UNIVERSITY OF RAJASTHAN STUDIES

CHEMISTRY

JAIPUR
1964-65

CONTENTS

ALKOXIDES OF METALS AND METALLOIDS

By

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Introduction

The alkoxides, $M(OR)_x$ are derivatives of alcohols (ROH), from which the hydroxylic hydrogen has been replaced by the metal (M). All of these involve $M^{\delta+}-O^{\delta-}-C$ bonds (the strongly electronegative oxygen atom induces considerable polarity). The polarity of the M^+-O^- bond may be partially offset in the cases of some electrophilic metals which undergo covalency expansion by co-ordination with donor (generally oxygen from other alkoxide molecules) atoms. The configuration of the alkyl group has also been found to affect markedly the stereochemistry of the alkoxides.

Methods of preparation :

The method chosen for the preparation of an alkoxide is generally determined by the electropositive character of the metal concerned. The more electropositive metals react spontaneously with alcohols whereas in the case of less electropositive metals or metalloids, the alkoxides are generally prepared by the reactions of their chlorides with alcohols either alone or in the presence of a hydrogen chloride acceptor.

(i) Action of metals on alcohols :

Alkali metals, beryllium, magnesium and aluminium react directly with alcohols (catalysts like iodine or mercuric chloride are required in the latter cases) :

$$M + xROH \rightarrow M(OR)_x + x/_2H_2$$

(ii) Action of oxides on alcohols :

Boron[157], selenyl[102] and vanadyl[143] alkoxides have been prepared in boiling alcoholic solutions from their oxides in the presence of benzene. The water formed is removed azeotropically with benzene :

$$V_2O_5 + 6\ ROH \longrightarrow 2\ VO(OR)_3 + 3\ H_2O$$

(iii) Action of chlorides on alcohols :

As typified by elements of group IV A, the halides show a gradation in their reactivity towards alcohols :

$$SiCl_4 + 4\ C_2H_5OH \longrightarrow Si(OC_2H_5)_4 + 4\ HCl \quad (72)$$

$$TiCl_4 + 3\ C_2H_5OH \longrightarrow TiCl_2(OC_2H_5)_2.C_2H_5OH + 2\ HCl \quad (88)$$

$$2\ ZrCl_4 + 5\ C_2H_5OH \longrightarrow ZrCl_2(OC_2H_5)_2.C_2H_5OH + ZrCl_3(OC_2H_5).C_2H_5OH + 3\ HCl \quad (42)$$

$$ThCl_4 + 4\ C_2H_5OH \longrightarrow ThCl_4.4C_2H_5OH \quad (17)$$

In some cases where the reaction with the alcohol alone is incomplete, the alkoxides can be prepared by carrying out the reaction in the presence of a hydrogen chloride acceptor like ammonia (Ti[131], Zr[19], Ge[21], Hf[20], Fe[16], Sb[82], Ce[23], V[75], Nb[24], Ta[25], U[26] and Pu[27]); pyridine (Ce[24](IV) and Pu[27]); and sodium (Fe[16](III), Sb[71,81], Th[17], Ni[130], U[18], Pr[123] and Nd[124]).

$$MCl_n + n\ C_2H_5OH + n\ NH_3 \longrightarrow M(OR)_n + n\ NH_4Cl \downarrow$$

$$(C_5H_5NH)_2MCl_6 + 6\ NH_3 + 4\ ROH \longrightarrow M(OR)_4 + 6\ NH_4Cl \downarrow + 2\ C_5H_5N$$

$$MCl_n + n\ NaOEt \longrightarrow M(OR)_n + n\ NaCl \downarrow$$

In all these cases, the ammonium (sodium or pyridinium hydro) chloride is precipitated; benzene is sometimes added to facilitate the separation of the insoluble material. In the case of insoluble alkoxides, solubility of lithium methoxide as well as lithium chloride is utilized in a reaction of the type (La[28], Nd[124], Pr[123], and U[77]) :

$$LaCl_3 + 3\ LiOCH_3 \longrightarrow La(OCH_3)_3 \downarrow + LiCl$$

(iv) Alcoholysis reactions :

The interchangeability of alkoxide group in an alkoxide with the lower straight chain alcohols has been found to be facile. This interchange becomes slow with highly branched alcohols in the final stages probably due to steric hindrance and thus mixed alkoxides are obtained. In this method of preparation, speed, reversibility and absence of side reactions play an important part. The reactions are usually carried out in inert solvents like benzene and the liberated lower alcohol (generally ethanol or isopropanol) is franctionated off azeotropically. Bains[6] prepared some alkoxides of aluminium while Bradley[18] *et al* used this method for uranium (V) alkoxides. Mehrotra and co-workers have employed this technique widely for the preparation of alkoxides of a number of elements (B[157], Si[136], Ti[36], Zr[37], Hf[112], V[127], Nb[90], Ta[30], Al[110,111], Sb[100], Pr[123], Nd[124], Sn[79], Se[101], Te[102], and Be[5]).

These authors have pointed out the following advantages of carrying out the reactions in the presence of benzene :

(a) Only a slight excess of higher alcohol is required for completing the reaction.

(b) Ethanol (or isopropanol) produced is removed continuously pushing the reaction to completion. The alcohol which is franctionated azeotropically can be estimated by a simple oxidimetric method and thus at any particular time, the progress of reaction can be checked.

(c) Side reactions like formation of alkyl chloride and water are avoided which lower the yields considerably in cases of branched alcohols.

(d) When a higher boiling alcohol is used, the reaction is carried out at a lower refluxing temperature due to the presence of benzene and thus side reactions are minimised.

(e) The technique has the unique advantage of the possibility of its use in stoichiometric ratios of the reactants ; mixed alkoxides of a number of elements (Ti^{169}, Sn^{79}, $Al^{110,111}$, B^{157}, C^{135}, V^{128}, Sb^{100}, Nb^{90}, Ta^{30}, and Se^{101}) have been successfully prepared.

(f) The oxidising properties of the metals are lowered when they are linked covalently; e. g., vanadyl trichloride will oxidise reactant alcohols much more than vanadyl trialkoxides.

The reactions may be represented, in general, as follows :

$$M(OR)_x + R'OH \longrightarrow \underset{H \cdots\cdots :O-R}{\overset{R'}{\diagdown}\!O:} \longrightarrow M(OR)_{x-1}$$

$$\longrightarrow (R'O)\,M(OR)_{x-1} + ROH$$

(v) Transesterification reactions :

Transesterification reactions have been utilised by Mehrotra and coworkers for preparing alkoxides of a number of metals (Al^{110}, Ti^{109}, Zr^{109}, Hf^{109}, V^{129}, Nb^{93} and Ta^{90}). The reactions can be represented as follows :

$$M(OR)x + x\ CH_3COOR' \rightleftharpoons M(OR')x + x\ CH_3COOR$$

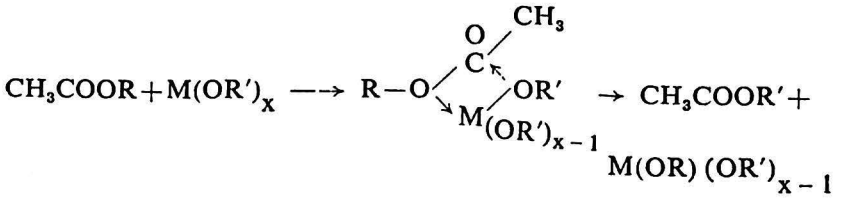
The method is particularly suitable for the preparation of the tertiary butoxide from the isopropoxide derivative as there is a larger boiling point difference between the esters, making fractionation easier. Another advantage appears to be the lower oxidisability of the esters compared to that of the alcohols; this aspect is of particular significance when the central element has oxidative properties like vanadyl.

The transesterification technique has been recently applied[93] in the presence of an inert solvent like cyclohexane which forms an azeotrope (b. p. 71–73°C) with ethyl acetate. This modified method can thus have the additional advantages mentioned for the alcoholysis reactions in the presence of benzene.

Bradley and Thomas[39] have extended the method to the preparation of trialkyl silyl acetate derivatives :

$$M(OR')_x + x\ CH_3COOSiR_3 \rightarrow M(OSiR_3)_x + x\ CH_3COOR'$$

The probable mechanism of these reactions may be indicated as below :



(vi) Other methods :

(a) Alkoxides of uranium (IV)[84] and vanadium (IV)[29] have been prepared by the reactions of their dialkyl amido derivatives with alcohols as given below :

$$U(NEt_2)_4 + 4\ ROH \rightarrow U(OR)_4 + 4\ Et_2NH$$

(b) Alkoxides of titanium[14] and silicon[176] have also been prepared by the action of alcohols on their disulphides.

(c) Zirconium alkoxides[57] have been prepared, recently, by the action of hexanol with its tetra-kis-acetylacetonate in vacuo at about 140°C.

(vii) Preparation of mixed alkoxides :

Mehrotra and co-workers prepared a number of mixed alkoxides of several elements (Al[110], Ti[169], Zr[111], B[157], V[128], Nb[90], Sn[79], Sb[100]

and C[125]) by alcoholysis reactions in stoichiometric quantities of the reactants in the presence of benzene; e. g.,

$Al(OPr^i)_3 + 2\ R^tOH \rightarrow Al\ (OPr^i)\ (OR^t)_2 + 2\ Pr^iOH\ \uparrow$ (removed azeotropically). Bradley and coworkers[38] extended the method to the preparation of mixed alkoxides of niobium and tantalum.

In certain cases (e. g., zirconium tertiary butoxide), the reaction with methanol and ethanol was found to be highly exothermic and the required mixed alkoxides could be prepared directly by mixing the reactants in the stoichiometric ratios as represented by the following equation :

$$Zr(OBu^t)_4 + n\ ROH \rightarrow Zr(OBu^t)_{4-n}\ (OR)_n + n\ Bu^tOH$$

(where R=Me, Et and n = 1 or 2)

Nesemeyanov and Nogina[133] prepared mixed alkoxides of titanium by the following reaction :—

$$TiCl\ (OR)_3 + R'OH + R''_3N \rightarrow Ti\ (OR')\ (OR)_3 + R''_3N.HCl$$

Ghosh *et al*[76] reported mixed alkoxides of titanium containing upto three different alkoxide groups by the following sequence of reactions :—

$$TiCl_2\ (OR)_2 + R'OH + C_5H_5N \rightarrow TiCl\ (OR')\ (OR)_2 + C_5H_5N.HCl$$
$$TiCl\ (OR')\ (OR)_2 + NaOR'' \rightarrow Ti\ (OR'')\ (OR')\ (OR)_2 + NaCl$$

(viii) Double alkoxides :

Uranium aluminium double alkoxides were prepared by Albers and co-workers.[1] These workers distilled them under reduced pressure. Double alkoxide of the type, $U_2Ca(OEt)_{12}$ could be sublimed under reduced pressure. Gilman *et al*[87] titrated uranium pentaethoxide with sodium ethoxide and isolated the double alkoxide of sodium and uranium :

$$NaOEt + U\ (OEt)_5 \rightarrow NaU(OEt)_6$$

Bartley and Wardlaw[10] obtained double alkoxides of zirconium by the action with alkali metal alkoxides; e.g.,

$$2Zr(OR)_4 + MOR \rightarrow MZr_2(OR)_9$$

These double alkoxides were found to be covalent and could be distilled under reduced pressure. Carter[59] titrated titanium alkoxides with sodium alkoxides and obtained $MTi_2(OR)_9$ in contrast to the formula, $KH[Ti\ (OBu)_6]$ suggested by Meerwein and Bersin.[107]

A. PHYSICAL PROPERTIES

I. Polarisation of M–O bond :

The metal alkoxides show a varying degree of ionic character. Sodium alkoxides[85] have been reported to ionise in alcohols whereas aluminium ethoxide[99] has been found to exhibit negligible conductance. The extent of polarisation of M–O bond will of course depend upon the electronegativity of the central element. In the following table are given the calculated ionic characters[142] of the M–O bonds taking the electronegativity value of oxygen as 3.44.

Table I

Element	Electronegativity[2]	% ionic character
Na	0.93	79
Li	0.98	77
Ca	1.00	76
Mg	1.31	67
Be	1.67	60
Al	1.51	56
Sb	1.80	48
Si	1.90	44
Ge	2.01	40

The covalent character of metal oxygen bond will, however, increase with the greater (+I) inductive effect of the alkyl group. The covalent alkoxides (e. g., those of Al, Ti, Zr, Th, Nb and Ta) are generally volatile and are soluble in organic solvents whereas the electrovalent alkoxides (e.g., those of Na, K, Be, Mg, Ca and Ba) are insoluble in inert organic solvents and are non-volatile. However, the methoxides of a number of metals (e g., Al, Ti, Zr) have been shown to be insoluble in common organic solvents. This might be due to the special inductive effect[169] of the methyl group, which brings about this spectacular change in the properties of the methoxide as compared to other alkoxides.

