

### 313. *Metal Oxide Trialkylsilyloxyde Polymers. Part II.<sup>1</sup> Zirconium Oxide Trimethylsilyloxyde Polymers.*

By D. C. BRADLEY and C. PREVEDOROU-DEMAs.

The partial hydrolysis of tetrakis(trimethylsilyloxy)zirconium in dioxan solution has been studied. Solid polymeric zirconium oxide trimethylsilyloxides,  $[\text{ZrO}_x(\text{O}\cdot\text{SiMe}_3)_{(4-2x)}]_n$ , which were soluble in organic solvents, were obtained. The variation of the number average degree of polymerization,  $n$ , as a function of the degree of hydrolysis,  $x$ , was analysed in terms of structural models. At  $150^\circ$  *in vacuo*, the polymers disproportionated to tetrakis(trimethylsilyloxy)zirconium and more highly condensed polymers  $[\text{ZrO}_y(\text{O}\cdot\text{SiMe}_3)_{(4-2y)}]_m$ , where  $y > x$ , and  $m > n$ .

PREVIOUSLY,<sup>1</sup> we reported on the limited hydrolysis of tetrakis(trimethylsilyloxy)titanium in dioxan. The initial products of hydrolysis underwent facile disproportionation, forming highly condensed but relatively low polymeric products,  $\text{Ti}_8\text{O}_{12}(\text{O}\cdot\text{SiMe}_3)_8$ , etc. Structures were proposed for these polymers involving 4-co-ordinated titanium, in contrast to the 6-co-ordination invoked for titanium oxide alkoxide polymers.<sup>2,3</sup> We now report on the hydrolysis, under similar conditions, of tetrakis(trimethylsilyloxy)zirconium.

#### RESULTS AND DISCUSSION

In Table 1 are summarized the data on zirconium oxide trimethylsilyloxides  $[\text{ZrO}_x(\text{OSiMe}_3)_{(4-2x)}]_n$  obtained by the room-temperature hydrolysis of tetrakis(trimethylsilyloxy)zirconium in dioxan (for conditions see Experimental section). The values of  $x$  were deduced from the zirconium and silicon analyses and those of  $n$ , the number average

<sup>1</sup> Part I, Bradley and Prevedorou-Demas, *Canad. J. Chem.*, 1963, **41**, 629.

<sup>2</sup> Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.

<sup>3</sup> Bradley, Gaze, and Wardlaw, *J.*, 1957, 469.

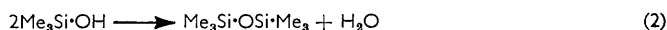
TABLE 1.

Zirconium oxide trimethylsilyloxyde polymers.

Initial products of hydrolysis			Residues from thermal disproportionation					
<i>h</i>	<i>x</i>	Mol. wt.	Degree of polymerization ( <i>n</i> )		<i>y</i>	Mol. wt.	Degree of polymerization ( <i>m</i> )	
			Found	Calc.			Found	Calc.
<i>0.00</i>	<i>0.000</i>	<i>916</i>	<i>2.05</i>	—	—	—	—	—
0.10	0.126	1016	2.39	2.31	1.486	2800	13.75	13.51
0.20	0.236	994	2.37	2.56	1.500	3044	15.20	15.38
0.30	0.320	1150	2.85	2.79	1.505	3457	17.34	16.13
0.40	0.478	1057	2.86	3.36	1.507	3778	18.80	16.56
0.50	0.518	1344	3.70	3.53	1.533	4025	20.69	22.73
0.75	0.617	1505	4.24	4.08	1.541	4839	24.93	25.64
1.00	0.675	1850	5.46	4.48	1.560	4130	26.97	—
1.33	0.948	2214	7.43	8.40	1.584	7615	40.69	—
2.00	1.107	2727	10.16	—	1.611	9511	51.16	—
2.50	1.221	2830	10.88	—	1.619	partially soluble	—	—
3.00	1.377	2790	12.36	—	1.632	insoluble	—	—

degree of polymerization, were calculated from the molecular weights, determined cryoscopically in cyclohexane. The molar proportion of water to tetrakis(trimethylsilyloxy)zirconium monomer in each experiment is designated by *h*. The data on the tetrakis-compound (in italics) are taken from ref. 4.

