METAL OXIDE ALKOXIDE POLYMERS

PART V. THE HYDROLYSIS OF SOME ALKOXIDES OF TIN (IV), CERIUM (IV), AND URANIUM (V)[1]

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ABSTRACT

The polymers formed by the hydrolysis of stannic isopropoxide, ceric isopropoxide, and uranium pentaethoxide have been studied by means of an ebulliometric method. The metal oxide alkoxide polymers formed from the tin (IV), cerium (IV), and uranium (V) alkoxides conform to the requirements of a structural theory. In view of the fundamental nature of the theory a formal mathematical presentation is now given.

INTRODUCTION

Previous work has shown that the remarkable variation of number-average degree of polymerization of the oxide alkoxides of titanium (1), zirconium (2), and tantalum (3) as a function of degree of hydrolysis may be satisfactorily explained on the basis of certain key structures in which the metal atom exhibits a higher coordination number. The success of the theory in explaining the behavior of compounds of both quadrivalent and quinquevalent elements on the same basic structural models suggested that it may be of fundamental importance in relation to metal oxide alkoxides in general and that it should have predictive ability. Accordingly we have set out in a formal manner the mathematical aspects of the theory, including a useful terminology for describing the various structural models. In an attempt to test the predictive possibilities of the theory we have extended the work to the hydrolysis of the isopropoxides of tin (IV), cerium (IV), and the pentaethoxide of uranium (V). The derivatives of tin and cerium both form dimeric solvates of the type $M_2(OPr^i)_8,(Pr^iOH)_2$ and should give polymeric oxide isopropoxides based on mixtures of the model II and model III or of the model II and model IV basic structures. Similarly, the uranium oxide ethoxides would be expected to conform to the same structural models as the tantalum oxide ethoxides, provided that the uranium exhibits a coordination number of six.

EXPERIMENTAL

Preparation of Metal Alkoxides

Stannic isopropoxide was prepared by alcoholysis of the ethoxide, which was obtained by the method of Bradley, Caldwell, and Wardlaw (4). The isopropoxide was purified by crystallization of the solvate $Sn_2(OPr^i)_8,(Pr^iOH)_2$, which lost the coordinated isopropanol when heated *in vacuo*. The resulting $Sn(OPr^i)_4$ was distilled *in vacuo*. Cerium isopropoxide was prepared from dipyridinium cerium hexachloride by the method of Bradley, Chatterjee, and Wardlaw (5). It was purified by recrystallization of the solvate $Ce_2(OPr^i)_8,(Pr^iOH)_2$. Uranium pentaethoxide was prepared by the three-stage synthesis from UCl_4 and sodium ethoxide using bromine as the oxidant, as developed by Jones *et al.* (6). The product was purified by distillation *in vacuo*. All of these compounds are extremely susceptible to hydrolysis and the usual precautions were adopted to control the hydrolysis in these experiments. The uranium compound is also susceptible to oxidation and the experiments were carried out under an atmosphere of oxygen-free nitrogen.

Ebulliometry

The previously described technique (3) was essentially followed throughout. Solutions of $Ce_2(OPr^i)_8,(Pr^iOH)_2$ and $Sn_2(OPr^i)_8,(Pr^iOH)_2$ in boiling isopropanol were prone to decomposition if the amount of

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superheating was high or if the heating was localized. However, by using a silicone oil heating bath and lagging the ebulliometer satisfactory conditions were obtained and the results were reproducible. With the exception of $Ce_2(OPr^i)_8,(Pr^iOH)_2$, which has a low volatility and was recrystallized immediately prior to use, the alkoxides were freshly distilled *in vacuo* immediately before an ebulliometric hydrolysis.

Stannic Isopropoxide

Three separate determinations of the molecular weight were carried out, each involving several additions of solute. Although the concentrations covered almost a 30-fold range there was no evidence of concentration dependence of the molecular weight. The values of n_0 (the number-average degree of polymerization of the metal alkoxide, i.e. n at zero degree of hydrolysis) were: 1.84, 1.88, 1.84. The mean value of $n_0 = 1.85$ was adopted. The results of two ebulliometric hydrolyses are recorded in Table I.

