202. *Parachors and Molecular Structure of Some Metal Alkoxides.*

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The densities and surface tensions of several alkoxides of titanium, zirconium, tin, cerium, and thorium have been measured over the temperature range 25—40° and the parachors have been calculated. Analysis of the parachors by the method used for alkyl orthogermanates [1] revealed some characteristic structural features. Parachor " contractions " in titanium *n*-alkoxides are consistent with the polymeric nature of these compounds and, in the monomeric tertiary alkoxides of titanium, zirconium, tin, cerium or thorium, suggest the presence of considerable intramolecular congestion accentuated by metal–oxygen bond contraction.

Recently [1] we reported the molar volumes and parachors of a representative range of alkyl orthogermanates and demonstrated the use of the parachor in the conformational analysis of molecules of that type. These monomeric germanium compounds were chosen as representative of the type $M(OR)_4$ containing the central atom M tetrahedrally bonded to oxygen because they were free from the complications of strong intermolecular bonding involving the metal and oxygen. We now report the results obtained with a number of liquid metal alkoxides with M = Ti, Zr, Ce^{IV}, Sn^{IV}, or Th over the temperature range 25—40°. Since the vapour pressures of these compounds are negligible in this region the parachor $[P]$ was calculated by using the simple equation $[P] = \gamma^{\frac{1}{4}}V$, where γ is the surface tension and V the molar volume. We have analysed these parachors by Gibling's method. This involves, first, subtraction of the expansion correction (E.C.) interpolated from Gibling's Table [2] to give the reduced parachor (R.P.). Next the sum of the reduced group parachors for the alkyl groups ($\sum$R.P. Alkyls) was calculated by using the following values: $CH_3(C) = 55{\cdot}2$; $(C)CH_2(C) = 39{\cdot}8$; $(C)CH_2(O) = 39{\cdot}3$; $(C)_2CH(C) = 22{\cdot}2$; $(C)_2CH(O) = 21{\cdot}2$; $(C)_2C(C)_2 = 2{\cdot}4$; and $(C)_3C(O) = 0{\cdot}9$. The reduced parachor for the pentatomic group of metal and four oxygen atoms was then obtained from the equation, R.P. $M(O_4)$ = R.P. − $\sum$R.P. Alkyls. In this procedure no assumptions are made concerning parachor values either for the metal or for oxygen attached to metal. It is clear that in the absence of volume anomalies the value of R.P.MO_4 should be constant for a given metal irrespective of the alkyl group. The results are given in Table 1 in which $[P]$ is the average parachor over the temperature range studied.

Table 1.

$M(OR)_4$		$[P]$	E.C.	R.P.	$\sum$R.P. Alkyls	R.P.$M(O_4)$
M	R					
Ti	Et	454	2·0	452	378·0	74
,,	Pr^n	616	3·7	612	537·2	75
,,	Bu^n	769	5·8	763	696·4	67
,,	Bu^t	844·5	7·0	837	666·0	171
,,	CMe_2Et	989	9·8	979	825·2	154
,,	CMe_2Pr^n	1154·5	13·3	1141	984·4	157
,,	$CMeEt_2$	1120·5	12·5	1108	984·4	124
Zr	Bu^t	851·5	7·0	844	666·0	178
,,	CMe_2Et	992	9·8	982	825·2	157
,,	CMe_2Pr^n	1154·5	13·3	1141	984·4	157
,,	$CMeEt_2$	1121	12·5	1109	984·4	125
Sn^{IV}	CMe_2Et	919·5	8·4	911	825·2	86
,,	CMe_2Pr^n	1088	11·8	1076	984·4	92
Ce^{IV}	$CMeEt_2$	1130·5	12·7	1118	984·4	134
,,	CEt_3	1269	16·1	1253	1143·6	109
Th	CEt_3	1231·5	15·2	1216	1143·6	72

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[1] Bradley, Kay, and Wardlaw, *J.*, 1956, 4916.

[2] Gibling, *J.*, 1941, 299.