II. General Properties :

(a) Density and Viscosity :

Due to their high susceptibility to hydrolysis which has a pronounced effect on the physical properties like density, viscosity,

surface tension, etc. of the alkoxides, their measurements present considerable experimental difficulties. Only a few attempts have been made to study these properties under rigorously controlled conditions. Cullinane *et al*[65] have reported the viscosities and densities of some titanium alkoxides. A perusal of their results (Table 2) shows that the density of normal alkoxides decreases with the increase of chain length and becomes minimum for the tertiary alkoxide. No such gradation was observed in the values of viscosity.

Table 2

Densities and Viscosities of some Titanium Alkoxides at 25°C.

R in $Ti(OR)_4$	Viscosity, poises	d, g/ml
Et	0.4445	1.1044
Pr^n	1.6135	1.0329
Bu^n	0.6174	0.9932
Am^n	0.7924	0.9735
Hex^n	0.6490	0.9499
Allyl	0.6225	1.1138
Bu^{iso}	0.9740≠	0.9601≠
Bu^t	0.0355	0.8834

≠ measured at 50°C.

A study of these properties for titanium, zirconium, tin, cerium and tin alkoxides was made by Bradley and co-workers [46,47] over a temperature range of 25–40°C and some of their results with molecular volume and parachor are given in table 3. They observed that the monomeric tertiary alkoxides of titanium and zirconium have nearly equal values for density, surface tension and viscosity. However these are considerably lower than the corresponding values for normal alkoxides (*cf.*, Table 3).

Table 3

Densities, Surface Tensions and Viscosities of some Metal Alkoxides at 25°C

Alkoxide	Density, g/ml.	Molecular Volume, cm^3	Surface tension dynes/cm.	Parachor	Viscosity poise.
$Ti(OEt)_4$	1.1066	206.2	23.1	454	0.4469
$Ti(OPr^n)_4$	1.0351	274.6	25.4	616	1.7490
$Ti(OBu^n)_4$	0.9958	341.6	25.5	769	0.6920
$Ti(OBu^t)_4$	0.8836	385.0	22.9	844.5	0.0352
$Ti(OAm^t)_4$	0.9049	438.1	25.8	989	0.0808
$Ti(OCMe_2Pr^n)_4$	0.8883	508.5	26.2	1154.5	0.0479
$Ti(OCMeEt_2)_4$	0.9265	488.5	27.6	1220.5	0.3453
$Zr(OBu^t)_4$	0.9570	400.8	20.3	851.5	0.0317
$Zr(OAm^t)_4$	0.9728	452.1	22.9	992.0	0.0759
$Zr(OCMe_2Pr^n)_4$	0.9514	521.2	23.9	1154.5	0.0464
$Zr(OCMeEt_2)_4$	0.9890	501.5	24.7	1121	0.2810
$Sn(OAm^t)_4$	1.0984	425.4	21.7	919.5	0.1664
$Sn(OCMe_2Pr^n)_4$	1.0499	498.3	22.5	1088.0	0.0986
$Sn(OCMeEt_2)_4$	1.1136	488.5	—	—	0.4127
$Ce(OCMe_2Pr^n)_4$	1.1768	462.2	—	—	8.1343
$Ce(OCMeEt_2)_4$	1.0774	505.6	24.3	1130.5	0.2161
$Ce(OCEt_3)_4$	1.0684	562.5	25.5	1269.0	0.5258
$Th(OCEt_3)_4$	1.2230	566.4	22.0	1231.5	0.4920

Similar detailed measurements for germanium[22] are given in Table 4.

Table 4

Densities, Surface tensions, Molecular Volumes and Parachors of some Germanium Alkoxides at 25°C.

Alkoxide	Density g/ml.	Surface tension dynes/cm.	Molecular volume, ml.	Parachor (P)	(P)/V
$Ge(OMe)_4$	1.3244	22.49	148.5	323.7	2.18
$Ge(OEt)_4$	1.1288	23.23	224.0	491.9	2.20
$Ge(OPr^n)_4$	1.0565	23.61	292.5	644.7	2.20
$Ge(OPr^i)_4$	1.0245	20.76	301.6	643.9	2.13
$Ge(OBu^n)_4$	1.0167	24.00	358.9	794.6	2.21
$Ge(OBu^i)_4$	1.0054	23.25	363.1	797.4	2.20
$Ge(OBu^s)_4$	1.0164	23.47	359.1	790.0	2.20
$Ge(OBu^t)_4$	1.0574	22.74	345.2	754.5	2.19
$Ge(OAm^n)_4$	0.9941	24.18	423.8	939.4	2.22
$Ge(OAm^t)_4$	1.0425	23.39	404.0	888.0	2.20

The values of parachors and reduced parachors given in the table were calculated using Gibling's[76a] method. In order to explain some abnormal deviations from additivity, a few atomic models were set up by these workers and the variations were explained on the basis of volume losses caused by the overlap of van der Waals fields in the preferred conformation.

The available measurements[139,173] on densities and refractive indices of some vanadyl alkoxides are given in table 5.

Table 5

Densities and Refractive Indices of some Vanadyl Alkoxides at 20°C

Alkoxides	Density g/ml.	Refractive Index
$VO(OEt)_3$	1.167	1.5103
$VO(OBu^n)_3$	1.031	1.4898
$VO(OBu^i)_3$	1.030	1.4889

$VO(OCHEtMe)_3$	1.012		1.4823
$VO(OAm^n)_3$	1.005		1.4887
$VO(OAm^i)_3$	0.999	"	1.484

(b) Dipole Moments :

Arbuzov and co-workers[1] determined the dipole moments of a large number of tetra-alkoxides of carbon, silicon and titanium and concluded that the steric hindrance to the free rotation of R–O bonds increases from titanium to silicon to carbon. The theoretical moments calculated by the formula $\mu^2=4m^2\ Sin^2\varphi$ (where m is the O–R bond moment and φ, the oxygen valency angle) depend on the oxygen valency angle and are appreciably affected by the ionic character of Ti–O bond.

In a latter publication, Caughlan *et al*[60] reported the electric moment of ethyl, n-propyl and n-butyl titanates and found them to have the values 1.50, 1.20 and 1.15 D respectively in hexane solution. The electric moments of ethyl orthocarbonate[73] and orthosilicate[156] have ceen reported as 1.10 and 1.70D respectively. However, assuming that the oxygen atoms are arranged around carbon, silicon and titanium (M) atoms in a regular tetrahedron and that the R–O groups are free to rotate about the M–O axis, the equation derived by Eyring[74] gave a value of 2.11D for the theoretical moment of all these alkoxides. Caughlan and co-workers suggested that the low values of the electric moment observed for the titanium compounds might be due to either an increment of the Ti-O-C bond angle, or alternatively, they may be due to restricted rotation of the R–O groups. Similar reasons would probably hold good for the low values for silicon and carbon alkoxides. However, electron diffraction study of silicon methoxide by Yamasaki and coworkers[179] showed that in this compound Si—O and C–O bond lengths are 1.64 ± 0.03 and 1.42 ± 0.04 A° respectively and Si–O–C angle is $113\pm2°$, which is close to the tetrahedral angle 109°28′. These data appear to indicate that at least in the silicon compounds, the low values seem to be mainly due to restricted rotation.

Tikatani [162] has calculated the Ti–O bond refraction for a number of titanium alkoxides by Denbigh's method[70] and has shown that the observed values for molar refractivity are in good agreement to those theoretically calculated except in a few cases like the isopropoxide, tertiary butoxide and tertiary amyloxide.

(c) Infra-Red Studies :

Recently, Wilhoit *et al*[175] studied the infra-red spectra of pure aluminium ethoxide and observed that the spectra of hydrolysed samples depend upon the proportion of aluminium present and the following changes in the spectra were observed with the increase in the degree of hydrolysis.

1. The intensity of all absorption bands except those at 3340 cm^{-1} (O–H stretching vibration) and 935 cm^{-1} (Al–O–Al stretching vibration) decreases.

2. The 3340 cm^{-1} peak becomes sharper, more intense and shifts to slightly higher frequencies.

3. The 935 cm^{-1} peak becomes broader and shifts to a slightly lower frequency.

The absorption frequencies for the Al–O–C vibrations in aluminium alkoxides reported by Guertin *et al*[78] and Bell *et al*[11] are given in the following table.

Table 6

Absorption Frequencies for the Al–O–C vibration in Aluminium Alkoxides

Alkoxide groups	Frequency (cm^{-1})
n–Propoxide	1015
Isopropoxide	1033
n–Butoxide	1048
Sec–Butoxide	1058
Ethoxide	1059
2–Pentoxide	1070

Barraclough *et al*[9] have measured the infra-red spectra of a number of Group IV and V metal alkoxides (e. g., Ti, Zr, Hf, Nb, Ta). The results obtained by these workers are in good agreement to those obtained by previous workers [11,182] for metal isopropoxides. These workers compared the spectra of metal alkoxides with those of corresponding alcohols and assigned the stretching frequencies of M–O and C–O bond for a number of alkoxides. The frequencies assigned for M–O bonds are given in the following table.

Table 7

M-O and C-O stretching frequencies of some Metal Alkoxides with the observed degree of polymerisation

Alkoxide	Degree of polymerisation	Observed frequencies in cm^{-1} C-O	M-O
$Ti(OCHMe_2)_4$	1.4	1005	619
$Zr(OCHMe_2)_4$	3.0	1011	559, 548
$Al(OCHMe_2)_3$	3-4	1036	699, 678, 610, 566, 535
$Ta(OCHMe_2)_5$	1.0	1001	540
$Zr(OCMe_3)_4$	1.0	997	557, 540,
$Hf(OCMe_3)_4$	1.0	990	567, 526
$Ti(OCEt_2Me)_4$	1.0	1011	615, 576
$Zr(OCEt_2Me)_4$	1.0	1010	586, 559, 521
$Ti(OEt)_4$	3.0	1064, 1042	625, 500
$Ta(OEt)_5$	2.0	1072, 1030	556
$Nb(OEt)_5$	2.0	1063, 1029	571

These workers have contradicted the explanation of Guertin *et al*[78] that the bonds at 1000 cm^{-1} in aluminium alkoxides are due to Al-O stretching frequency. They observed that 1000 cm^{-1} is due to C-O stretching in Al-O-C group and assigned five new frequencies for Al-O bond. If aluminium isopropoxide is monomeric, then there can be only three Al-O stretching vibrations but the presence of five bonds clearly indicates the presence of bridging oxygen atoms which are essential for polymerisation.

Infra-red study of methyl (trimer), ethyl and tertiary butyl (monomer) orthotitanates at different concentrations was carried out by Brini-Fritz *et al*[58] in order to evaluate the association of these alkoxides. These workers have assigned a band at 1100 cm^{-1} to the Ti-O...Ti-O association.

Johnson and Fritz[86] have made a study of the infra-red spectra for pure liquid as well as for dilute solutions of some germanium alkoxides in carbon disulphide and observed a strong absorption line near 1040 cm^{-1} and a strong band near 680 cm^{-1} which presumably arise from the vibrational characteristic of the central GeO_4^{-4} configuration.

Siminov and coworkers[153] have reported the infra-red spectra for lithium tertiary butoxide [$LiOC.(CH_3)_3$] in hexane, carbon tetrachloride, cyclohexane, dioxane, triethylamine, di-ethylamine and

in the absence of any solvent at different temperatures. These workers have not observed any band for the free Li–O bond and have assigned the intense bands at 580 and 510 cm^{-1} to...Li–O...Li–O...intermolecular bridges. They have also found that the normal alkoxides (e. g., MeOLi, EtOLi, PrOLi and BuOLi), which are less soluble than the tertiary butoxide, show absorption bands in the same region.

III. VOLATILITY :

The alkoxides of monovalent alkali metals like sodium and potassium are not volatilised even at higher temperatures due to their ionic nature. Similarly the bivalent metal alkoxides also cannot be distilled and are insoluble in organic solvents. This extraordinary behaviour of the latter group of compounds may be due to either appreciable ionisation (for example in the cases of alkaline earth elements) or it may be due to the formation of giant covalent molecules (for example in the case of beryllium alkoxides). In a recent communication, Bains[8] has reported the volatility of some lithium alkoxides. The methoxides are generally quite different in their properties compared to the other alkoxides. They are insoluble in non-polar organic solvents and are nonvolatile, except in the cases of niobium and tantalum pentamethoxides. The alkoxides of Group IV (e. g., Ti[20,36,48], Zr[20,36,48], Hf[20], Ge[49], Sn[17,23], Th[23], Ce[24],) and Group V metals (V[127,139,173], Nb[25], Ta[25]) have been studied in detail from these points of view.

