26. *Structural Chemistry of the Alkoxides. Part X.* Primary Alkoxides of Tervalent Iron.*

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Ferric alkoxides, $Fe(OR)_3$ where R = Me, Et, Pr^n, Bu^n, Bu^i, $CH_2{\cdot}CMe_3$, $CH_2{\cdot}CHMeEt$, $CH_2{\cdot}CH_2{\cdot}CHMe_2$, and $[CH_2]_4Me$, have been obtained either from ferric chloride, the alcohol, and ammonia, or by alcohol interchange. All except the methoxide volatilise unchanged under reduced pressure. Molecular weights were determined ebullioscopically in benzene and all the compounds, except the *neo*pentyloxide (dimer), were found to be trimeric.

Little is known about ferric alkoxides. Although Grimaux[1] and then Vorlander[2] attempted to prepare ferric ethoxide by treating ferric chloride with sodium ethoxide they did not isolate it pure, and it was not until 1929 that Thiessen and Koerner[3] obtained it by the same method. Meerwein and Bersin[4] reported that ferric ethoxide could be titrated

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* Part IX, *J.*, 1957, 2600.

[1] Grimaux, *Bull. Soc. chim.*, 1884, 157.

[2] Vorlander, *Ber.*, 1913, **46**, 181.

[3] Thiessen and Koerner, *Z. anorg. Chem.*, 1929, **180**, 65.

[4] Meerwein and Bersin, *Annalen*, 1929, **476**, 113.

with sodium ethoxide in alcoholic benzene, thymolphthalein being the indicator. Their end-point corresponded to the formation of the double alkoxide $Na[Fe(OEt)_4]$ but this was not isolated. As no other ferric alkoxides had been mentioned it seemed worth while systematically to study their preparation and properties, and in particular to compare ferric alkoxides with aluminium alkoxides.

We now report results on the primary alkoxides mentioned in the summary. The above method for preparing ferric ethoxide was found to be unsuitable because of its low solubility in alcohol, and, although the ethoxide was soluble in benzene, it was difficult to filter off sodium chloride from alcoholic benzene. Ferric chloride in alcoholic solution reacted exothermically on treatment with ammonia, but the ferric ethoxide appeared to be completely coprecipitated with the ammonium chloride. This was due to the formation of an insoluble ammoniate of ferric ethoxide $Fe(OEt)_3,xNH_3$ (where $x = 1$—3), but removal of solvent under reduced pressure led to dissociation of the ammoniate. The ferric ethoxide was then isolated by extraction with benzene, in which it is very soluble. The formation of the ammoniate was demonstrated by exposing the ferric ethoxide, dissolved in either ethyl alcohol or benzene, to ammonia vapour, whereupon a precipitate was formed. This was shown to be a reversible system by pumping off the ammoniacal solvent; ferric ethoxide was regenerated and could be redissolved. A number of ferric primary alkoxides were then prepared by the ammonia method:

$$FeCl_3 + 3ROH + 3NH_3 \longrightarrow Fe(OR)_3 + 3NH_4Cl$$

where R = Me, Et, Pr^n, Bu^n, Bu^i, $CH_2{\cdot}CHMeEt$, $CH_2{\cdot}CH_2{\cdot}CHMe_2$, and $[CH_2]_4Me$.

Several alkoxides were also prepared by alcohol interchange from ferric ethoxide:

$$Fe(OEt)_3 + 3ROH \longrightarrow Fe(OR)_3 + 3EtOH$$

where R = Me, Pr^n, Bu^n, Bu^i, $[CH_2]_4Me$, and $CH_2{\cdot}CMe_3$.

Ferric methoxide was an orange microcrystalline solid soluble in methyl alcohol and in benzene, thus differing from the methoxides of aluminium, titanium, zirconium, hafnium, cerium, and thorium which are insoluble. However, ferric methoxide was involatile and decomposed at 250°/0·05 mm. Ferric ethoxide was a dark brown crystalline compound which melted at 120° and volatilised at 155°/0·1 mm. in a molecular still. It is soluble in benzene and can be recrystallised from ethyl alcohol. Ferric *n*-propoxide was a brown solid which crystallised from benzene and volatilised at 162°/0·1 mm. in the molecular still. Ferric *n*-butoxide and *n*-pentyloxide were both brown, highly viscous liquids which were soluble in benzene and volatilised at 171°/0·1 mm. and 178°/0·1 mm. respectively. The other primary alkoxides (R = Bu^i, $CH_2{\cdot}CMe_3$, $CH_2{\cdot}CHMeEt$, and $CH_2{\cdot}CH_2{\cdot}CHMe_2$) were brown solids which sublimed under reduced pressure. The molecular weights of ferric alkoxides were determined ebullioscopically in benzene and their molecular complexities are given in Table 1, together with their volatilities (the temperature at which condensate was first observed on the cold-finger of the molecular still). The molecular complexities and b. p.s of the corresponding aluminium alkoxides obtained by Mehrotra [5] are also shown.