We consider first the values of the reduced parachor for the group $Ti(O)_4$. The most striking feature is the enormous difference between values for the *n*-alkoxides and *tert.*-alkoxides. This is undoubtedly a consequence of the polymeric nature of the *n*-alkoxides compared with the monomeric *tert.*-alkoxides. For example, it has been shown that titanium tetraethoxide approaches a limiting trimeric state in either benzene [3] or ethanolic [4] solutions and it is probable that the liquid ethoxide consists mainly of trimeric molecules. Further, it has been suggested [3,4] that the trimeric ethoxide contains titanium 6-co-ordinated by oxygen in approximately octahedral configuration and it is evident that the formation of such a trimer leads to a considerable loss of volume relative to that of the monomer. The value of R.P.$Ti(O)_4$ is not constant for the *n*-alkoxides but is in the order: *n*-propyl > ethyl > *n*-butyl. The appearance of a maximum value of R.P.$Ti(O)_4$ in the *n*-propoxide is consistent with the operation of two structural phenomena in the titanium *n*-alkoxides, as was previously suggested to explain trends in the entropies of vaporisation.[6] Thus it has been shown by molecular-weight determinations that the degree of polymerisation in titanium *n*-alkoxides decreases with increase in length of alkyl chain [3, 5, 6] and this should cause a variation in R.P.$Ti(O)_4$ in the order: *n*-butyl > *n*-propyl > ethyl. On the other hand it was suggested [6] that in ascending the homologous series another type of interaction involving the *n*-alkyl chains becomes increasingly important. This alkyl interaction which we visualised as an intermolecular " entanglement " of the alkyl chains will cause a volume loss leading to a variation in R.P.$Ti(O)_4$ in the order: ethyl > *n*-propyl > *n*-butyl, and it is the simultaneous operation of these two opposed structural effects which results in the *n*-propoxide's having the maximum value of R.P.$Ti(O)_4$ and the minimum entropy of vaporisation.

A second notable feature of the results on titanium alkoxides is the pronounced decrease in R.P.$Ti(O)_4$ with the increased branching of the alkyl group in the *tert.*-alkoxides. This effect is also clearly apparent in the values of R.P.$Zr(O)_4$ for zirconium *tert.*-alkoxides and in R.P.$Ce^{IV}(O)_4$ for the two cerium compounds. Moreover a similar effect of chain branching was observed in the alkyl orthogermanates [1] and it is evidently a consequence of a fundamental structural feature of this type of molecule. Previously [1] we showed that this effect was caused by intramolecular congestion which by virtue of the overlap of van der Waals volumes of some of the atoms led to an effective loss of volume. This was confirmed by measurements on molecular models which showed qualitative agreement between volume losses calculated for conformations of minimum intramolecular congestion and the observed parachor losses. Similarly, in the series $M(O{\cdot}CMe_xEt_{3-x})_4$ where $M = Ti$ or Zr and $x = 3, 2,$ or 1, the value of R.P.$M(O)_4$ decreases sharply as x decreases. It is particularly noteworthy that the derivatives of 2-methylpentan-2-ol have values of R.P.$M(O)_4$ greater than those of the derivatives of the isomeric 3-methylpentan-3-ol. In fact the derivatives of the former alcohol gave values equal to, or slightly higher than, those of *tert.*-amyl alcohol. This behaviour agrees with the predictions of conformational analysis, it being assumed that the molecules are predominantly in the conformations of minimum intramolecular congestion (see ref. 1 for illustrations of these conformations for *tert.*-butyl and *tert.*-amyl orthogermanates). Thus in converting the *tert.*-amyloxide into the derivative of 2-methylpentan-2-ol the molecule is extended at peripheral positions and no additional volume loss is involved, whereas in the formation of the derivative of 3-methylpentan-3-ol there is more intramolecular congestion.