The boiling points of some lower alkoxides under reduced pressure are given in the tables 8 and 9. The degrees of association of the different alkoxides are shown in parentheses below the observed boiling points (which are given in.....^{0}C/.....mm); these values of 'n' are generally in boiling benzene unless otherwise stated.

A perusal of the data in the tables 8 and 9 shows that for any metal, the boiling point of the n-alkoxides increases with the increase in the length of the alkyl chain, but the molecular complexity remains almost unaltered. For the same alkyl group, the degrees of association and the boiling points show a marked lowering as the ramification in the alkyl chain increases. The association of these alkoxides has been ascribed to the tendency of metals to increase their covalency by forming bonds of the type inter-molecularly :

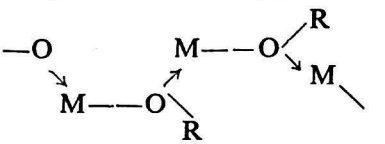


Table 8

Volatilities at Reduced Pressure and Degrees of Polymerisation of some lower Alkoxides.

Elements	R in $M(OR)_x$							
	Me	Et	$Me(CH_2)_2$	Me_2CH	$Me(CH_2)_3$	MeEtCH	Me_3C	Reference
Al	—	162/1.3 (4.1)	205/1.0 (4.0)	106/1.5 (3.0)	242/0.7 (3.9)	172/5.0 (2.4)	160/1.0* (1.95)	110
Fe	— (2.9)	155/0.1 (2.9)	162/0.1 (2.9)	149/0.1 (2.9)	171/0.1 (3.0)	159/0.1 (1.9)	136/0.1 (1.5)	16
Sb(III)	118/0.3*	94–5/10.0	115–16/15.0	89/3.0	148–9/11.0	119–20/6.5	91/9.5	71, 100
Ti	—	103/0.1 (2.4)	124/0.1	49/0.1 (1.4)	142/0.1	81/0.1	81/2.0 (1.0)	36, 43, 48
Zr	—	180/0.1 (3.6)	208/0.1	160/0.1 (3.0)	243/0.1 (3.4)	164/0.1 (2.5)	86/4.0 (1.0)	36, 43, 48
Ce(IV)	—	—	— (4.30)	165±5/0.5* (3.13)	— (4.20)	— (2.99)	—	23
Th	—	—	—	200±5/0.1* (3.8)	— (6.44)	— (4.2)	160/0.1* (3.4)	17, 23
Ge	66–67/36.0	71–72/11.0 (1.0)	108–9.5/9.0 (1.03)	91/8.5 (1.0)	140–3/8.0 (1.0)	—	—	20, 86
Sn	— (4.1)	— (4.0)	— (3.85)	131/1.6 (3.10)	— (3.70)	—	99/4.0	105
V(IV)	—	105±5/0.5	145±5/0.5	75±5/0.1	155±5/0.5	81/0.05	65±5/0.1	53
V(V)	120/0.1*	82.5/5.0	—	102/9.0	131/3.5	167/2.0	110/10.0	127, 139, 173
Nb	153/0.1 (2.11)	155/0.05 (2.02)	166/0.05 (2.02)	122/0.1 (1.00)	195/0.1 (2.01)	115.5/0.1 (1.83)	90/0.1	24
Ta	189/10.0 (1.98)	202/10.0 (1.98)	232/10.0 (1.95)	122/0.1 (0.99)	215/0.1 (2.02)	138/0.1 (2.04)	96/0.1* (1.00)	25

*Sublimed.

Table 9

Volatilities at Reduced Pressure and Degrees of Polymerisation of some Amyloxides.

Elements	R in $M(OR)_x$								
	$Me(CH_2)_4$	$Me_2CH(CH_2)_2$	$MeEtCHCH_2$	Me_3CCH_2	Et_2CH	$MePr^nOH$	$MePr^iCH$	Me_2EtC	References
Al	255/0.1 (4.0)	195/0.1 (4.0)	200/0.6 (4.1)	188/0.8 (2.07)	165/1.0 (2.08)	162/0.5 (2.06)	162/0.6 (1.98)	—	111
Fe	178/0.1 (3.0)	200/0.1 (3.0)	178/0.1 (3.0)	159/0.1 (2.0)	163/0.1 (2.0)	165/0.1 (1.9)	162/0.1 (1.9)	131/0.1 (1.5)	16
Ti	175/0.8 (1.4)	148/0.1 (1.2)	154/0.5 (1.1)	105/0.05 (1.3)	112/0.05 (1.0)	135/1.0 (1.0)	135/0.5 (1.0)	98/0.1 (1.0)	36, 43, 48
Zr	256/0.01 (3.2)	247/0.1 (3.3)	238/0.1 (3.7)	188/0.2 (2.0)	178/0.05 (2.4)	175/0.05 (2.0)	156/0.01 (2.0)	95/0.1 (1.0)	36, 43, 48
Ce(IV)	— (4.20)	—	—	— (2.53)	— (2.90)	— (3.11)	— (3.00)	— (2.4)	23
Th	— (6.20)	—	—	— (4.0)	—	—	—	208/0.3 (2.8)	17, 23
Sn	230/0.7 (1.5)	204/2.0 (1.05)	—	—	203/1.5 (1.15)	205/1.5 (1.15)	—	170/0.5 (1.0)	105
V(IV)	160/0.5	112/0.1	142/0.5	—	108/0.05	110/0.5	104/0.05	83/0.05	53
Nb	228/0.1 (2.0)	199/0.1 (1.81)	183/0.1 (1.81)	126/0.1 (1.52)	138/0.1 (1.16)	137/0.1 (1.03)	139/0.1 (1.05)	—	24
Ta	233/0.1 (2.01)	210/0.1 (1.98)	204/0.1 (1.97)	130/0.1 (1.35)	153/0.1 (1.02)	148/0.1 (0.99)	137/0.1 (1.02)	139/0.1 (1.00)	25

This tendency will obviously be hindered sterically with ramified alcohols. Another possible explanation of lower association and greater volatility of tertiary alkoxides can be sought in the greater +I inductive effect of these groups.

The latent heats and entropies of vaporisation of a number of metal akoxides (e. g., Al[110], Ti[36,48], Zr[36,48,50], Ge[22]) have been calculated by the vapour pressure measurements. The boiling points of alkoxides were measured at several pressures between 0.1 and 10.0 mm of mercury and in all cases, the data fitted approximately to a straight line of the form 'Log p_{mm} = a—b/T' where a and b are constants and T is the boiling temperature at the absolute scale. Some of these values are given in tables 10, 11 and 12 .

Table 10.

Latent Heats and Entropies of Vaporisation of some Aluminium Alkoxides [110].

Alkoxide	Boiling point °C/5.0 mm	Latent Heat	Entropy	Molcular association.
$Al(OEt)_3$	184.5 (189.0)	23.9 (20.2)	52.2 (43.7)	4.1
$Al(OPr^n)_3$	232.5 (222.7)	27.5 (22.3)	54.5 (45.0)	4.0
$Al(OPr^i)_3$	124.0 (139.1)	19.4 (21.1)	48.9 (51.2)	3.0
$Al(OBu^n)_3$	270.0 (259.6)	29.9 (24.9)	55.0 (46.7)	3.9
$Al(OBu^{sec})_3$	172.0 (167.3)	21.6 (19.5)	48.5 (44.3)	2.4

In the above table are given the respective values for different aluminium alkoxides reported by Mehrotra[110] and the values in brackets are those obtained by Wilhoit[174] using isoteniscope method the agreement between these two sets of data has been shown by the latter workers[175] to be within the experimental errors of the pressure measurements.

The latent heats and entropies of vaporisation with the respective boiling points of some normal[48], secondary[20] and tertiray alkoxides[36] of titanium and zirconium are given in the table 11.

Table 11

Latent Heats and Entropies of Vaporisation of some Titanium and Zirconium Alkoxides

Alkoxide	Boiling point °C/5.0 mm	Latent Heat	Entropy	Molecula Association
$Ti(OEt)_4$	138.3	21.6	52.5	2.4
$Ti(OPr^i)_4$	91.3	14.7	40.5	1.4
$Ti(OCHMeEt)_4$	127.8	19.9	49.6	—
$Ti(OCHEt_2)_4$	157.3	21.4	49.6	1.0
$Ti(OCMe_3)_4$	93.8	14.5	39.5	1.0
$Ti(OCMe_2Et)_4$	142.7	16.7	40.0	1.0
$Ti(OCMeEt_2)_4$	170.4	19.0	43.0	1.0
$Ti(OCMe_2Pr^n)_4$	167.0	19.5	44.0	1.0
$Zr(OEt)_4$	234.8	30.2	59.4	3.6
$Zr(OPr^i)_4$	203.8	31.5	66.1	3.0
$Zr(OCMe_3)_4$	89.1	15.2	42.0	1.0
$Zr(OCMe_2Et)_4$	138.4	16.3	39.5	1.0
$Zr(OCMeEt_2)_4$	171.4	19.0	43.0	1.0
$Zr(OCMe_2Pr^n)_4$	161.6	19.0	44.0	1.0

A persual of the above table shows that the entropies of vaporisation become lower with the decrease in molecular association; they are found to be of order of about 40 for the monomeric alkoxides of titanium and zirconium. The latent heat of vaporisation also decreases with the degree of polymerisation. These results support the view that the inter-molecular forces in the alkoxides are effectively reduced by the screening effect of the organic groups. The values of entropy of vaporisation for aluminium alkoxides are generally lower than those for zirconium alkoxides in spite of the degrees of association being higher in the former cases. This reversal of expected behaviour may be explained by the observations[110,36] that aluminium and zirconium isopropoxides show dimeric and monomeric behaviour respectively in the vapour phase.

According to Bradley[20], the monomeric alkoxides of approximately the same size and shape, i.e., same number of carbon and hydrogen atoms, have similar boiling points [e.g., $TaO_5C_{20}H_{45}$ (b.p. 149.5°/5.5mm) and $TiO_4C_{20}H_{44}$ (b.p. 143°/5.0mm)]. Similar behaviour was observed in the cases of tetra-tertiary amyloxides of zirconium and hafnium and in a number of higher alkoxides of titanium, niobium and tantalum, etc.

Bradley and Swanwick[50] have determined the vapour pressure of some monomeric alkoxides of titanium, zirconium and hafnium using both static and dynamic methods and have shown that the results follow the relation :

$$\text{Log } P = a + b/T + c \log T$$

The volatilities of these alkoxides follow the order $P_{Hf} > P_{Zr} > P_{Ti}$. An attempt has been made by Bradley[52] to explain this anomalous behaviour in terms of the fundamental effects of mass on volatility.

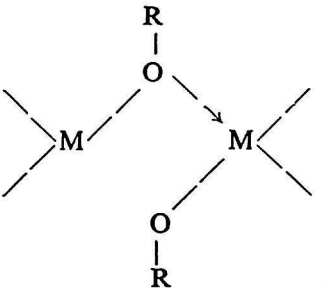
Bradley *et al*[51] have also measured the vapour pressures and viscosities of some germanium alkoxides over a range of temperature (20–45°C) and have calculated the energies for the entropies of vaporisation and entropies of activation for their viscous flow.

IV. Molecular Association and Structure of Metal Alkoxides :

Bradley and coworkers have determined the molecular weights of a number of metal alkoxides (e.g., Ti[20,36,48], Zr[20, 36,48], Th[17,23], Ce[23], Nb[24], Ta[25]) generally in benzene by the ebullioscopic method and have shown that the degree of association varies with the change in both the metal atom and the alkoxide groups. The alkoxides of first group are ionic in character; lithium methoxide has been recently shown[178] to have a layer structure with tetrahedral 4-coordination. The alkoxides of second group like beryllium and magnesium are generally insoluble in organic solvents and so their molecular weights have not been reported as yet.

Molecular association values of some metal alkoxides in boiling benzene are given in tables 8 and 9. Generally, the alkoxides show polymeric behaviour and their complexities depend upon the ramification of the alkyl groups and the atomic radii of the metals. The extent of polymerisation decreases as we proceed from primary to secondary and to tertiary alkoxides.