It is noteworthy that for *h* = 0.1—0.5, *x* > *h*, evidently due to additional hydrolysis resulting from some condensation of trimethylsilanol:



The silanol condensation is acid-catalysed, and in this system the tetrakis(trimethylsilyloxy)zirconium, which tends to form co-ordination polymers, would be a weak Lewis acid. For *h* = 0.75—3.00, *h* > *x* and the hydrolysis is incomplete as was also found in the hydrolysis of the titanium compound. This behaviour could be due to increasing resistance to hydrolysis as *x* is increased, or to reversibility of the system, or both. Moreover, it is possible that the zirconium oxide trimethylsilyloxyde polymers do not effectively catalyse the condensation of the silanol and the Lewis-acid character of zirconium is reduced when Zr-O-SiMe<sub>3</sub> groups are replaced by Zr-O-Zr groups.

Heating the initial zirconium polymers at 150°/0.1 mm. caused disproportionation to the volatile tetrakis-compound and the non-volatile, more highly condensed zirconium oxide trimethylsilyloxyde polymers  $[\text{ZrO}_y(\text{O}\cdot\text{SiMe}_3)_{(4-2y)}]_m$ . Some data on these products are presented in Table 1.

It is interesting to note that the degree of hydrolysis in the initial polymers, *x* = 0.126—1.377, covered a much wider range than in the final polymers, *y* = 1.486—1.632. It suggests that for *y* > ~1.45, further rearrangement of the polymer becomes difficult although the number average degree of polymerization, *m*, is not very high and the products are soluble in cyclohexane. Insoluble polymers were obtained when *y* > ~1.6.

Previous results with polymeric metal oxide alkoxides<sup>2-9</sup> were interpreted in terms of certain structural models. Bradley and Holloway<sup>9</sup> derived a mathematical approach to polymeric systems which conformed to their definition of regular polymer series. Each species in a regular polymer series contains the same repeating unit involving *p* metal atoms, and each repeating unit is bonded to an adjacent unit by *q* M-O-M bridges. It

<sup>4</sup> Bradley and Thomas, *J.*, 1959, 3404.

<sup>5</sup> Bradley and Carter, *Canad. J. Chem.*, 1961, **39**, 1434.

<sup>6</sup> Bradley and Holloway, *Canad. J. Chem.*, 1961, **39**, 1818.

<sup>7</sup> Bradley and Carter, *Canad. J. Chem.*, 1962, **40**, 15.

<sup>8</sup> Bradley and Holloway, *Canad. J. Chem.*, 1962, **40**, 62.

<sup>9</sup> Bradley and Holloway, *Canad. J. Chem.*, 1962, **40**, 1176.

then follows that the number average degree of polymerization,  $n$ , is related to the degree of hydrolysis or condensation,  $x$ , by the equation  $(n)^{-1} = p^{-1} - q^{-1}(x)$ , and for a given value of  $x$  the value of  $n$  is independent of the distribution of polymer sizes. Thus, it is possible to deduce structural information from the experimentally determined degree of polymerization as a function of the degree of hydrolysis if the system involves a regular polymer series. The results for  $x = 0.126-0.948$  in Table 1 gave a straight line

$$(n)^{-1} = 0.480 - 0.381(x), \quad (3)$$

suggesting a regular polymer series. Extrapolation to  $(n)_0$  for  $(x) = 0$  gave  $(n)_0 = 2.08$ , in agreement with the experimental value of 2.05 for  $Zr(O\cdot SiMe_3)_4$ . The non-integral values of  $p$  and  $q$ , calculated from eqn. (3), suggested that more than one regular polymer series was present. Bradley and Holloway<sup>9</sup> showed that, for a system containing a proportion,  $\alpha$ , of the metal in the regular polymer series  $(p_a, q_r)$  (*i.e.*,  $p = a$ ;  $q = r$ ) and the remaining  $(1 - \alpha)$  in another series  $(p_b, q_s)$ , the relationship between  $(n)^{-1}$  and  $(x)$  should be:

$$(n)^{-1} = [\alpha p_a^{-1} + (1 - \alpha)p_b^{-1}] - [\alpha q_r^{-1} + (1 - \alpha)q_s^{-1}](x).$$