A third notable feature of Table 1 is revealed in a comparison of values of R.P.$M(O)_4$ in a series of alkoxides containing the same alkyl group but different metals. In terms of purely stereochemical factors it would be predicted that volume losses due to intramolecular congestion in the tertiary alkoxides should decrease with increase in size of

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[3] Caughlan, Smith, Katz, Hodgson, and Crowe, *J. Amer. Chem. Soc.*, 1951, **73**, 5652.

[4] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.

[5] Cullinane, Chard, Price, Millward, and Langlois, *J. Appl. Chem.*, 1951, **1**, 400.

[6] Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025.

the central atom and that for a given alkyl group the value of R.P.M$(O)_4$ should depend on the atomic radius of M. Hence we should expect the R.P. order: $Th(O)_4 > Ce^{IV}(O)_4 > Zr(O)_4 > Sn^{IV}(O)_4 > Ti(O)_4$. This is clearly not the case because our results show $Ti(O)_4 \gg Sn^{IV}(O)_4$, and $Ce^{IV}(O)_4 > Th(O)_4$, while $Ti(O)_4$ is almost as large as $Zr(O)_4$. In view of the results on titanium *n*-alkoxides which showed the striking effect of polymerisation it could be argued that, contrary to the apparent monomeric nature of the *tert.*-alkoxides in solution, they might not be exactly monomeric in the liquid state and that a small degree of polymerisation would explain these anomalies. However there are two reasons for rejecting such an argument. First, the degree of polymerisation for a given metal would decrease with increase in branching of the alkyl group and this would cause an increase in R.P.M$(O)_4$ instead of the observed decrease. Secondly, the monomeric nature of several of these *tert.*-alkoxides is confirmed by data on vapour pressures and entropies of vaporisation. It appears that electronic factors must also be considered and it seems reasonable to suggest that the M–O bonds are thus shortened so that the covalent atomic radii are not applicable. In particular it is considered that intramolecular covalency expansion occurs in the form of double bonding $^{-}M{=}O^{+}R$ and that this is stabilised by electron release from the *tert.*-alkyl group. The extent of partial double bonding will vary according to the metal involved, but at present there is a dearth of reliable data on interatomic distances for these molecules and it would be unwise to speculate further on this aspect. It is of interest to apply Gibling's method to the problem of the " anomalies " found by Mann and Purdie [7] in the parachors of some complexes of palladous chloride. We offer the following interpretation of Mann and Purdie's results. We have treated their data in the same manner as for the metal alkoxides, using the same values for reduced group parachors. In the case of *trans*-bis(dialkyl sulphide) palladous chlorides the reduced group parachor for the pentatomic system $[S_2PdCl_2]$ was calculated by using $(C)CH_2(S) = 39{\cdot}3$ and $CH_3(S) = 54{\cdot}7$. For the trialkylphosphine complexes the reduced group parachor for $[\{(CH_2)_3P\}_2PdCl_2]$ was deduced because the value for $(C)CH_2(P)$ has not been determined. Similarly for the trialkylarsine complexes the value for $[\{(CH_2)_3As\}_2PdCl_2]$ was calculated. These results are given in Table 2.

TABLE 2.

	trans-$(R_2S)_2PdCl_2$			*trans*-$(R_3P)_2PdCl_2$			*trans*-$(R_3As)_2PdCl_2$		
R	[*P*]	$[S_2PdCl_2]$	Δ	[*P*]	$[\{(CH_2)_3P\}_2PdCl_2]$	Δ'	[*P*]	$[\{(CH_2)_3As\}PdCl_2]$	Δ'
Me	463	242	0	—	—	—	—	—	—
Et	613	231	−11	775	438	0	793	456	0
Pr^n	760	217	−25	994	414	−24	1014	434	−22
Bu^n	906	198	−44	1217	393	−45	1243	419	−37
Bu^i	914	218	−24	—	—	—	—	—	—
n-C_5H_{11} ...	1054	187	−55	1452	383	−55	1467	398	−58