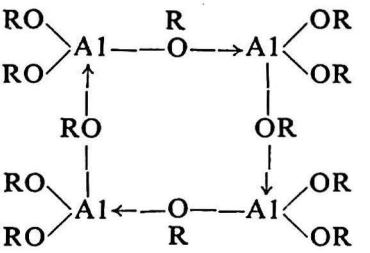
The molecular association of the alkoxides must be arising by formation of bonds of the type :



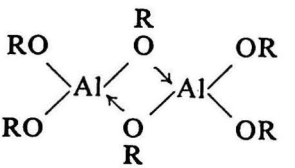
which help the central metal atoms to achieve higher covalency also. The lowering of the degree of molecular association with ramification in the alkyl chain can be ascribed to either steric hindrance or higher +I inductive effect of the branched alkyl groups. This would tend to endow a varying degree of double bond character on the metal-oxygen bonds M⇌OR; this type of back coordination involving overlap between a filled p_π orbital of oxygen and a vacant p_π or d_π orbital of the metal will allow it to achieve a higher covalency without recourse to association intermolecularly. However, in a detailed study of the amyloxides of titanium and zirconium [36] and of aluminium[111], it has been shown that the neopentyloxides show a closer similarity to the secondary alkoxides. This observation appears to give greater emphasis to the steric factors. Similar conclusions have been arrived at in a detailed study of the mixed alkoxides of titanium [169]. Obviously, it would be difficult to sort out the factors completely as both these effects are complementary to each other. With the same alkyl group the molecular association of the alkoxide increases with the radius of the metal atom; for example, n-butoxides of silicon, titanium, zirconium and thorium show average moleoular associations of the order of 1,1.4, 3.4 and 6.4 respectively in boiling benzene. Similarly, although zirconium tertiary butoxide is a monomer, the corresponding thorium derivative is almost tetrameric and it is only the tertiary heptyloxide which exhibits monomeric character in the case of thorium derivatives.

The tetrameric molecular association of the thallous alkoxide was reported by Sidgwick and Sutton[154] in the year 1930. Robinson and Peak[150] in 1935 suggested the following type of structure for

the observed tetrameric character of a number of aluminium alkoxides :



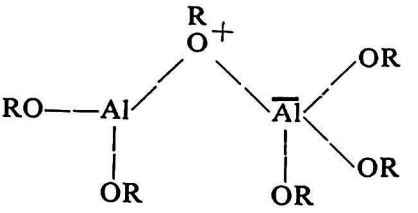
The confusion in the reported values[106,150,165] of the molecular association of aluminium alkoxides has been resolved to a large extent by the detailed studies of Mehrotra[110,111] who has also found an ageing phenomenon in these compounds. This latter effect may be responsible at least partially to the differences in the results of many earlier workers. The lowest degree of polymerisation (in the case of tertiary butoxide) has been found to be 2 and this has been ascribed by Mehrotra to the greater stability of the bridge structure



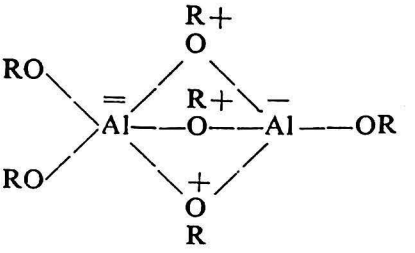
in the case of aluminium. A preliminary measurement of the vapour density of aluminium isopropoxide appears to lend support to this conclusion.

Shiner, Whittaker and Fernadez[155] have confirmed the views of Mehrotra[110] by molecular weight and nuclear magnetic resonance measurements that aluminium tertiary butoxide exists as a dimer in a number of organic solvents over a considerable range of temperature (-40° to 74°C). Bains[6] had shown the presence of two different types of bridging and non-bridging tertiary butyl groups by N.M.R. spectroscopy. O'Reilly[138] has measured the aluminium resonance spectrum of aluminium isobutoxide and concludes that the environment of the aluminium atom shows some tetrahedral or octa-hedral symmetry. Shiner and coworkers have determined the molecular weight of freshly distilled aluminium isopropoxide and observed the rate of rearrangement from trimeric to tetrameric form by taking the

spectra at different intervals in the pure melt as well as in solution. The N.M.R. spectrum of the benzene solution of the melt after 48 hours of preparation was found to consist of characteristic peaks of the trimer, tetramer and two small peaks at 79 and 73 c.p.s. showing the probability of a third form of aluminium isopropoxide. On the basis of these measurements the above workers have assumed that the mechanism of the intermolecular exchange of the alkoxide groups proceeded by the fission of a bridging Al—O bond to give the intermediate structure :



followed by the formation of another Al—O bond or by the formation of another alkoxide bridge giving an intermediate structure :



followed by the fission of one of the bridging Al-O bond.

The results of the above workers are in close conformity with the earlier observations of Mehrotra[110,111]. The N.M.R. studies have also confirmed the proposed structures for tetrameric alkoxides[47], having 6 coordination state for the central and 4-coordination state for the three surrounding aluminium atoms.

In a recent publication, Amma[3] has reported on the basis of his X-ray diffraction studies that the unit cells of aluminium alkoxides (methoxide, ethoxide and isopropoxide) consist of a tetrameric entity and they are not chain type of polymers.

Amongst other trivalent metals, the data on molecular association of only ferric[16] and some lanthanon[123,124] alkoxides are available. The ferric alkoxides appear to be generally a little less

polymerised than the corresponding aluminium compounds. The covalent radii of aluminium (1.26 A°) and iron (1.22 A°) are nearly of the same order and the differences may be ascribed to the greater strength of the inter-molecular bonding in the case of aluminium.

A perusal of the tables 8 and 9 shows that the titanium alkoxides have a maximum polymerisation of 2.4 whereas Caughlan *et al*[60] have shown that molecular association of titanium normal alkoxides inereases with concentration and attains a maximum value of three. Bradley and coworkers do not appear to have come across this concentration effect in their experimental work. However, Martin and Winter[104] have carried out a detailed study of the temperature and concentration dependence of the molecular association of titanium tetra-butoxide measured in benzene by cryoscopic and calorimetric methods. In the following table are summarised the data of molecular complexities of some normal titanium alkoxides determined by different workers.

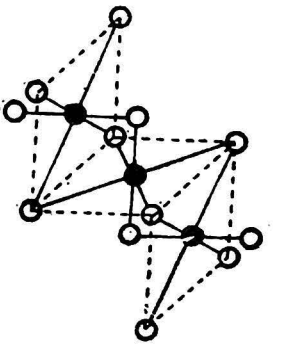
Table 12

Molecular complexities of some n-alkyl titanates, $Ti(OR)_4$

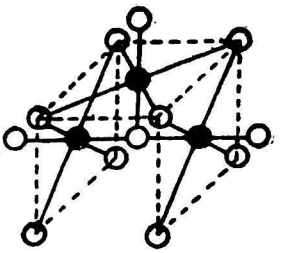
R in $Ti(OR)_4$	Method	Solvent	Concn. (10^{-3} mole fraction)	Molecular association	Author
Ethyl	Ebullioscopic	Benzene	1.3-8.0	2.4	Bradley *et al*[43]
Butyl	„	Butanol	5.9	1.14	
			6.7	1.17	
			10.3	1.28	
			11.7	1.29	Winter[177]
			16.1	1.40	
			18.1	1.41	
Butyl	„	„	5.0	1.0	
Pentyl	„	Benzene	1.1-7.0	1.4	Bradley *et al*[43,55]
Octyl	„	„	2.5-8.1	1.4	
Propyl	Cryoscopic	„	3.7	1.0	
			8.9	2.4	
			13.3	3.0	Caughlan
			17.8	2.9	*et al*[60]

			21.7	2.8	
			28.3	2.7	
			36.1	2 5	
Butyl	„	„	6.0	2.01	
			11.4	2.04	Cullinane
			14.5	2.05	*et al*[65]
Butyl	„	„	3.1	1.0	
			5.0	1.3	
			8.3	3.0	Caughlan
			12.2	3.0	*et al*[60]
			22.0	2.8	
			23.0	2.8	

Caughlan *et al*[60] had proposed two probable structures (I and II) for the trimeric titanium alkoxides based on the structure of rutile, TiO_2 :

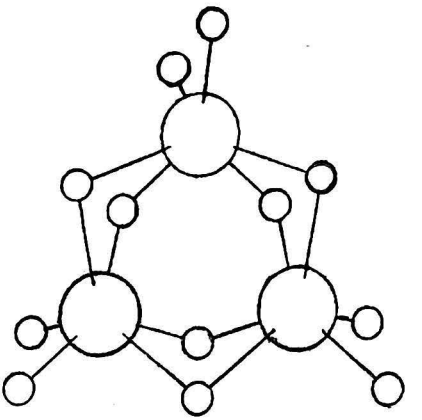


(I) $Ti_3(OR)_{12}$. ●, Ti ; ○, O in OR



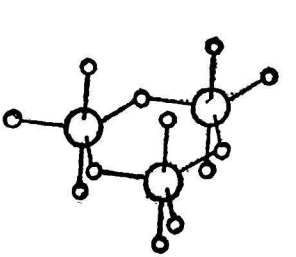
(II) $Ti_3(OR)_{12}$. ●, Ti ; ○, O in OR

In both these structures, titanium has attained its maximum coordination number of six. In the first structure, two titanium atoms are connected through three alkoxy bridges and in the second, one oxygen is attached to three titanium atoms and one alkyl group. The first structure was adopted by Bradley *et al*[55] for explaining the various reaction products obtained by the hydrolysis of titanium normal alkoxides. But this type of molecular arrangement was not found suitable by Martin and Winter[104] for explaining the structure and behaviour of the compound, $Ti_3Cl_3(OBu)_9$, which can be better represented by a symmetrical arrangement of titanium atoms. In both the structures of Caughlan, the central titanium atom contains six bridged alkoxy groups and the two terminal titanium atoms have three bridged and three alkoxy groups. Martin and Winter[101] have suggested a symmetrical structure (III) based on trigonal prisms for explaining the structure of $Ti_3Cl_3(OBu)_9$ which can accomodate one terminal chlorine atom per titanium :



(III) Proposed cyclic structure for $Ti_3(OR)_{12}$ based on TiO_6 trigonal prisms

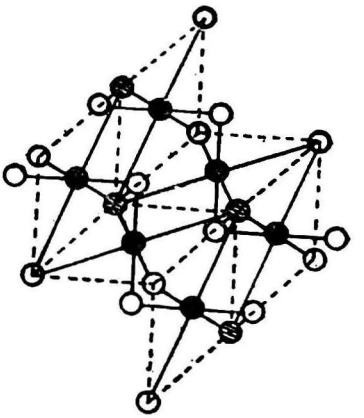
These authors have also suggested a cyclic structure for 5-covalent titanium which is based on a trigonal bipyramidal TiO_5



(IV) Alternative Cyclic structure for $Ti_3(OR)_{12}$ based on TiO_5 trigonal bipyramids.

grouping, as an alternative configuration for $Ti_3(OR)_{12}$. This differs from the structure III, not only in the five covalency of titanium, but also in that only one alkoxy bridge per titanium atom is present.

Bradley, Gaze and Wardlaw[55] have obtained $Ti_6O_4(OR)_{16}$, as the first stage hydrolysis product of $Ti_3(OR)_{12}$ and have proposed the following structure for this derivative :



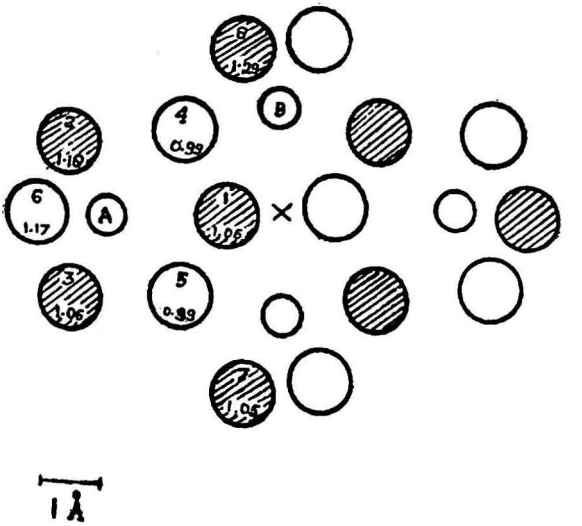
$Ti_6O_4(OR)_{16}$. ●, Ti; ○, O in OR; ◉, O in Ti-O-Ti

These workers have assumed that two trimer units $Ti_3(OR)_{12}$ are hydrolysed and they first form entities with the formulae $Ti_3(OR)_8(OH)_4$. The mutual bridging of these molecules with elimination of water would give a derivative of the above type, $Ti_6O_4(OR)_{16}$. In this representation, all the titanium atoms have attained the maximum coordination number of six. These plausible concepts have easily explained all the results obtained by these workers in the course of their detailed hydrolysis studies of some normal titanium alkoxides.

Martin and Winter[104] in a latter communication have claimed that the hydrolysis of $Ti_3(OR)_{12}$ can also be explained by the structure III without any difficulty and the formation of the oxides of the type $Ti_6O_4(OR)_{16}$, $Ti_9O_8(OR)_{20}$ and $Ti_{12}O_{12}(OR)_{24}$ obtained by Bradley and coworkers can be easilty accounted for on the same basis.