Hence,  $\alpha$  may be calculated from the intercept  $(n)_0^{-1}$  at  $x = 0$  and cross-checked against the value determined from the slope  $d(n)^{-1}/d(x)$ . Inspection shows that the experimentally determined equation [eqn. (3)] is near to that for a  $(p_3, q_4)$  regular polymer series based on a trimeric repeating unit containing octahedral zirconium and with four Zr-O-Zr bridges between adjacent units. A section of a  $(p_3, q_4)$  polymer is shown in Fig. 1. Combinations of the  $(p_3, q_4)$  series with other feasible series were investigated and only one combination gave agreement with the results. The second series was one of the two which explained the behaviour of the titanium oxide trimethylsilyloxides.<sup>1</sup> It is based on the octamer  $Ti_8O_{12}(O\cdot SiMe_3)_8$  (Fig. 2) as the repeating unit, with one Ti-O-Ti group between adjacent octamers and  $(n)^{-1} = 0.125 - 1.00(x - 1.50)$ . From the intercept  $(n)_0^{-1}$  at  $x = 0$  of the experimental line, the value of  $\alpha$ , the proportion of metal in the  $(p_3, q_4)$  series, is 0.887. By the use of this value of  $\alpha$ , the slope  $d(n)^{-1}/dx$  is calculated to be  $-0.335$ , comparing favourably with the experimental value of  $-0.381$ . In Table 1 the values of  $(n)_{calc.}$  were obtained by substituting experimental values of  $(x)$  in eqn. (3). The coefficient of variation for  $(n)$  was  $\sigma = \pm 11\%$ , which is reasonable considering the possible errors in determining  $(x)$  and  $(n)$ . The data on the initial polymers are thus consistent with about 90% of the zirconium adopting the  $(p_3, q_4)$  regular polymer series with octahedral co-ordination, in marked contrast to the behaviour of the titanium oxide trimethylsilyloxide polymers. At the higher degrees of hydrolysis,  $(x) = 1.107-1.377$ , the observed values of  $(n)$  are much smaller than  $(n)_{calc.}$  and suggest that the proportion of the second regular polymer series, based on  $Zr_8O_{12}(O\cdot SiMe_3)_8$  as the repeating unit, is increasing.

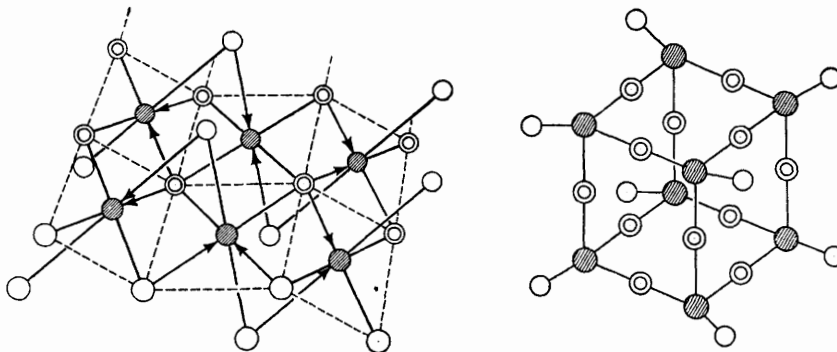
When the data in Table 1 for the final polymers were similarly treated, the values for  $(y) = 1.486-1.541$  gave a straight line