TABLE I

A. Initial concentration of $Sn(OPr^i)_4 = 0.264$ g-mol./kg						
h	0.100	0.190	0.332	0.507	0.724	0.919
n	1.87	2.06	2.43	2.98	3.81	4.95
n_{calc}	1.95	2.09	2.35	2.78	3.59	4.86
B. Initial concentration of $Sn(OPr^i)_4 = 0.310$ g-mol./kg						
h	0.204	0.483	0.822	1.078	1.449	
n	1.98	2.73	4.02	6.14	17.0	
n_{calc}	2.11	2.71	4.13	6.84		

Ceric Isopropoxide

The two determinations of the molecular weight of the solvate $Ce_2(OPr^i)_8,(Pr^iOH)_2$ gave $n_0 = 1.86, 1.87$. The value of 1.86 was adopted. The results of four ebulliometric hydrolyses are recorded in Table II.

TABLE II

A. Initial concentration of $Ce_2(OPr^i)_8,(Pr^iOH)_2 = 0.109$ g-mol./kg					
h	0.111	0.271	0.506	0.704	1.026
n	2.02	2.26	2.79	3.51	6.34
n_{calc}	2.02	2.28	2.83	3.55	6.08
B. Initial concentration of $Ce_2(OPr^i)_8,(Pr^iOH)_2 = 0.127$ g-mol./kg					
h	0.109	0.265	0.471	0.688	1.042
n	2.02	2.26	2.71	3.46	5.90
n_{calc}	2.02	2.27	2.74	3.48	6.25
C. Initial concentration of $Ce_2(OPr^i)_8,(Pr^iOH)_2 = 0.205$ g-mol./kg					
h	0.088	0.217	0.413		
n	1.98	2.21	2.62		
n_{calc}	1.98	2.19	2.59		
D. Initial concentration of $Ce_2(OPr^i)_8,(Pr^iOH)_2 = 0.173$ g-mol./kg					
h	0.128	0.289	0.505		
n	2.04	2.37	2.91		
n_{calc}	2.04	2.32	2.83		

Uranium Pentaethoxide

The molecular weight of uranium pentaethoxide was determined in boiling ethanol in two separate experiments covering a 15-fold range in concentrations but no evidence of concentration dependence was found. The values of n_0 were 1.47 and 1.49. The average value, $n_0 = 1.48$, was adopted. The results for two ebulliometric hydrolyses of uranium pentaethoxide are given in Table III.

TABLE III

A. Initial concentration of $U(OEt)_5 = 0.217$ g-mol./kg									
h	0.093	0.219	0.349	0.478	0.630				
n	1.56	1.70	1.85	2.03	2.31				
n_{calc}	1.61	1.69	1.85	2.03	2.31				
h	0.804	0.969	1.163	1.339	1.500				
n	2.72	3.28	4.25	6.07	10.0				
n_{calc}	2.73	3.30	4.55	6.21	10.7				
B. Initial concentration of $U(OEt)_5 = 0.167$ g-mol./kg									
h	0.075	0.226	0.354	0.482	0.655	0.779	0.866	0.992	1.081
n	1.55	1.70	1.86	2.00	2.32	2.62	2.98	3.42	4.14
n_{calc}	1.55	1.70	1.85	2.04	2.36	2.66	2.92	3.40	3.84

DISCUSSION

A General Structural Theory for Metal Oxide Alkoxide Polymers

A formal presentation of the theoretical aspects of the metal oxide alkoxides will simplify the discussion of the latest experimental results.

First we define a regular polymer series as a set of metal oxide alkoxides having structures which fulfill the following requirements: (*a*) Each polymer in the series may be considered as derived from an integral number of unhydrolyzed metal alkoxide units linked together by metal–oxygen–metal bridges formed in the condensation $M(OR) + H_2O + (RO)M \rightarrow M{\cdot}O{\cdot}M + 2ROH$. (*b*) The metal alkoxide repeating units may themselves be polymers but they must have integral values of degree of polymerization which remain constant throughout the polymer series. (*c*) The number of $M{\cdot}O{\cdot}M$ links between adjacent units of the metal oxide alkoxide polymer must be constant. Secondly, we define the following variables: (i) the degree of polymerization of the metal oxide alkoxide (i.e. number of metal atoms per molecule) $= n$; (ii) the degree of polymerization of the metal alkoxide repeating unit $= p$; (iii) the degree of hydrolysis (i.e. ratio of water molecules added per metal atom) $= h$; (iv) the number of $M{\cdot}O{\cdot}M$ links between adjacent repeating units $= q$.