In a recent publication, Bradley and co-workers[56] have discussed various aspects of structure III on the basis of some infra-red spectra and high resolution proton magnetic resonance measurements on the polymeric titanium (IV) ethoxide and titanium (IV) oxide ethoxides. The proton magnetic resonance studies of $Ti_3(OEt)_{12}$ in carbon disulphide at room temperature reveal the presence of only one type of ethoxide groups. This gives the confirmation of the fact that the bridging and terminal ethoxide groups are changing their positions rapidly. The infra-red studies have revealed that as the degree of hydrolysis increases, there is a decrease in the intensity of bands near 2960, 2900, 2840, 2680, 1370, 1350, 1135, 1102, 1063, 1038, 915 and 890 cm^{-1} which involve in various ways the ethoxide groups. On the other hand there is an increase in the intensity of bands 790 and 770 cm^{-1} which are absent in $Ti_3(OEt)_{12}$. These new bands are understood to be due to Ti–O–Ti systems. These studies appear to lend greater support to the structure suggested by Caughlan and coworkers[60].

The X-ray crystallographic study has recently shown[83a] titanium ethoxide to be tetrameric in the solid state with the following structure :

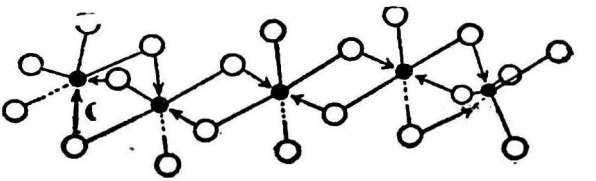


The tetrameric titanium (IV) ethoxide molecule projected on to the ab plane. The four titanium atoms (smaller circles) are in the plane. The cross-hatched oxygen atoms are below the plane ; the clear oxygen atoms are above the plane at distances (in A) from the plane given beneath the atom number. The "x" marks the centre of symmetry of the molecule.

While Martin and Winter[104] have adduced some new experimental evidence for the tetrameric titanium ethoxide as one of the species determining the association equilibrium in solution also, Bradley and Holloway[56a] reconfirm that the molecular association of Ti $(OC_2H_5)_4$ is independent of concentration over the range $2-100\times10^{-3}$m. These latter authors, therefore, suggest that a single trimeric species is present in solution contrary to the tetrameric nature of the crystalline solid.

In a detailed investigation on the scrambling tendencies of the alkoxyl, dimethylamino and halogen substituents on titanium, Weingarten and Van Wazer[173a] have concluded that both the cryoscopic as well as N. M. R. data suggest that titanium methoxide molecules in benzene or chloroform solution are tetrameric and have a structure similar to that described for crystalline titanium ethoxide by Ibers[83a] from X-ray studies. For the trimeric titanium ethoxide species in solution, these N. M. R. studies appear to support the structure (IV) given on page 24.

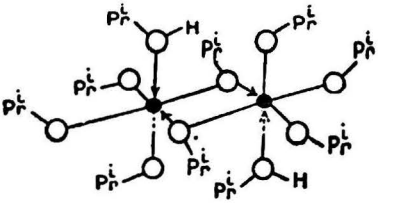
Zirconium alkoxides also show a molecular complexity ranging from 1 to 3.6. A structure similar to the one suggested by Caughlan *et al*[60] for the trimeric titanium alkoxides was suggested by Bradley and coworkers[43]. These workers are of the opinion that molecular complexities greater than three suggest that species of higher molecular weights are present and have predicted a possible structure for a pentameric unit in which the zirconium has a coordination number of six :



R Groups omitted. $[Zr(OR)_4]_5$; ●= *Zr*; O=Oxygen

These workers have observed that zirconium isopropoxide crystallised out with one mole of isopropanol and this solvated

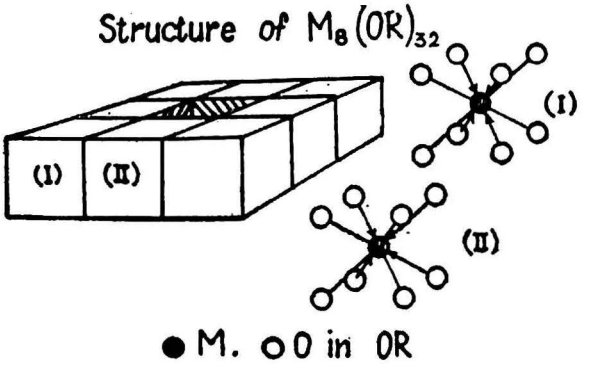
compound is dimeric in nature. They have suggested the following octahedrally coordinated structure for this compound :-



$[Zr(OPr^i)_4 \cdot Pr^iOH]_2$; ●=Zr

A similar structure was suggested by Bradley *et al*[25] for dimeric tantalum alkoxides.

In the fourth group, cerium and thorium have atomic radii of the same order (1.65A°). However, ceric alkoxides appear to show greater resemblance to the corresponding zirconium derivatives in the formation of solvated compounds and to some extent in the order of molecular complexity (tables 8 and 9) also. Zirconium, cerium and thorium have been reported to show coordination numbers of eight in their tetra-acetylacetonate derivatives and the minimum polymer which can show the 8-coordinated value will be octameric in nature. The molecular complexities of titanium, zirconium, cerium and thorium normal alkoxides have been found to be between 3-8 depending on the proportion of 6-coordinated to 8-coordinated atoms present in the molecule. These workers have suggested the following structure for an octameric metal alkoxide,



in which the corner cubes (I) and side cubes (II) differ only in the arrangement of the primary covalent and coordinated OR groups around each thorium atom.

Bradley[52] has suggested that metal alkoxides show a minimum degree of polymerisation consistent with the attainment of higher covalency of the metal. This simple theory appears to account in an excellent manner the different molecular complexities exhibited by various metal alkoxides.

Bradley and coworkers[25] have studied the effect of some solvents like benzene, toluene, acetonitrile, pyridine and corresponding alcohols on the molecular complexities of some tantalum normal alkoxides. In the following table are given some of their results :

Table 13

R in $Ta(OR)_5$	Molecular complexity in : C_6H_6 (b.p.80°, D 2.28)	PhMe (b.p.110°, D 2.38)	MeCN (b.p.82°, D 38.8)	Pyridine (b.p. 114°, D 12.5)	Pr_2^iO (b.p. 68°, D 3)	ROH
Me	1.98	1.83	1.50	1.01	1.75	1.20
Et	1.98	1.83	1.50	0.99	1.84	1.78
Pr^n	1.95	1.83	1.50	0.99	1.84	1.70
Bu^n	2.02	1.83	1.48	0.99	1.84	1.40

They have studied the effect of boiling points, dielectric constant and the donor power of the solvents on the molecular association of the solutes. The molecular complexity decreases with the increase in boiling point of the solvent due to dissociation of polymeric alkoxides. The dielectric constant value of the solvent does not appear to have any pronounced effect but the donor power of the solvent has a major influence in determining the molecular complexity. A perusal of the table shows that in pyridine (having lower dielectric constant in comparison to acetonitrile), the metal alkoxides exhibit minimum complexity due to strong donor tendency of pyridine. A similar explanation can be given in the case of alcohols also when they are used as solvents.

B. CHEMICAL PROPERTIES

I. Reactions with hydroxy compounds :

The alkoxides show a very powerful tendency of reacting with compounds, having a hydroxy group, like water, alcohols, phenols, glycols, substituted alcohols (like ethanolamines), carboxylic acids (and substituted carboxylic acids) and enolic forms of beta—diketones and ketoesters.

(a) Reactions with water :

Metal alkoxides show a very pronounced hydrolysable character and the hydrated oxide is generally precipitated when these are treated with an excess of water. However, with limited quantities of water, oxide alkoxides are obtained.

Bradley and co-workers have recently, made a very detailed physico-chemical study of the hydrolysis of alkoxides of some elements (Ti[35], Zr[31,33], Ta[32,34], Sn[34](IV) and Ce[34](IV)) a brief account of the structural aspects of the hydrolysis reactions have been already given in an earlier section. Kandelaki and co-workers[96] prepared gels by hydrolysing alkoxides of manganese, cobalt, chromium and iron. Hydrolysis of antimony (V) ethoxide was studied by Kolditz and Engles[97].

(b) Reactions with alcohols :

Mehrotra and co-workers studied the reactivity of alcohols on a number of alkoxides of metals (Zr[111], Ti[169], V[128], Sb[100], Sn[79](IV), and Nb[90]). The order of reactivity in the cases of zirconium and titanium has been found to be $OMe > OEt > OPr^i > OBu^t$. In the case of vanadium, the order was found to be opposite of the above. This reversal in the order of reactivity may be ascribed to be due to the monomeric nature of vanadyl trialkoxides in contrast to the associated nature of the alkoxides of titanium and zirconium. In the cases of tin, titanium and antimony alkoxides the order of reactivity was found[105] to be n-hexanol>cyclohexanol>phenol.

(c) Reactions with phenols :

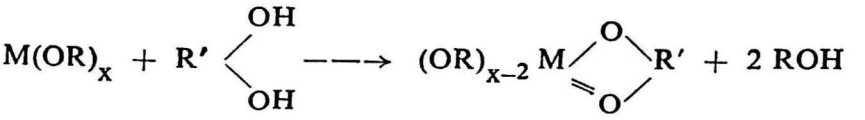
It has been revealed that the hydroxy group of phenol shows much greater reactivity than the hydroxy group of aliphatic compounds when the reactions of phenols were carried out with alkoxides of

some elements (B^{160}, Ti^{171}, Ge^{63}, Nd^{124} and Pr^{123}) by Mehrotra and co-workers in these laboratories. The solubility of the products is decreased in benzene as the number of phenoxide groups increased in the molecule. The reaction may be written in general as follows :

$$M(OR)_x + x\, C_6H_5OH \longrightarrow M(OC_6H_5)_x + x\, ROH$$

(d) Reactions with glycols :

Reactions of alkoxides of a number of elements (B^{158}, C^{136}, $Si^{136,141}$, Ti^{144}, Sn^{79}, Ge^{61}, Fe^{152}, Al^{113}, Pr^{123}, Nd^{124}, V^{128}, Nb^{90}, Sb^{12} and Se^{102}) with glycols have been investigated by Mehrotra and co-workers. Deluzarche[68] studied these reactions with orthotitanates. It has been noted that two moles of alcohol are liberated when the reactants are taken in 1 : 1 molar ratio according to the following equation :



Hexylene and pinacol derivatives of most of the above elements were found to be soluble in benzene and also could be distilled under reduced pressure while others were insoluble and non-volatile probably due to polymerisation.

(e) Reactions with ethanolamines :

The reactions of alkoxides of some elements (B^{159}, Al^{119}, Ti^{148}, Ge^{62}, and Sn^{79}) have been carried out with these substituted alcohols (mono, di and tri, 2,hydroxy ethylamines) and it was found that the reactions are similar to the alcohol interchange reactions. In the cases of boron and titanium alkoxides the amino group does not appear to take part in the replacement reactions, while in the cases of germanium and tin (IV) it does react as represented by the following equations :

$$Ti(OR)_4 + HOC_2H_4NH_2 \longrightarrow (RO)_3Ti\,(OC_2H_4NH_2) + ROH$$

$$Ge\,(OR)_4 + HOC_2H_4NH_2 \longrightarrow (RO)_2Ge\,(OC_2H_4NH) + 2\,ROH$$

(f) Reactions with carboxylic and substituted carboxylic acids :

Mehrotra and Pande[140] have established the preparation of

aluminium trisoaps by the action of carboxylic acids on aluminium isopropoxide :

$$Al(OPr^i)_3 + 3\ RCOOH \longrightarrow Al(OOCR)_3 + 3Pr^iOH$$

Similar attempts for the preparation of titanium[140] and vanadium[128] soaps were made but these always resulted in the formation of oxide-carboxylates. In the case of zirconium[91], tetra-soaps could not be prepared starting from the isopropoxide due to side reactions. The overall reaction of zirconium isopropoxide with excess of fatty acids could be represented as:

$$2\ Zr(OPr^i)_4 + 7\ RCOOH \longrightarrow (RCOO)_3\ Zr\text{-}O\text{-}Zr\ (OOCR)_3 + 7\ Pr^iOH + RCOOPr^i$$

The zirconium tetrasoaps could, however, be prepared by the reaction of zirconium tetrachloride with excess of fatty acids.

Reactions of alkoxides of some elements (Si[137], Ti[140], Zr[92], Al[140], V[128], and Be[5]) and carboxylic acid anhydrides were studied by Mehrotra and co-workers and it was found that metal carboxylates and alkyl esters were formed:

$$M(OR)_x + x\ (R^1CO)_2O \longrightarrow M(OOCR^1)_x + x\ R^1COOR$$

In the case of silicon alkoxides[137], only a dialkoxy diacylate derivatives were obtained in spite of the excess of acid anhydride employed.

Reactions of benzoic acid with titanium alkoxides[166] were found to be straightforward upto the formation of dialkoxy dibenzoate derivative and then an oxide derivative was obtained.