$$(m)^{-1} = 1.025 - 0.64(y) \quad (4)$$

Assuming the same two regular polymer series to be present as was suggested for the initial polymers, the new equation gave, from the intercept  $(m)_0$  at  $(y) = 0$ , the value  $\alpha = 0.465$ . From this value of  $\alpha$ , the slope  $d(m)^{-1}/d(y)$  was calculated to be  $-0.65$ , in excellent agreement with the observed slope of  $-0.64$ . Values of  $(m)_{calc.}$  are listed in Table 1, and the coefficient of variation for  $(m)$  was  $\sigma = \pm 7.5\%$ . Solving by extrapolation for  $(y)_\infty$  at  $(m)^{-1} = 0$  gave the value  $(y)_\infty = 1.6$  for the formation of infinite polymers, and it was observed that products with  $(y) > \sim 1.6$  were insoluble, which seems reasonable on the basis of their being infinite polymers.

We conclude that the zirconium oxide trimethylsilyloxides conform to two regular polymer series, one based on trimeric repeating units containing octahedral zirconium and the other based on a highly condensed octamer,  $Zr_8O_{12}(O\cdot SiMe_3)_8$ , containing

4-co-ordinated zirconium. The initial products of hydrolysis contain predominantly, (90% of Zr) the octahedral species, but thermal disproportionation produces a more highly condensed polymer with a lower proportion (*ca.* 50% of Zr) of octahedral zirconium. This suggests that the  $(p_3, q_4)$  regular polymers preferentially undergo thermal disproportionation, and this seems reasonable when the structures (Figs. 1 and 2) are compared. The formation of volatile tetrakis(trimethylsilyloxy)zirconium requires certain zirconium atoms to acquire exclusive primary bonding to four trimethylsilyloxy-groups. This appears to be almost impossible for the polymers based on the octamer repeating units, because no zirconium atom in this species is bonded to more than one trimethylsilyloxy-group and each is bonded to three oxygen atoms in Zr-O-Zr groups. Inspection of the  $(p_3, q_4)$  polymers reveals that each "end" of the molecule contains two zirconium atoms bonded to four trimethylsilyloxy-groups, of which two are terminal and two



- Zr    ○ Oxygen in Zr·O·Zr groups  
 ○ Oxygen in Zr·O·SiMe<sub>3</sub> groups (Me<sub>3</sub>Si groups omitted)

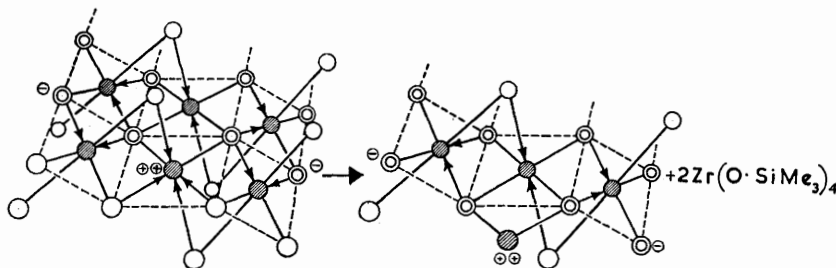
FIG. 1.

FIG. 2.

FIG. 1. Section of a  $(p_3, q_4)$  polymer  $[\text{Zr}_{3(z+1)}\text{O}_{4z}(\text{OSiMe}_3)_{4(z+3)}]$ , where  $z = 0, 1, 2, 3, \dots$

FIG. 2. The octamer  $\text{Zr}_8\text{O}_{12}(\text{O-SiMe}_3)_8$ .

bridging, and only two oxide oxygen atoms, of which one bridges two zirconium atoms and the other bridges four. Assuming that Zr-O-SiMe<sub>3</sub> bonds are shorter and stronger than Zr ← O(Zr)·SiMe<sub>3</sub> bonds, it is clear that only a slight electronic rearrangement is required to give an external zirconium atom four strong primary bonds to trimethylsilyloxy-groups and only two weak co-ordinate bonds to oxide oxygen atoms (Fig. 3). It



- Zr    ○ Oxygen in Zr·O·Zr groups  
 ○ Oxygen in Zr·O·SiMe<sub>3</sub> groups (Me<sub>3</sub>Si groups omitted)

FIG. 3. Disproportionation of a  $(p_3, q_4)$  polymer.

is thus entirely feasible that, at higher temperatures, such a zirconium atom should dissociate out of the polymer as the volatile tetrakis(trimethylsilyloxy)zirconium.