It follows from the definition of the regular polymer series that $n = p(x+1)$, where x is 0, 1, 2, 3, etc. Since one water molecule produces one $M{\cdot}O{\cdot}M$ link between adjacent repeating units, it also follows that $hn = xq$. By eliminating x we obtain the following general description of the members of the regular polymer series:

$$n^{-1} = p^{-1}-q^{-1}h. \tag{1}$$

The regular polymer series will consist of a distribution of the members of the series so that the number-average degree of polymerization $\bar{n}$ and the average degree of hydrolysis $\bar{h}$ need not necessarily have integral values. Consider a regular polymer series comprising a mole fraction N_1 of the species with $n = n_1$ and $h = h_1$; N_2 of the species with $n = n_2$ and $h = h_2$; and N_i of the species with $n = n_i$ and $h = h_i$. The number-average degree of polymerization

$$\bar{n} = \sum N_i n_i / \sum N_i = \sum N_i n_i \tag{2}$$

and the average degree of hydrolysis $\bar{h} = \sum h_i n_i N_i/\bar{n}$. Equation [1] will hold (p and q are constant) for each member of the series, i.e. $n_i^{-1} = p^{-1}-q^{-1}h_i$, which may be rearranged to $pq = qn_i - pn_ih_i$. Summation over the whole series gives the following expression:

$$\sum pqN_i = \sum qn_iN_i - \sum pn_ih_iN_i, \tag{3}$$

i.e.

$$pq = q\bar{n} - p\bar{n}\bar{h}. \tag{4}$$

Equation [4] may be rearranged to [5].

$$(\bar{n})^{-1} = p^{-1}-q^{-1}\bar{h} \tag{5}$$

An important feature of equation [5] is the determination of the number-average degree of polymerization $\bar{n}$ by the average degree of hydrolysis $\bar{h}$, since p and q are constant for any given regular polymer series. This is important because it has the consequence that once $\bar{h}$ is fixed then $\bar{n}$ is fixed irrespective of the distribution of polymer sizes in the system. Thus a redistribution of the polymer sizes for a given value of $\bar{h}$ will not affect $\bar{n}$. Another consequence of equation [5] is a simple classification of regular polymer series. Thus the system can be defined as (p_x,q_y), where x is the numerical value of p, and y the numerical value of q. For example, the regular polymer series based on trimeric titanium ethoxide and termed Model I by Bradley, Gaze, and Wardlaw (1) would simply be the system (p_3,q_4) with $(\bar{n})^{-1} = 0.333_4 - 0.25\bar{h}$. The regular polymer series called model II and based on either the solvated dimeric metal tetraalkoxide $M_2(OR)_8,(ROH)_2$ (1, 2) or the dimeric tantalum pentaalkoxide $M_2(OR)_{10}$ (3) would be (p_2,q_3) with $(\bar{n})^{-1} = 0.5 - 0.333_4\bar{h}$. Model III based on the solvated monomeric alkoxides $M(OR)_4,2ROH$ or $M(OR)_5,ROH$ would be (p_1,q_3) with $(\bar{n})^{-1} = 1.0 - 0.333_4\bar{h}$, whilst the alternative model IV is (p_1,q_2) with $(\bar{n})^{-1} = 1.0 - 0.5\bar{h}$. The fundamental aspect of the theory of regular polymers is the consequence that the classification (p_x,q_y) fixes the variation of $\bar{n}$ with $\bar{h}$, which will be the same for all systems with the same values of x and y irrespective of the valency of the metal or the geometrical structures involved. It follows that with a knowledge of the structure of the original metal alkoxide and hence the value of x the possible values of y may be deduced from geometrical considerations. Having fixed x and y the variation of number-average degree of polymerization with degree of hydrolysis for the metal oxide alkoxides may be predicted by means of equation [5]. The structures of polymeric metal alkoxides have been discussed by Bradley (7) in terms of the valency of the metal, its higher coordination number, and stereochemistry. The fact that some metal alkoxides have non-integral values of n suggests that more than one value of x may be adopted. However, it is readily shown that the metal oxide alkoxides may still conform to an equation of the same general form as [5]. For example, let us consider a metal alkoxide existing in two polymeric species with $n = a$ and $n = b$ together in a system and let them form metal oxide alkoxides which conform to the regular polymer series (p_a,q_r) and (p_b,q_s). The proportions of the a-mer and b-mer initially present are defined by α_a, where $\alpha_a =$ the ratio of the number of metal atoms present in a-mers divided by the total number of metal atoms in the system. Obviously $\alpha_b = 1-\alpha_a$. Then