In the case of hydroxy carboxylic acids when reactions were carried out with alkoxides of some elements (Si[141], Ti[168], Zr[92], Al[149], Ge[62], Nd[124] and Pr[123]), it has been observed that both hydroxyl and carboxylic groups are reactive. The carboxylic group has been, however, found to be more reactive[62] compared to the hydroxyl group :

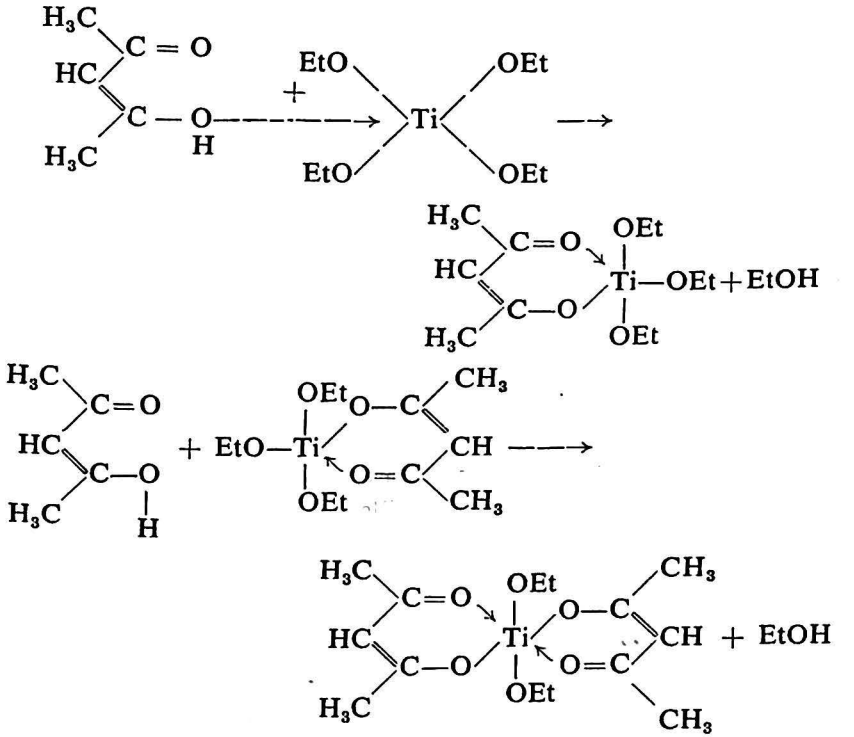
$$M(OR)_x + RCH(OH)COOH \longrightarrow (RO)_{x-2}MOOC(O)CHR + 2ROH$$

(g) Reactions with beta-diketones and keto-esters :

Compounds of the type of beta di-ketones, interact with metal alkoxides in their enolic forms to produce chelate derivatives.

Kambara *et al*[180] have reported the $Ti(ac.ac)(OR)_3$ complex in which co-ordination number of titanium is five. Puri, Pande and Mehrotra[145] found that only $Ti(OR)_2(ac.ac)_2$ derivative was formed even when an excess of acetylacetone was added. The diethoxide or diisopropoxide diacetylacetonate derivatives intercharge their alkoxide groups with higher alcohols quantitatively. This indicates that the six co-ordination structure is sufficiently labile to co-ordinate and react with higher alcohols. It may be due to the weak co-ordination from the ketonic oxygen of the acetylacetone group that the maximum covalency of titanium has not fully achieved in these derivatives. The non-reactivity of the di-acetylacetonate derivative with a third molecule of acetylacetone would, then, be due to steric factors.

A plausible mechanism for the reaction may be of the SN_2 type as represented below :



Besides acetylacetone, the reactions of benzoylacetone were also carried out with the alkoxides of a number of metals (Ti[146], Ge[62], Sn[79], Al[118], Fe[152], Nd[124], Pr[123], V[128] and Nb[90]) by Mehrotra and co-workers.

The pattern of the reactions between alkoxides of a number of metals (Sn^{79}, Nd^{124}, Pr^{123}, Nb^{95} and Ta^{90}) and ketoesters is analogous to the one described for acetylacetone and similar derivatives were obtained. Mehrotra and coworker[118] also synthesised mixed derivatives of the type Al(acac) $(etac)_2$ and Al(etac) $(acac)_2$ (where etac and acac stand for ethyl acetoacetate and acetylacetone respectively).

II. Reactions with other compounds :

(h) Reactions with halogens and halides :

Reactions of hydrogen halides on metal alkoxides produce halide derivatives as represented below :

$$M(OR)_x + y\,HX \longrightarrow MX_y(OR)_{x-y} + y\,ROH$$

Nesmeyanov and co-workers[134] found that $TiX_2(OR)_2.ROH$ derivatives were obtained by the reactions of halogens on titanium alkoxides. Mehrotra and co-workers investigated the reactions of hydrogen halides on the alkoxides of a number of elements (Al^{114}, Ti^{115}, Zr^{115}, Si^{115}, Ge^{64}, Sn^{79} (IV), Nd^{124}, Pr^{123} and Nb^{90}). In the cases of titanium and zirconium, the products were the same as those obtained in the reactions between their metal chlorides and alcohols :

$$Ti(OR)_4 + 2\,HX \xrightarrow[(X=Cl \text{ or } Br)]{} TiX_2(OR)_2.ROH + ROH$$

$$TiX_4 + 3ROH \xrightarrow[(R=Et \text{ or } OPr^i)]{} TiX_2(OR)_2.ROH + 2HCl$$

Chloride derivatives of alkoxides were first prepared by Wardlaw *et al*[88] by the action of acetyl chloride on titanium alkoxides. Bradley *et al*[43] extended this work and obtained $TiCl_4CH_3COOEt$ by the reaction of an excess of acetyl chloride on titanium ethoxide which was distilled under reduced pressure. Similar reactions were investigagted in the cases of alkoxides of a number of elements (Ti^{41}, Zr^{112}, Ge^{64}, Sn^{79} (IV), Be^{5}, Al^{116}, V^{129}, Nb^{90}, Pr^{123} and Nd^{124}) by Mehrotra and co-workers.

The different chloride alkoxides obtained in these reactions exhibit an increasing tendency to add molecules of organic ester of addition as the alkoxide group is gradually replaced by the chloride radical. This is understandable as the replacement of the alkoxide group by the more electronegative chloride group would tend to decrease the electron density round the metal atom and thus increase

its capacity for acceptance of donor bonds from the organic esters. A probable mechanism for the reaction of aluminium alkoxides with acetyl halides has been given by Mehrotra *et al*[116] :

$$Al(OR)_3 \rightleftharpoons Al^+(OR)^2 + OR^-$$

$$CH_3COX \rightleftharpoons CH_3CO^+ + X^-$$

$$Al^+(OR)_2 + X^- + OR^- + CH_3CO^+ \rightarrow Al(OR)_2X + CH_3COOR$$

The isolation of the single molecular entities based on the stoichiometric ratios of the reactants taken shows a ready radical interchangeability which has been confirmed in a large number of cases[94] by facile reactions of the type :

$$ZrBr_2(OPr^i)_2.Pr^iOH + Zr(OPr^i)_4.\ Pr^iOH \longrightarrow 2\ ZrBr(OPr^i)_3.Pr^iOH$$

It has been found that the primary and secondary alkoxides of most elements reacted readily with the stoichiometric replacement of alkoxide groups by chloride. The reactivity in the cases of tertiary alkoxides has been found to be slow. This behaviour of tertiary alkoxides was attributed to steric factors by Bradley *et al*[42]. However, it has been argued by Mehrotra and Misra that steric factors should have been most operative in the replacement of the first alkoxide group. Misra and Mehrotra[125] have shown in a recent study with tertiary alkoxides of aluminium, titanium and zirconium that side reactions occur which result in the formation of acetate derivatives. A plausible mechanism of the reaction has also been suggested by these workers :

$$Zr(OBu^t)_4 + CH_3COCl \xrightarrow{\text{slow}} ZrCl(OBu^t)_3 + CH_3COOBu^t$$

$$ZrCl(OBu^t)_3 + x\ CH_3COCl \longrightarrow ZrCl_{(1+x)}(OBu^t)_{3-x} + x\ CH_3COOBu^t$$

$$ZrCl_{1+x}(OBu^t)_{3-x} + xCH_3COOBu^t \longrightarrow ZrCl(OOCCH_3)_x(OBu^t)_{3-x} + xBu^tCl$$

Chloride derivatives of alkoxides of titanium[40,132] germanium[64] and vanadium[75,129] have also been prepared by the action of metal chlorides on their alkoxides :

$$Ti(OR)_4 + 3\ TiCl_4 \longrightarrow 4\ TiCl_3(OR)$$

The reaction of acetyl bromide with metal alkoxides follows the same pattern as described already with acetyl chloride. Mehrotra

and co-workers obtained bromide alkoxide derivatives of several metals (Zr^{94}, Ti^{170}, Ge^{62}, Al^{117}, Sn^{79} (IV), V^{129} and Nb^{90}) by the action of acetyl bromide on their alkoxides.

(i) Reactions with Carbonyl compouuds :

Tishchenko[163] reported the oxidaton of aldehydes into carboxylic esters by aluminium alkoxides :

$$2RCHO \longrightarrow RCOOCH_2R$$

Aluminium ethoxide[172] being a Lewis acid produces simple esters by the straight-forward Tishchenko reaction while the mildly basic double alkoxides such as $Mg\,[Al\,(OEt)_4]_2$ caused the formation of trimeric glycol esters :

$$3RCH_2CHO \longrightarrow RCH_2\text{–}\underset{OH}{CH}\text{–}ROOCH_2R$$

Meerwein-Ponndorf-Verley reaction involves catalytic reduction of ketones and aldehydes into secondary and primary alcohols respectively in the presence of metal alkoxides :

$$R_2CO + R'_2CHOH \rightleftharpoons R_2CHOH + R'_2CO$$

Mehrotra and co-workers investigated reactions of salicylaldehyde with titanium[167] and aluminium[120] alkoxides. In the case of titanium, disalicylaldehyde derivatives were obtained by straight-forward reactions. The ethyl and isopropyl products have been shown to undergo an intramolecular Meerwein-Ponndorf type of oxidation reaction. In the case of aluminium, trisalicylaldehyde derivatives were obtained at the room temperature. The ethyl and isopropyl products tend to decompose in refluxing benzene due to the internal oxidation of the type described above. The tertiary butyl derivatives in both cases were found to be stable.

(j) Co-ordination complexes of alkoxides :

The alkoxides have a predominant tendency of polymerisation due to the expansion of covalency of the metal, which they try to attain through co-ordination of oxygen from the nearby alkoxide groups, while they show very little tendency of forming co-ordination compounds with donor molecules. It appears that steric limitations are more effective in preventing a particular branched alkoxide from polymerisation but the formation of addition compounds can occur even in such cases [e. g., $Ti\,(OBu^i)_4.Bu^iOH$].

Bradley and Bains[7] reported a number of co-ordination complexes of aluminium, titanium, zirconium and tantalum alkoxides with ethylenediamine : $Al_8(OPr^i)_{24}.(en)_4$; $Ti_2(OEt)_8.en$; $Zr_2(OPr^i)_8$ en; $Ta_2(OPr^i)_{10}.en$. Srivastava and Mehrotra[161] reported a number of pyridine and diethylamine complexes of triaryl borates. Gupta and Mehrotra[79] have shown the reactivity of amino groups in ethylenediamine similar to that in ethanolamines. They obtained disubstituted products when reactions of ethylenediamine were carried out with tin (IV) alkoxides in equimolar ratio.

[e. g., $Sn(OPr^i)_2(en)$].

(k) Thermal stability of alkoxides :

The methoxids of lithium, magnesium and lanthanum were not affected when they were heated for several hours at 360°C while those of aluminium, zirconium, titanium, vanadium and antimony could be sublimed under reduced pressure. The pyrolysis of aluminium alkoxides was studied by Tishchenko[163] while their thermal decomposition was investigated by Schulman and co-workers[151] in the range of 166-265°C. Meerwein and Geschke[108] carried out pyrolysis studies of the alkoxides of tin (IV), iron (III), cobalt, nickel and copper. On thermal decomposition, it has been observed that sodium and potassium alkoxides form olefins and hydroxides by the removal of beta-hydrogen atoms in the cases of ethoxide or isopropoxide while in tertiary butoxide and other highly branched alkoxides 98, 183, acetone and methane are formed. Similar studies were also carried out by Bradley and co-workers[44] for zirconium alkoxides. They have reported the following order of stabilities of zirconium alkoxides, $Zr(OEt)_4 \gg Zr(OPr^i)_4 > Zr(OBu^t)_4$. $Zr(OAm^t)_4$.

Conclusions :

A perusal of the above account shows that there has been a brisk activity in the alkoxide field during the last two decades. However, as could be expected in the initial stages, work has been centred mainly round the synthetic aspects. With the beginning of the applications of physico-chemical tools to these new compounds, a start is being made in the understanding of their structural aspects.