## EXPERIMENTAL

Tetrakis(trimethylsilyloxy)zirconium was synthesized by Bradley and Thomas's method<sup>4</sup> and purified by vacuum sublimation. Dioxan was refluxed over sodium for several hours and fractionally distilled. Cyclohexane was fractionally distilled and dried over "molecular sieve" reagent. Molecular weights were determined cryoscopically in a Beckman apparatus modified to exclude atmospheric moisture. Products were analysed for zirconium and silicon by the previously described methods.<sup>4</sup>

*Hydrolysis of Tetrakis(trimethylsilyloxy)zirconium.*—Aqueous dioxan [25 c.c. (containing 0.0100—0.300 g. H<sub>2</sub>O)] was added, with stirring, to tetrakis(trimethylsilyloxy)zirconium (2.00—

TABLE 2.  
Zirconium oxide trimethylsilyloxyde polymers.

$x$	Zr (%)		Si (%)		$y$	Zr (%)		Si (%)	
	Found	Calc.	Found	Calc.		Found	Calc.	Found	Calc.
0.126	21.47	21.34	24.8	24.65	1.486	44.7	44.1	14.2	14.0
0.236	21.77	22.27	23.7	24.2	1.500	45.5	44.6	14.0	13.75
0.320	22.64	23.03	23.4	23.85	1.505	45.9	44.8	14.0	13.65
0.478	24.74	24.63	23.2	23.1	1.507	45.4	44.9	13.8	13.65
0.518	25.00	25.07	22.85	22.9	1.533	46.9	45.85	13.5	13.2
0.617	25.70	26.20	21.9	22.35	1.541	47.0	46.15	13.3	13.05
0.675	27.03	26.96	22.1	22.0	1.560	47.95	46.85	13.0	12.7
0.948	30.60	31.04	19.85	20.1	1.584	48.75	47.8	12.5	12.25
1.107	33.98	34.01	18.7	18.7	1.611	49.1	48.95	11.75	11.75
1.221	35.09	36.53	16.85	17.55	1.619	50.2	49.3	11.8	11.6
1.377	40.40	40.65	15.5	15.6	1.632	51.15	49.9	11.6	11.3

2.50 g.) in dioxan (25 c.c.) at *ca.* 23°. After standing for 30 min., the solution was evaporated rapidly under reduced pressure, leaving a white powder,  $[\text{ZrO}_x(\text{O}\cdot\text{SiMe}_3)_{(4-2x)}]_n$ , which was soluble in cyclohexane, benzene, or carbon disulphide. This product was analysed for silicon and zirconium, and its molecular weight was determined cryoscopically in cyclohexane. No concentration-dependence of molecular weight was found. The product was then heated at 0.1 mm. and, at a bath temperature of *ca.* 110°, a sublimate appeared. The bath temperature was raised to 150° and the experiment was continued until no more sublimate appeared (about 5 hr.). Analysis confirmed that the sublimate was tetrakis(trimethylsilyloxy)zirconium. The non-volatile residue,  $[\text{ZrO}_y(\text{O}\cdot\text{SiMe}_3)_{(4-2y)}]_m$ , was a white powder, soluble, except for the more highly condensed materials, in benzene, cyclohexane, or carbon disulphide. Since all the experiments were carried out in the same manner, the relevant analytical details are given in Table 2.

We thank the Defence Research Board of Canada for generous financial support.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WESTERN ONTARIO,  
LONDON, ONTARIO, CANADA.

[Received, September 2nd, 1963.]