$$(\bar{n})^{-1} = \alpha n_a^{-1} + (1-\alpha)n_b^{-1},$$

where

$$n_a^{-1} = p_a^{-1} - q_r^{-1}h,$$

and

$$n_b^{-1} = p_b^{-1} - q_s^{-1}h.$$

Therefore,

$$(\bar{n})^{-1} = \alpha_a p_a^{-1} - \alpha_a q_r^{-1}h + (1-\alpha_a)p_b^{-1} - (1-\alpha_a)q_s^{-1}h.$$

$$[6] \qquad = [\alpha_a p_a^{-1} + (1-\alpha_a)p_b^{-1}] - [\alpha_a q_r^{-1} + (1-\alpha_a)q_s^{-1}]h.$$

Substitution of

$$(\bar{p})^{-1} = \alpha_a p_a^{-1} + (1-\alpha_a)p_b^{-1}$$

and

$$(\bar{q})^{-1} = \alpha_a q_r^{-1} + (1-\alpha_a)q_s^{-1}$$

in equation [6] results in [7], which is identical in form with [5]:

$$[7] \qquad (\bar{n})^{-1} = (\bar{p})^{-1} - (\bar{q})^{-1}h.$$

Since α_a may be evaluated from the number-average degree of polymerization of the original metal alkoxide the values of $\bar{p}$ and $\bar{q}$ may be calculated for the metal oxide alkoxides. By similar reasoning it may be shown that for a metal alkoxide existing as three different polymeric species giving rise to the regular polymer series' (p_a,q_r),(p_b,q_s), and (p_c,q_t), equation [8] may be derived:

$$[8] \qquad (\bar{n})^{-1} = [\alpha_a p_a^{-1} + \alpha_b p_b^{-1} + (1-\alpha_a-\alpha_b)p_c^{-1}] - [\alpha_a q_r^{-1} + \alpha_b q_s^{-1} + (1-\alpha_a-\alpha_b)q_t^{-1}]h,$$

where α_a, α_b, and $(1-\alpha_a-\alpha_b)$ are the proportions of metal atoms in species (p_a,q_r), (p_b,q_s), and (p_c,q_t) respectively. By determining the intercept $(\bar{p})^{-1}$ and the slope $(\bar{q})^{-1}$ of equation [7] from the experimental plot of $(\bar{n})^{-1}$ versus h, it is possible to solve equation [8] for α_a and α_b and hence calculate $1-\alpha_a-\alpha_b$. It is clear that we cannot solve a system containing a mixture of more than three regular polymer series.

Stannic Oxide Isopropoxides

Since stannic isopropoxide forms a solvate, $Sn_2(OPr^i)_8,(Pr^iOH)_2$, which is practically dimeric in boiling isopropanol we should expect the variation of $\bar{n}$ with $\bar{h}$ for the oxide isopropoxides to be close to the equation for the (p_2,q_3) regular polymer series. The results plotted in Fig. 1 show that this is indeed the case. A least-squares fit of $(\bar{n})^{-1}$ versus $\bar{h}$ gave the equation $(\bar{n})^{-1} = 0.5505 - 0.3751\bar{h}$ with a coefficient of variation $\sigma_n = \pm 5.2\%$. There are five changes in sign in the error $\delta\bar{n} = \bar{n}_{calc} - \bar{n}$ ($\bar{n}_{calc}$ given in Table I) when the 11 points are arranged in ascending order of $\bar{h}$. From the intercept $(\bar{n})_0^{-1} = 0.5505$ at $\bar{h} = 0$, a value of $(\bar{n})_0 = 1.82$ was calculated, which compares favorably with the value of 1.85 determined from the molecular weight of stannic isopropoxide.