Acknowledgements :

Thanks of the senior author (R.C.M.) are due to the Council of Scientific and Industrial Research, University grants Commission, Atomic Energy Establishment and the U. P. Scientific Research Committee for their financial assistance during the last 12–13 years on various aspects of alkoxide chemistry.

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REACTION OF MIXED CARBOXYLIC-CARBONIC ANHYDRIDES WITH SODIUM AZIDE

by

D. S. DEORHA AND (MISS) PADMA GUPTA.

The use of mixed carboxylic-carbonic anhydrides in peptide synthesis and in the place of acid chlorides for the preparation of amides and esters, of sensitive acids is well known[1]. We have, now, found that mixed anhydrides of α-benzoylamino-β-2-benzofuryl-acrylic acids react with sodium azide under very mild conditions to form acid azides in excellent yield. These can be rearranged to the 4-[(2'-benzofuranyl) methyl]-6-phenyl-2H-1, 3, 5-oxadiazin-2-ones on heating in benzene.

EXPERIMENTAL

Preparation of α-benzoylamino-β-2-benzofurylacrylic acid:-

A mixture of 4-[(2'-benzofuranyl) methylene]-2-phenyloxazolin -5-one(0.5 g.) and 20 ml. of 20% potassium hydroxide was heated on water bath for 45 mins. The resulting solution was filtered an the filtrate acidified. The solid that separated was crystallised from ethanol.

A few acids obtained by this procedure are described in table I.

Reaction with sodium azide:-

α-Benzoylamino-β-2-benzofurylacrylic acid (0.86 mole) was suspended in water (15 ml.) and sufficient acetone was added to complete the solution. The solution was cooled to 0° (ice salt bath) and triethylamine (0.1 mole) in acetone (175 ml.) was added. The mixture was stirred for 30 mins. at 0°and then a solution of sodium azide (0. 13 mole) in water (30 ml.) was added dropwise. After the mixture was stirred (0°) for 1 hour, it was poured into an excess of ice water. The solid that separated was filtered and dried in air. As the azides are difficult to be purified, their formation was confirmed by converting them to oxadiazines.

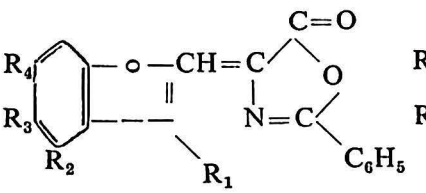
1. Barnden et al., *J. Chem. Soc.*, 1953, 3733; Evans et al, *ibid*, 1954, 403; Johnson, *J. Amer Chem. Soc.*, 1953, **75**, 3636; Vaughan, *ibid*, 1951, 73, 3547; 1952, 74, 676.

For this purpose the above azide was heated in benzene on a steam bath until no more nitrogen was evolved. Concentration of benzene solution afforded a solid which was shown to be a pure oxadiazine.

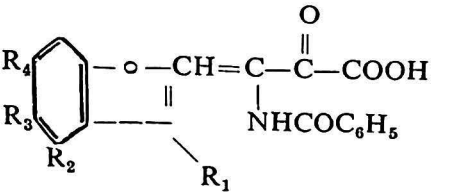
A few oxadiazines prepared by this procedure are described in table II.

Table 1

α—Benzoylamino-β—2—Benzofurylacrylic acids



(a)



(b)

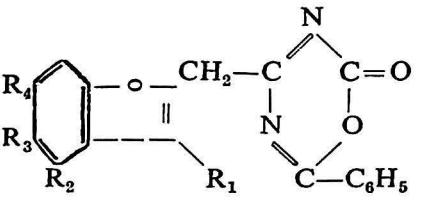
*Azlactones used formula (a)	Acrylic acids formed Formula (b)	M. P.	Formula	% Nitrogen Found	% Nitrogen Reqd.
I.	$R_1 = CH(CH_3)_2$, $R_2=R_4=CH_3$, $R_3=H$.	205°	$C_{23}H_{23}O_4N$	3.57	3.71
II.	$R_1 = CH(CH_3)_2$, $R_2=R_3=H$, $R_4=OCH_3$.	198°	$C_{22}H_{21}O_5N$	3.67	3.69
III.	$R_1 = CH_2CH_3$, $R_2=R_4=CH_3$, $R_3 = Cl$.	230°(d)	$C_{22}H_{20}O_4NCl$	3.22	3.52
IV.	$R_1 = CH(CH_3)_2$, $R_2=R_3=H$, $R_4 = CH_3$.	210°	$C_{22}H_{21}O_4N$	3.82	3.85
V.	$R_1 = CH_2CH_3$, $R_2=R_4=CH_3$, $R_3 = H$.	224°(d)	$C_{22}H_{21}O_4N$	3.90	3.85
VI.	$R_1 = CH_3=R_4$, $R_2=H$, $R_3=Cl$	173–5°	$C_{20}H_{16}O_4NCl$	3.93	3.79
VII	$R_1 = CH_2CH_3$, $R_2=H$, $R_3=Cl$, $R_4 = CH_3$.	180–1°	$C_{21}H_{18}O_4NCl$	3.46	3.65

*Groups correspond to those in the coloumn of acrylic acids.

VIII	$R_1 = CH_3$, $R_3 = Cl$, $R_2 = R_4 = H$.	198°	$C_{19}H_{14}O_4NCl$	4.09	3.93
IX	$R_1 = CH_3 = R_4$, $R_2 = R_3 = H$	168°	$C_{20}H_{17}O_4N$	4.29	4.17
X	$R_1 = CH_3$, $R_2 = R_3 = R_4 = H$.	144-5°	$C_{19}H_{15}O_4N$	4.15	4.36

Table II

4-[(2'—Benzofuranyl) methyl]-6-phenyl-2H-1,3,5-oxadiazin-2-ones.



*S. No.	M.P.	Colour	Formula	% Nitrogen Found	% Nitrogen Reqd.
1.[2]	226°	Deep yellow	$C_{23}H_{22}O_3N_2$	7.72	7.48
II.[2]	208°	Orange yellow	$C_{22}H_{20}O_4N_2$	7.81	7.44
III.[2]	246°	Orange	$C_{22}H_{19}O_3N_2Cl$	7.31	7.09
IV.[2]	206°	Deep yellow	$C_{22}H_{20}O_3N_2$	7.42	7.77
V.[2]	174°	Red	$C_{22}H_{20}O_3N_2$	7.98	7.77
VI.[3,a]	262°	Orange yellow	$C_{20}H_{15}O_3N_2Cl$	7.86	7.64
VII.[3,b]	233°	Yellow	$C_{21}H_{17}O_3N_2Cl$	7.12	7.36
VIII.[3,c]	251-2°	Yellow	$C_{19}H_{13}O_3N_2Cl$	8.19	7.94
IX.	218-19°	Red	$C_{20}H_{16}O_3N_2$	8.67	8.43
X.[3,d]	222-3°	Orange	$C_{19}H_{14}O_3N_2$	8.51	8.80

Thanks of the authors are due to Prof. R. C. Mehrotra, Head of the Chemistry Department, University of Rajasthan, for providing facilities and to the authorities of the University of Rajasthan for awarding scholarship to one them. (P.G.)

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*Number corresponds to that of an acrylic acid in Table I.

2. Dean et al., J: Chem. Soc., 1961, 327.

3. Deorha and Gupta, (a) Rec. Trav. Chim., (1964, 83, 1056); (b) J. Indian Chem. Soc., (1964, 41, 371); (c) Indian J. Chem. (1964, 2, 459); (d) Chem. Ber., (1964, 97, 3577).

4. Foster et al., *J. Chem. Soc.*, 1948, 2254.

REPLACEMENT OF THE HYDRAZINO-GROUP IN SUBSTITUTED NITROPHENYLHYDRAZINES BY CHLORINE OR HYDROGEN

by

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The behaviour of a few substituted phenylhydrazines with potassium chlorate in hydrochloric acid and with cupric acetate in acetic acid has been studied.

Soon after the discovery of phenylhydrazine, Fischer[1] attempted to study the behaviour of halogens on it, but he found that the reaction was very vigorous and its course was difficult to follow. Chattaway et al[2]. continued this work more systematically and were able to obtain polyhalogenated benzene derivatives in which hydrazino group was not present. Brady and Bowman[3] described the replacement of hydrazino-group by iodine atom in case of 2,6-dinitro-3 methylphenylhydrazine. They also effected the substitution of the hydrazino-group by chlorine and hydrogen atoms in a few cases. Joshi and Deorha[4] reported the replacement by iodine and bromine in a number of nitrophenylhydrazines. No further attempts appear to have been made to utilise the reaction in other cases.

In the present investigation, methods have been developed to effect the replacement of hydrazino-group by chlorine and hydrogen in polynitrophenylhydrazines. It has been found that when the nitrophenylhydrazines are treated with potassium chlorate in hydrochloric acid suspension, the hydrazino-group gets replaced by chlorine. Replacement by hydrogen has been effected by cupric acetate and acetic acid.

As expected due to the deactivating influence of the nitro group, the replacement of the hydrazino-groupby chlorine proceeds smoothly (except in case of mononitrophenylhydrazines) and no

1. *Annalen*, 1878, **190**, 87
2. *J. Chem. Soc.*, 1908, **93**, 852; 1909, **94**, 1066
3. *ibid*, 1921, **116**, 894.
4. *ibid*, 1957, 2414

nuclear chlorination takes place. Thus, 2,4-dinitro- (I)[5], 2-chloro-4, 6-dinitro-(II)[6], 2-bromo-4,6-dinitro-(III)[6], 4,6-dinitro-3-methyl-(IV)[7], 2,4,6 trinitro-3-methyl-(V)[7], 6-bromo-2, 4-dinitro-3-methyl-(VI)[7], 6-chloro-2,4-dinitro-3-methyl-(VII)[8], 4-chloro-2,6-dinitro-(VIII)[8], 4-bromo-2,6-dinitro-(IX)[8], 3-chloro-4,6-dinitro-(X)[9] and 4,6-dinitro-2-methyl-(XI)[10] phenylhydrazines on reacting with potassium chlorate and concentrated hydrochloric acid form the corresponding chloroderivatives described in table I. 0-(XII)[11], m-(XIII)[11] and p-(XIV)[12] -Nitrophenylhydrazines on reaction with chlorine yield 1,2,4-trichloro-6-nitro-, 1,2,4-trichloro-5-nitro-, and 1,2,3-trichloro-5-nitrobenzenes respectively. It, thus, appears that one nitro group does not deactivate the benezene nucleus sufficiently with the result that in this reaction, in addition to the substitution by chlorine atom of the hydrazino-group, hydrogen atoms in the benzene ring are also replaced. Even in the compound 1,3-dihydrazino-4,6-dinitrobenzene (XV)[9] containining two hydrazino-groups, the replacement of both the hydrazino-groups takes place by chlorine.

The replacement of the hydrazino-group by hydrogen in II, III, IV, VI, VII, VIII, IX, X and XV has been effected by heating them with cupric acetate in acetic acid to provide the corresponding hydrazino free compounds (vide Table II).

The replacement of hydrazino-group by hydrogen or chlorine in substituted phenylhydrazines, therefore, provides an excellent method for preparing compounds having definite structures.

EXPERIMENTAL

Replacement of Hydrazino group by chlorine :

Nitrophenylhydrazine (0.01M) was suspended in concentrated hydrochloric acid (12 ml.) and was treated with a saturated solution of potassium chlorate (0.04M). On leaving the mixture overnight the chloronitrobenzene separated. It was filtered, washed with water and crystallised from ethanol.

5. Purgotti, *Gazzetta*, 1894, **24**, 113.
6. Joshi and Deorha, *J. Ind. Chem. Soc.*, 1951, **28**, 34.
7. Joshi and Deorha, *ibid.*, 1952, **29**, 46.
8. Joshi and Deorha, *ibid*, 1957, **34**, 14.
9. Borsche, *Ber.*, 1921, **54**, 669.
10. Brady and Bowman, *J. Chem. Soc.*, 1921, **119**, 894.
11. Hantzsch and Borghaus, *Ber.*, 1897, **30**, 90, Bischler, *Ber*, 1889, **22**, 280.
12. Bamberger and Kraus, *Ber.*, 1896, **29**, 1834.

Chloronitrobenzenes obtained by the above procedure are recorded in Table I.

Replacement of Hydrazino group by Hydrogen :

A solution of nitrophenylhydrazine (0.01M) in acetic acid (20ml.) and cupric acetate (0.03M) were heated on water bath for 45 minutes. The mixture was diluted with water, filtered and the residue was extracted by hot ethanol. On concentrating and cooling the extract, the hydrocarbon separated in crystals.

The hydrocarbons obtained by this procedure from a few phenylhydrazines are recorded in Table II.