These results show clearly for each type of compound that there is a parachor contraction between each homologue in ascending the *n*-alkyl series. This is shown by the increments Δ or Δ'. We are convinced that this is a genuine structural phenomenon caused by the alignment of the *n*-alkyl chains and that it is not due to the fact that the central atom is a metal. The same behaviour is shown by *n*-alkyl orthocarbonates and orthosilicates (Arbusov and Vinogradova [8]); and for dialkyl carbonates, malonates, sulphates, and sulphites, and for trialkyl phosphates and phosphites Gibling [9] has observed similar effects in the *n*-alkyl derivatives. It appears that *n*-alkyl chains radiating from a central atom or group tend to align themselves in parallel so that they sweep out a smaller van der Waals volume than in the pure hydrocarbon. We discussed this in terms of models for the *n*-alkyl germanates [1] and showed that reasonable agreement was obtained between observed and calculated molar volumes. Returning to Mann and Purdie's compounds we

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[7] Mann and Purdie, *J.*, 1935, 1549.

[8] Arbusov and Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, 1948, **60**, 799.

[9] Gibling, *J.*, 1941, 304; 1944, 383.

find strong support for our views in the behaviour of *trans*-bis(di*iso*butyl sulphide) palladous chloride which has a much smaller Δ than the *n*-butyl isomer. This is because the *iso*butyl groups can only align themselves to the same degree as *n*-propyl groups, a view confirmed by the Δ value for the *n*-propyl derivative which is practically the same as for the *iso*butyl derivative. Mann and Purdie [7] also determined parachors for a number of *n*-alkylthiomercury compounds and we have deduced the corresponding values of $[S_2Hg]$ (Table 3). Again there is a contraction between each homologue, and the increment Δ becomes more negative in ascending the series. However, the increment Δ′ between succeeding members shows an alternating magnitude reminiscent of the alternation found in the *n*-alkyl orthosilicates (see ref. 1). Unfortunately Mann and Purdie did not study this series with branched alkyl groups but we would predict that branching would lead to higher values of $[S_2Hg]$ than for the *n*-alkyl isomers.

TABLE 3.

R in $Hg(SR)_2$	$[P]$	$[S_2Hg]$	Δ	Δ′	R	$[P]$	$[S_2Hg]$	Δ	Δ′
Et	334	144	0	0	n-C_6H_{13}	620	109	−35	−5
Pr^n	402	131	−13	−13	n-C_7H_{15}	692	100	−44	−9
Bu^n	475	125	−19	− 6	n-C_8H_{17}	772	99	−45	−1
n-C_5H_{11}	545	114	−30	−11					

EXPERIMENTAL

Preparation of Metal Alkoxides.—The alkoxides of titanium,[6, 10] zirconium,[6, 10] tin,[11] cerium,[12] and thorium [13] were prepared, purified, and analysed by the methods already described.

Density and Surface-tension Measurements.—An all-glass dilatometer of *ca.* 11 c.c. capacity fitted with two limbs of "Veridia" capillary tubing was used. It differed from that described in the germanium work [1] by having only one standard joint. Since the capillaries (r_1 = 0·0245 cm., r_2 = 0·1246 cm.) differed markedly in bore it was possible to calculate the density and surface tension of the liquid from the same measurement. The cleaning, drying, and weighing technique was similar to that described earlier.[1] The alkoxide was collected in the dilatometer by fractional distillation under 0·05 mm. pressure, in an all-glass apparatus fitted with a variable take-off still-head and a device for taking fractions without interrupting the distillation. At least three separate determinations were carried out over the whole temperature range on each alkoxide. The results are presented in Table 4 in the abbreviated form, involving the appropriate constants d_0, α, γ_0, and β, where d_t (density at $t°$) $= d_0 - \alpha t$, and γ (surface tension at $t°$) $= \gamma_0 - \beta t$.

TABLE 4.