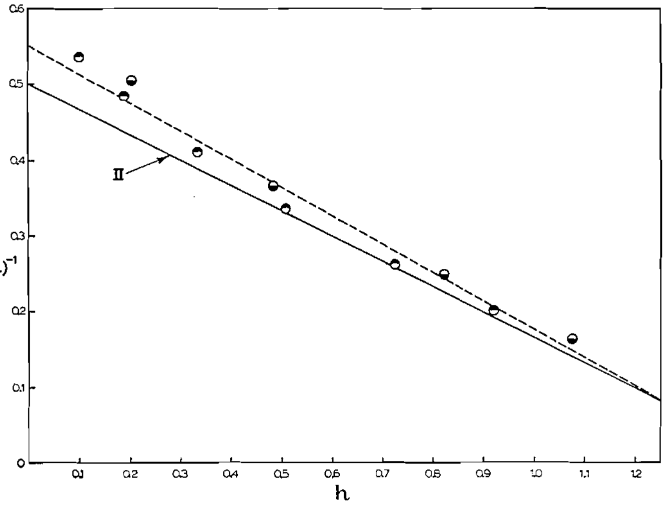

FIG. 1. The variation of $\bar{n}$ with $\bar{h}$ for the hydrolysis of stannic isopropoxide: ◓, data from Table 1A; ◒, data from Table IB. Curve II, $\bar{n} = 6/(3-2\bar{h})$.

Assuming that the (p_2,q_3) regular polymer series is accompanied by either the (p_1,q_2) or (p_1,q_3) series we derive the value of $\alpha_{II} = 0.899$ for the proportion of tin atoms in the (p_2,q_3) series. If the (p_1,q_3) series is present then the slope $d(\bar{n})^{-1}/d\bar{h}$ should be -0.333_4. If the (p_1,q_2) series is present then $d(\bar{n})^{-1}/d\bar{h}$ is calculated from equation [6] to be -0.350. The "least-squares" value of -0.375 is obviously closest to that predicted for the mixture of (p_2,q_3) and (p_1,q_2) series.

Ceric Oxide Isopropoxides

Ceric isopropoxide also forms a solvate, $Ce_2(OPr^i)_8,(Pr^iOH)_2$, which is practically dimeric in boiling isopropanol and hence would be expected to produce oxide isopropoxides conforming nearly to series (p_2,q_3). The plot of $\bar{n}$ versus $\bar{h}$ in Fig. 2 shows that such is the case. The least-squares fit of $(\bar{n})^{-1}$ versus $\bar{h}$ gave the equation $(\bar{n})^{-1} = 0.5358-0.3608\,\bar{h}$, with a coefficient of variation $\sigma_n = \pm2.1\%$. In fact a considerable part of the error resides in the two points of highest and next-highest value of $\bar{h}$, and the coefficient of variation for the first 14 points is only $\pm1.2\%$, with 8 changes in sign of $\delta\bar{n}$. Values of $(\bar{n})_{\text{calc}}$ are listed in Table II. The intercept $(\bar{n})_0 = 0.5358$ at $\bar{h} = 0$ leads to a value of $(\bar{n})_0 = 1.87$, in good agreement with the value 1.86 calculated from the molecular weight of ceric isopropoxide. Accordingly the proportion of cerium in the (p_2,q_3) series is $\alpha_{II} = 0.928$. The slope $d(\bar{n})^{-1}/d\bar{h} = 0.3608$ is much closer to the figure of -0.3456 calculated (eq. [6]) for the (p_1,q_2) series than the -0.3334 calculated for the (p_1,q_3) series. It appears from these calculations that the ceric oxide isopropoxides resemble the stannic oxide isopropoxides in conforming to a mixture of the regular polymer series' (p_2,q_3) and (p_1,q_2).