Table I

Phenyl* hydrazine used	Chloronitrobenzene† formed	Yield %	M.P. °C	Formula	Found	Calcd.
I	1-Chloro-2,4-dinitro-	80	52	$C_6H_3O_4N_2Cl$	Cl : 17.32	17.53
II	1,2-Dichloro-4,6-dinitro-	72	56	$C_6H_2O_4N_2Cl_2$	Cl : 29.57	29.95
III	1-Chloro-2-bromo-4,6-dinitro-	75	62	$C_6H_2O_4N_2ClBr$	Cl+Br: 41.31	41.03
IV	1-Chloro-4,6-dinitro-3-methyl-	71	90	$C_7H_5O_4N_2Cl$	Cl : 16.18	16.39
V	1-Chloro-2,4,6-trintro-3-methyl-	72	147	$C_7H_4O_6N_3Cl$	Cl : 13.39	13.57
VI	1-Chloro-6-bromo-2,4-dinitro-3-methyl-	68	81	$C_7H_4O_4N_2ClBr$	Cl+Br : 38.86	39.06
VII	1,6-Dichloro-2,4-dinitro-3-methyl-	64	94	$C_7H_4O_4N_2Cl_2$	Cl : 28.46	28.28
VIII	1,4-Dichloro-2,6-dinitro-	64	105	$C_6H_2O_4N_2Cl_2$	Cl : 30.29	29.95
IX	1-Chloro-4-bromo-2,6-dinitro-	62	94	$C_6H_2O_4N_2ClBr$	Cl+Br : 41.28	41.03
X	1,3-Dichloro-4,6-dinitro-	67	101	$C_6H_2O_4N_2Cl_2$	Cl : 29.78	29.95
XI	1-Chloro-4,6-dinitro-2-methyl-	69	58	$C_7H_5O_4N_2Cl$	Cl : 16.25	16.39
XII	1,2,4-Trichloro-6-nitro-	73	86	$C_6H_2O_2NCl_3$	Cl : 46.71	47.02
XIII	1,2,4-Tricholoro-5-nitro-	70	57	$C_6H_2O_2NCl_3$	Cl : 47.37	47.02
XIV	1,2,3-Trichloro-5-nitro-	74	71	$C_6H_2O_2NCl_3$	Cl : 46.88	47.02
XV	1,3-Dichloro-4,6-dinitro-	77	103	$C_6H_2O_4N_2Cl_2$	Cl : 30.27	29.95%

† All the chloronitrobenzenes are colourless except the last which is yellow.

* The number corresponds to those of phenylhydrazines given in the text.

Table II

Phenyl hydrazine used *	Nitrobenzenes formed †	Yield %	M.P. °C	Formula	Found	Calcd.
II	1-Chloro-3,5-dinitro-	30	56	$C_6H_3O_4N_2Cl$	Cl : 17.11	17.53
III	1-Bromo-3,5-dinitro-	26	77	$C_6H_3O_4N_2Br$	Br : 32.00	32.36
IV	2,4-Dinitro-1-methyl-	75	70	$C_7H_6O_4N_2$	N : 15.16	15.38
VI	1-Bromo-3,5-dinitro-4-methyl-	32	91	$C_7H_5O_4N_2Br$	Br : 31.12	30.62
VII	1-Chloro-3,5-dinitro-4-methyl-	30	77	$C_7H_5O_4N_2Cl$	Cl : 16.20	16.39
VIII	1-Chloro-3,5-dinitro-	28	54	$C_6H_3O_4N_2Cl$	Cl : 17.24	17.53
IX	1-Bromo-3,5-dinitro-	25	77	$C_6H_3O_4N_2Br$	Br : 32.14	32.36
X	1-Chloro-2,4-dinitro-	60	50	$C_6H_3O_4N_2Cl$	Cl : 17.34	17.53
XV	1,3-Dinitro-	85	89	$C_6H_4O_4N_2$	N : 16. 81	16.66%

The authors' sincere thanks are due to Prof. R. C. Mehrotra, Head of the Chemistry Department for providiug facilities and to the authorities of this University for awarding a scholarship to one of them (S. P. S.)

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† All the compounds are colourless except the last which is light yellow.

* The number corresponds to those of phenylhydrazines given in the text.

PREPARATION OF 3-HYDROXY-2,5-DIMETHYL-1, 4-BENZOQUINONE

by

D. S. DEORHA AND (MISS) SNEH PRABHA SAREEN

The title compound, required in connection with a project under way in these laboratories on the synthesis of depsidones, has been prepared by three methods. In the first method 2,5-dimethyl-cyclohexane-1, 4-dione[1] has been oxidised to the hydroxyquinone by selenium dioxide. The second method involves the oxidation of 2,5-dimethyl resorcinol[2] under similar conditions. The third method consists in the catalytic reduction of 4,6-dinitro-2,5-dimethylphenol followed by oxidation of the product with Fremy's salt or ferric chloride. The latter method is found to be superior to others in quality and yields of the product.

EXPERIMENTAL

3-Hydroxy-2,5-dimethyl-1,4-benzoquinone :

(1) A mixture of 2,5-dimethylcyclohexane-1,4-dione[1] (3.6g) in ethanol (150 ml.) and selenium dioxide (2 g.) dissolved in enthanol (10 ml) was refluxed for 10 hours on a water bath. On removing ethanol, the residue was taken in ether (100 ml). The ethereal layer was extracted with 10% potassium hydroxide solution. Neutralisation of the aqueous extraot with dilute sulphuric acid provided the hydroxyquinone which on crystallisation from ethanol gave orange plates (0. 3 g.) m.p. 138°. (Found : C, 63.42; H, 5.43. $C_8H_8O_3$ requires C, 63.15; H, 5.26%).

(2) Similarly 2,5-dimethyl resorcinol[2] gave the quinone m.p. and mixed m.p. with the above 138°.

(3) (a) 4,6-Dinitro-2,5-dimethylphenol[2] (4.2g.) was dissolved in ethanol (100 ml) and catalytically reduced on Adams catalyst. On filtration, the filtrate was concentrated in vacuum and

1. Baeyer, *Ber*, 1892, **25**, 2122.
2. Kostanecki, *ibid*, 1886, **19**, 2321.

The acetone solution of the residue was added slowly with stirring to a solution of Fremy's salt (25 g.) and sodium acetate (1.6 g.) in water (250 ml.). The mixture was stirred for one hour at room temperature and then extracted with ether. The ether layer was extracted with 10% potassium hydroxide solution. Acidification of the alkaline extract furnished a solid which sublimed at 120°/15 mm. to give a semicrystalline solid. This crystallised from ethanol in orange plates (1 g.), m.p. and mixed m.p. with the above 138°.

(b) The residue obtained above by reduction of the dinitrophenol was taken in 5N–hydrochloric acid (12 ml.) and a solution of ferric chloride (16 g.) in water (50 ml.) was then added. The mixture was quickly steam distilled. The solid was collected and crystallised from ethanol to afford the hydroxyquinone in orange plates (0.9 g.), m.p. and mixed m.p. with the above 138°.

3—Hydroxy–2,5-dimethylhydroquinone :

To a vigorously stirred solution of the preceeding quinone (1.2 g.) in ether (30 ml.), sodium hydrosulphite (3 g.) in water (8 ml.) was gradually added. After stirring ($\frac{1}{2}$ hr.), the ether phase was separated and the aqueous phase extracted with ether (2×20 ml.). The residue left after evaporation of the dried ether extracts was crystallised from benzene giving 3–hydroxy–2,5–dimethylhydroquinone (0.6 g.) in colourless needles, m.p. 155° (Found : C, 62.18; H, 6.36. $C_8H_{10}O_3$ requires C, 62.33; H, 6.50%).

The author's sincere thanks are due to Prof. R. C. Mehrotra, Head of the Chemistry Department for providing facilities and to the authorities of this University for awarding scholarship to one of them (S.P.S.)

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EBULLIACHOR

A New Physical Constant

by

D . S. DEORHA

Several attempts have been made to find properties of atoms or of linkages which are additive in the sense that the total measured value of some such property for a molecule may be calculated by adding together the constant contributions of each atom or linkage. One might think that the molar volume would be an additive function of the atomic volumes, but experiment shows that it is only too frequently far from the case. This frequent inability of the molar volume to be additive has been attributed to the polarity in the molecule, to the internal pressure under which different molecules exist and to several other factors. With this point in view, attempts were, therefore, made to correct the molar volume by multiplying it with certain function of refractive index, function of surface tension, function of viscosity etc. as a result of which properties like Molar refraction, Parachor, Rheochor etc. are already in existence.

As boiling point of substance is chiefly determined by the constitutive factor it was considered of interest to corelate molar volume with certain function of boiling point and see whether any such property proves to be of any help in elucidating the structure of organic compounds.

A new physical constant, for which the name "EBULLIACHOR" and symbol (E) is proposed, has been obtained by associating molar volume with the logarithm of the boiling point on absolute scale according to the expression $E=\frac{M}{d}\log_e T$ (Where M is the Molecular weight of a substance, d is its density at 20° and T, its boiling point on absolute scale at 760 mm.).

As a result of the study of a large number of compounds, it is found that the observed Ebulliachor of any compound is made up of two constants, one dependent on the atoms and the other on structural factors such as type of linkage, size of rings etc. Some of

the atomic, group, and structural Ebulliachor, derived by the author are given in table I below. In deriving these, the density and boiling point values given by Vogel[1] and in International Critical Tables have been used throughout and the procedure employed by him in the calculation of atomic and structural parachors have been adopted.

Table I

CH_2	20.46
C (in CH_2)	0.00
H (in CH_2)	10.23
O (in aliphatic ethers)	7.86
OH (in aliphatic alcohols)	9.24
CO (in methyl ketones)	16.00
CO (in ketones)	16.90
CO_2 (in esters)	26.17
O (in acetals)	8.19
O (in aromatic ethers)	6.94
COOH	33.46
Cl (in aliphatic)	22.79
Cl (in aromatic)	27.20
Br (in aliphatic)	27.70
Br (in aromatic)	32.44
I (in aliphatic)	37.33
I (in aromatic)	41.17
F (in aliphatic)	12.08
F (in aromatic)	16.33
C–C (in double bond)	13.09
C–C (in triple bond)	23.54
C–C (in three membered ring)	5.67
C–C (in four ,, ,,)	3.45
C–C (in five ,, ,,)	0.00
C–C (in six ,, ,,)	—2.64
N–NO(in nitrosoamines)	22.39
NH_2 (in aliphatic primary amines).	16.56
NH_2 (in aromatic primary amines).	17.35
NH (in secondary aliphatic amines).	10.47
NH (in secondary aromatic amines).	7.99

1. A. Vogel, J. Chem. Soc., 333, 4758 (1934); 1323 (1938); 171, 1528 (1940); 636 (1943); 133 (1946); 607, 1804 (1948).

N (in tertiary aliphatic amines).	1.54
N (in tertiary aromatic amines).	—3.42
O.NO (in nitrite).	36.33
NO_2 (in nitro aliphatic)	29.00
NO_2 (in nitro aromatic)	31.28
S (in aliphatic sulphides)	17.09
S_2 (in aliphatic disulphides)	38.21
SH (in thiols aliphatic)	27.40
SH (in thiols aromatic)	29.67
NO_3 (in nitrate)	39.98
SO_3 (in sulphite)	44.51
CO_3 (in carbonate)	34.74
SO_4 (in sulphate)	49.39
$C_3H_7^i$ (in isopropyl)	73.34
$C_4H_9^i$ (in isobutyl)	93.05
$C_5H_{11}^i$ (in isoamyl)	113.03
C_6H_5 (in phenyl)	87.72

As slight structural variations result in marked differences in Ebulliachors, the constant may prove more useful than parachor alone when applied to problems of Chemical constitution. A few cases in which its utility has been studied so far, are given below.

(i) Distinction between Stably Linked & Reactive Halogen Atoms -

Two sets of Ebulliachor values are obtained for halogen atoms according as they are reactive as in alkyl halides etc. or are stably linked as in halogenated benzenes etc. Comparison of observed and calculated Ebulliachor values for say, a halogenated homologue of benzene shows whether the halogen is in the nucleus or in the side chain.

(ii) Ebulliachor and Structural Variations :

Isomeric groups and compounds, in which the mode of linking of multivalent atoms is different, show appreciable difference in their Ebulliachors. Thus, Ebulliachors for nitro and nitrite groups are 29.09 and 36.33 respectively and for two double bonds and one triple bond are 26.19 and 23.54 respectively, whereas the parachors for the same are 73.8, 75.3, 46.4 and 46.6 respectively. Ebulliachor

can, therefore, prove of some help in the study of the structure of isomeric compounds.

Its possible use to calculate the resonance energy of a system will form part of another communication.

The author expresses his grateful thanks to Prof. R.C. Mehrotra, Head of the Department of Chemistry, University of Rajasthan for providing necessary facilities.

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