f orbitals in the uranides are reasonably well inside the atom, only at small uranide–oxygen distances will the f bonding be appreciable. Double bonding will tend to bring about this condition. While the formation of π bonds enhances the participation of the f orbitals, conversely the contribution of the f orbitals to the bonding will strengthen the π-bonds. These π-bonds are doubtless such that the valence electron density in the vicinity of the oxygens is considerably larger than near the uranium. Thus, we picture these π orbitals as giving rise to an ionic contribution to the uranium–oxygen bonds.[18] With two oxygens about the uranium one π bond can be formed between each oxygen and the metal atom if it is assumed that p orbitals are used. With three oxygens around the uranium only one-third of a π bond can be formed per oxygen. It seems reasonable that the participation of the f orbitals in the σ-bonds would be significant only if each oxygen were double bonded to the uranium and, in this case, the coördination number could not exceed two.

Qualitatively the same result is obtained if it is assumed that each oxygen is held to the uranium by a σ-bond and electrostatic attraction. The electrostatic energy per bond decreases rapidly as the coördination number is increased, therefore, only a small coördination number will give sufficiently short bonds to allow participation of f orbitals. That this limit should be two seems reasonable although not calculable.

Thus, the concept of a short σ-bond in which an f orbital can participate appreciably accounts satisfactorily for the low coördination number and the great stability of the M–O bonds in the MO_2^{++} and MO_2^+ ions.

Structure of UO_3.—The relationship of the UO_3 structure to the uranyl ion structure is of interest. The linear chains of . . . U—O—U—O . . . may be considered as formed by placing U^{+6} ions between uranyl groups along an axis. The electrostatic effect of the U^{+6} will be to lengthen the uranium–oxygen bonds in the uranyl groups. This is consistent with the observed *ca.* 0.2 Å. lengthening of the uranium–oxygen distance in the UO_3 chains compared to uranyl ion.

In addition, bond lengthening in UO_3 probably occurs because of the difficulty of forming two linear σ-bonds on the oxygens. The formation of sp hybrid orbitals would require a large promotion energy. Possibly there is only *circa* half a σ-bond between each uranium and oxygen. Because of the increased bond distance the participation of the f orbitals of the uranium would be expected to be less than in uranyl ion.

Charge Distribution and Entropy.—If we assume a distribution of charge between the uranium and the oxygens of a uranyl ion, it is possible to calculate from simple electrostatics the electric field at various points in the vicinity of the ion. In aqueous solution, waters should be arranged about the uranyl ion in approximately the same manner as are the oxide ions in $CaUO_4$. That is, about the equator of the uranyl ion a puckered ring of six oxygens will be arranged at about 2.3 Å. from the uranium. With the assumed charges of +4 on the uranium and −1 on each uranyl oxygen the field at each of the equatorial oxygens is found to be approximately that of a +3 charge located at the uranium. The field at the ends of the uranyl ion is found to be quite small; at 2.8 Å. from the nearer oxygen (*ca.* the distance of closest approach for a water molecule) it approximates the field of a charge of +0.3 at the location of the uranium. Thus a uranyl ion appears as a +3 ion to waters about its equator, and interacts but weakly with the waters at the ends.

On the basis of such a picture we may estimate the entropy of uranyl ion if we assume that over some fraction of the solid angle about the uranyl ion the electric field is so weak that essentially no waters are sufficiently restricted to cause a decrease in the partial molal ionic entropy. For a spherical ion with a radius equal to the equatorial radius (0.89 Å.) of uranyl ion, eight nearest water molecules would be expected. Consequently, for uranyl ion only about 6/8 of the entropy decrease due to the electrostatic effect would be expected as for the hypothetical +3 ion with a radius of 0.89 Å.

Powell and Latimer[19] have given an empirical

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(15) Z. Z. Hugus, Jr., THIS JOURNAL, **74**, 1076 (1952).

(16) R. E. Connick, *J. Chem. Soc.*, supplementary Issue No. 2, S235 (1949).

(17) H. W. Crandall, *J. Chem. Phys.*, **17**, 603 (1949).

(18) Evidence for such a charge distribution in uranyl ion is given in a succeeding section "Charge Distribution and Entropy."

(19) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

expression for the partial molal entropy of a monatomic positive ion of charge, Z, and crystal radius, r

$$\bar{S}^0 = \frac{3}{2} R \ln M - 270 \frac{Z}{(r + 2.00)^2} + 37$$

For uranyl ion we should reduce the electrostatic contribution to the entropy (the second term on the right of the above expression) by the factor of 6/8 as stated above. The empirical equation for the partial molal entropy of UO_2^{++} is then

$$\bar{S}^0 = \frac{3}{2} R \ln 270 - \frac{6}{8} \times 270 \times \frac{3}{(0.89 + 2.00)^2} + 37 + S_{int}$$

Here we have inserted the mass of UO_2^{++} in atomic weight units, the equatorial radius, 0.89 Å., the effective charge at the equator, 3, and a term, S_{int}, to take care of the vibrational and rotational (or, more probably, librational) contributions to the entropy of the aqueous ion. The contribution of these modes to the entropy of UO_2^{++} would only be a few entropy units and to the accuracy of our calculation would not alter the fact that the calculated entropy, $-19 + S_{int}$, and the experimental entropy, -17 e.u., are in approximate agreement. In fact, the closeness of this agreement is doubtless fortuitous.