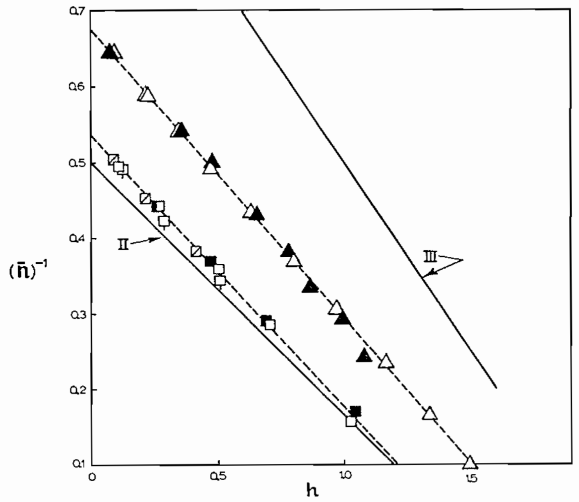

FIG. 2. The variation of $\bar{n}$ with $\bar{h}$ for the hydrolysis of ceric isopropoxide and uranium pentaethoxide: □, data from Table IIA; ■, data from Table IIB; ⊠, data from Table IIC; ◻, data from Table IID; △, data from Table IIIA; ▲, data from Table IIIB. Curve II, $\bar{n} = 6/(3-2\bar{h})$; Curve III, $\bar{n} = 2/(2-\bar{h})$.

Uranium (V) Oxide Ethoxides

Although uranium pentaethoxide is practically dimeric in boiling benzene its molecular weight in boiling ethanol ($\bar{n} = 1.48$) suggests that a considerable proportion of monomeric species is present in the alcohol, no doubt due to solvation to $U(OEt)_5,EtOH$. This is extremely interesting because the two previously discussed alkoxides were predominantly dimeric and a quantitative distinction between the alternative series (p_1,q_2) and (p_1,q_3) was not favored. However, with the larger proportion of monomer species in the uranium pentaethoxide, discrimination between the alternative series should be facilitated. The plot of $\bar{n}$ versus $\bar{h}$ in Fig. 2 for the uranium oxide ethoxides appears to follow a path almost midway between curves II and III. The least-squares fit for the 20 points between $\bar{h} = 0$ to 1.500 was in accordance with the equation $(\bar{n})^{-1} = 0.6755-0.3841\bar{h}$, with a coefficient of variation $\sigma_n = \pm 3.2\%$ and 10 changes of sign in $\delta\bar{n}$ ($\bar{n}_{\text{calc}}$ values are listed in Table III). A major portion of the errors in $\bar{n}$ occurred for the highest four values of $\bar{h}$. Thus, $\sigma_n = \pm 1.4\%$ for the first 16 points ($h = 0$ to 0.992) and there are 9 changes of sign. From the intercept $(\bar{n})_0^{-1} = 0.6755$ ($\bar{h} = 0$), the value of $(\bar{n})_0 = 1.48$ was calculated in exact agreement with the value determined from the molecular weight of the pentaethoxide. The low value of $\alpha_{\text{II}} = 0.649$, calculated from $(\bar{n})_0$, predicts a slope $d(\bar{n})^{-1}/d\bar{h} = 0.3919$ if series (p_1,q_2) is present with (p_2,q_3) and this is close to the least-squares slope of -0.3841. The results thus point unambiguously to the presence of the (p_1,q_2) series and the absence of the alternative (p_1,q_3).

It should be noted that the theory is not confined to metal oxide alkoxide systems but is applicable to any system involving regular polymer series as defined in the text. For example, it is evident that the formation of linear polydialkylsiloxanes by hydrolysis and condensation of dialkyldialkoxysilanes should conform to the requirements of the theory since (p_1,q_1) series will be formed. In this particular system the "central" atom (silicon) of the monomer has a coordination number which is the same as its group valency.

CONCLUSIONS

A general theory to account for the number-average degree of polymerization of metal oxide alkoxides has been formulated mathematically. In addition to explaining the properties of some oxide alkoxides of titanium, zirconium, and tantalum reported earlier, the theory also provides a rational interpretation of some oxide alkoxides of tin, cerium, and uranium. A characteristic feature of the metal oxide alkoxide polymers, namely the formation of relatively low polymers, appears to be a logical consequence of the theory.

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