Compound	d_0	α	γ_0	β
$Ti(OEt)_4$	1·1321	0·00102	23·77	0·027
$Ti(OPr^n)_4$	1·0564	0·00086	27·38	0·079
$Ti(OBu^n)_4$	1·0160	0·00081	27·00	0·060
$Ti(OBu^t)_4$	0·9060	0·00090	24·38	0·059
$Ti(O{\cdot}CMe_2Et)_4$	0·9239	0·00076	27·33	0·061
$Ti(O{\cdot}CMe_2Pr^n)_4$	0·9085	0·00075	27·15	0·038
$Ti(O{\cdot}CMeEt_2)_4$	0·9437	0·00069	29·22	0·065
$Zr(OBu^t)_4$	0·9845	0·00110	22·34	0·080
$Zr(O{\cdot}CMe_2Et)_4$	0·9960	0·00093	24·11	0·050
$Zr(O{\cdot}CMe_2Pr^n)_4$	0·9719	0·00082	25·40	0·060
$Zr(O{\cdot}CMeEt_2)_4$	1·0092	0·00081	25·79	0·042
$Sn(O{\cdot}CMe_2Et)_4$	1·1229	0·00098	23·26	0·061
$Sn(O{\cdot}CMe_2Pr^n)_4$	1·0724	0·00090	23·52	0·042
$Ce(O{\cdot}CMeEt_2)_4$	1·1064	0·00114	24·55	0·011
$Ce(O{\cdot}CEt_3)_4$	1·0879	0·00078	25·83	0·014
$Th(O{\cdot}CEt_3)_4$	1·2505	0·00110	22·61	0·027

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[10] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4204.
[11] Bradley, Caldwell, and Wardlaw, *J.*, 1957, 4775.
[12] Bradley, Chatterjee, and Wardlaw, *J.*, 1957, 2600.
[13] Bradley, Saad, and Wardlaw, *J.*, 1954, 3488.

Parachors.—The values for the parachor at various temperatures are given in Table 5. It is difficult to estimate the probable error in these measurements. Although separate experiments on the same compound gave results which agreed within ~0·2% it is possible, in view of the ease of hydrolysis of these compounds, that the absolute error could be 0·5—1·0%. Apart from titanium *n*-propoxide and zirconium *tert.*-butoxide which gave remarkably constant values, there is a small but general drift towards higher values of the parachor at higher temperatures and this is most marked for the two cerium compounds. For all of the other compounds the variation of parachor with temperature (~0·03% per degree) is much smaller than the variation of molar volume with temperature (~0·1% per degree) and it seems reasonable to choose the average parachor for comparative purposes.

TABLE 5. *Parachors* [*P*].

Compound	25°	30°	35°	40°
$Ti(OEt)_4$	452·1	453·6	454·6	456·3
$Ti(OPr^n)_4$	616·4	616·5	616·4	616·4
$Ti(OBu^n)_4$	767·7	768·3	769·1	770·0
$Ti(OBu^t)_4$	842·0	844·0	845·3	846·7
$Ti(O{\cdot}CMe_2Et)_4$	987·5	988·6	990·0	991·0
$Ti(O{\cdot}CMe_2Pr^n)_4$	1150·5	1153·5	1155·7	1158·7
$Ti(O{\cdot}CMeEt_2)_4$	1119·5	1120·2	1121·2	1121·5
$Zr(OBu^t)_4$	851·0	851·5	852·1	851·3
$Zr(O{\cdot}CMe_2Et)_4$	988·8	990·7	993·2	994·4
$Zr(O{\cdot}CMe_2Pr^n)_4$	1152·5	1153·8	1155·0	1156·8
$Zr(O{\cdot}CMeEt_2)_4$	1118·0	1120·2	1122·2	1125·0
$Sn(O{\cdot}CMe_2Et)_4$	918·2	919·2	920·0	920·9
$Sn(O{\cdot}CMe_2Pr^n)_4$	1085·2	1087·8	1088·5	1091·0
$Ce(O{\cdot}CMeEt_2)_4$	1122·5	1127·5	1133·3	1138·5
$Ce(O{\cdot}CEt_3)_4$	1263·8	1267·3	1270·7	1275·5
$Th(O{\cdot}CEt_3)_4$	1226·8	1230·0	1234·0	1235·2

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