The sensitivity of the model to a change in the charge distribution is such that a shift of 0.1 of an electronic charge to each oxygen from the uranium would cause a decrease of 3 e.u. in the calculated entropy of UO_2^{++}. Therefore the charge distribution cannot be fixed with any great accuracy but it would appear that it approximates to +4 on the uranium and -1 on each oxygen.

The Relative Hydrolysis of PuO_2^{++} and UO_2^{++}.—Kraus and Dam[20] have found that uranyl ion appears to hydrolyze more extensively than plutonyl ion, although the complication of polymerization in the case of uranyl may make this conclusion incorrect. Kraus and Dam comment that the observed greater hydrolysis of uranyl seems anomalous since "Pu(VI) should be the smaller ion and thus have the larger acid constant."

Since the structural evidence shows that the six oxygen neighbors of uranyl ion (in $CaUO_4$, for example) are in contact with the oxygens of the uranyl group rather than in contact with the uranium, the fact that PuO_2^{++} is a smaller ion than UO_2^{++} does not follow from the expected actinide contraction. A calculation based on the packing of hard spheres about a uranyl group also composed of hard spheres shows that, in the case where the uranium cannot contact the six peripheral neighbors, a decrease in the radius of the uranium causes an increase in the uranium–peripheral oxygen distance. The relevant formula obtained by straightforward geometrical considerations is

$$a^2 = 4b^2 - \frac{(b + c)^2}{3}$$

where a is the uranium–peripheral oxygen neighbor distance, b is the radius of oxygen, c is the radius of uranium, and $b + c$ is the uranium–uranyl oxygen distance. Obviously then a will decrease as c is increased, and we must conclude that plutonyl behaves as a larger ion than uranyl toward oxygens or water molecules about the equator.

Provided that the charge distribution is not appreciably altered in going from uranyl to plutonyl one must then conclude that uranyl ion should indeed be more acidic than plutonyl ion.

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(20) K. A. Kraus and J. R. Dam, National Nuclear Energy Series, "The Transuranium Elements," Division IV, Volume 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, Part I, pp. 528–549.

[CONTRIBUTION FROM KING COLLEGE AND THE OAK RIDGE NATIONAL LABORATORY]

Bispentanedione Diaquo Manganese(III) Compounds

BY G. H. CARTLEDGE

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Salts of a new cationic manganese(III) complex with 2,4-pentanedione have been prepared. The acidic ionization constant of the diaquo-ion previously reported has been confirmed. The equilibrium constant for the interconversion of the bis- and tris-complexes has been determined at different temperatures for the estimation of the ΔH and ΔS of the reaction.

In a previous paper[1] it was shown that trispentanedione manganese(III) resembles the trioxalato and trimalonato complexes in that one of the bidentate organic ligands may be reversibly replaced by two water molecules under proper conditions of acidity. The equilibrium constant was determined for the reaction $MnPn_3 + 2H_2O + H^+ \rightleftarrows MnPn_2(H_2O)_2^+ + HPn$, in which Pn^- is used to represent the anion of 2,4-pentanedione.

This reaction is of particular interest in that it produces a cationic complex. Previously only neutral or anionic complexes of tervalent manganese had been prepared, though Taube[2] had postulated the formation, in solution, of a monoöxalato manganese(III) cation, $MnC_2O_4^+$, in order to account for the catalytic effect of manganese in the oxidation of oxalic acid. The isolation and properties of a few salts of the bispentanedione diaquo ion will be described in this paper, together with a determination, at different temperatures, of the equilibrium constant of the reaction for its conversion to the tris-complex.

Preparation of the Complex Perchlorate.—The first attempt to isolate the complex salt was based upon the possibility that the large univalent cation might form a perchlorate of sparing solubility. The equilibrium measurements indicated that at a *p*H of 2 the trispentanedione complex is totally converted to the bis-ion, even in the presence of much free pentanedione. After a few experiments had demonstrated that the perchlorate has a surprisingly high solubility, a convenient method of preparation was developed as follows. Three grams of the tris-complex was tri-

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[1] G. H. Cartledge, THIS JOURNAL, **73**, 4416 (1951).

[2] H. Taube, *ibid.*, **69**, 1418 (1947); **70**, 1216, 3928 (1948).