TABLE 1.

R in $M(OR)_3$	Mol. complexity		Volatility	
	Fe	Al	Fe	Al
Me	2·9	—	—	—
Et	2·9	4·1	155°/0·1	162°/1·3
Pr^n	3·0	4·0	162°/0·1	205°/1·0
Bu^n	2·9	3·9	171°/0·1	242°/0·7
Bu^i	3·0	—	173°/0·1	—
$Me{\cdot}[CH_2]_4$	3·0	4·0	178°/0·1	255°/1·0
$Me_2CH{\cdot}[CH_2]_2$	3·0	4·0	(decomp.) 200°/0·1	195°/0·1
$MeEtCH{\cdot}CH_2$	3·0	4·1	178°/0·1	200°/0·6
$Me_3C{\cdot}CH_2$	2·0	2·0	159°/0·1	180°/8·0

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[5] Mehrotra, *J. Indian Chem. Soc.*, 1953, **30**, 585; 1954, **31**, 85.

The molecular complexities of the ferric normal alkoxides being considered first, it is noteworthy that they are all trimeric independently of chain length from methyl to *n*-pentyl. Moreover, a moderate degree of branching in the pentyl group does not affect the molecular complexity but the effect of pronounced branching on the β-carbon atom is revealed in the *neo*pentyloxide which is dimeric. It seems reasonable to assume that the complex ferric alkoxides arise through covalency-expansion of the ferric atom which is involved in intermolecular bonding with alkoxide oxygen. In this respect ferric alkoxides behave similarly to those of aluminium, titanium, zirconium, hafnium, cerium, thorium, niobium, and tantalum. Furthermore, in each case the *neo*pentyloxide was characterised by abnormal behaviour due to the steric effect of the *neo*pentyloxide group. The comparison between alkoxides of iron and aluminium is especially interesting because these metals have practically the same covalent radius (1·22 Å and 1·26 Å, respectively [6]) and from the stereochemical viewpoint their alkoxides should have similar properties. However, Table 1 shows that the aluminium alkoxides (mol. complexity 4·0) are more polymerised than the ferric compounds (mol. complexity 3·0) and only the *neo*pentyloxides behave the same. It appears from these data that the intermolecular bonding must be stronger in aluminium alkoxides than in the ferric compounds. The data on volatilities are not strictly comparable because the values quoted for the aluminium compounds are b. p.s of liquids whereas the values for the ferric compounds were obtained under different conditions. Nevertheless, it is clear that in ascending the homologous series from methyl to *n*-pentyl there is a much greater change in volatility in the aluminium compounds than in the ferric compounds.

EXPERIMENTAL

The usual precautions [7] were taken to avoid hydrolysis. Ferric chloride was resublimed in nitrogen at 300° immediately before use (Found: Fe, 34·4; Cl, 65·6. Calc. for Fe_2Cl_6: Fe, 34·4; Cl, 65·6%). Iron was determined gravimetrically as ferric oxide after dissolving the sample in dilute nitric acid. Methoxide and ethoxide determinations were carried out by the chromic acid method [8] with a correction for the reduction of ferric iron by iodide in the back titration.

Preparation of Alkoxides by the Ammonia Method.—The detailed preparation of ferric ethoxide is given as typical. Ferric chloride (15 g.), dissolved in benzene (150 g.) and ethyl alcohol (60 g.), was treated with excess of ammonia. After completion of the exothermic reaction the excess of ammonia and solvents were evaporated off under reduced pressure. The residue was extracted with benzene (150 c.c.), and the ammonium chloride filtered off. The filtrate was evaporated to dryness under reduced pressure and gave a viscous brown residue which dissolved in ethyl alcohol (30 c.c.). Dark brown crystals (4·2 g.) of *ferric ethoxide* were slowly deposited [Found: Fe, 29·3; EtO, 70·7. $Fe(OEt)_3$ requires Fe, 29·3; EtO, 70·7%]. The data concerning the other alkoxides prepared by this method are given in Table 2.

TABLE 2.

					Fe (%)	
R in $Fe(OR)_3$	Fe_2Cl_6 (g.)	C_6H_6 (g.)	ROH (g.)	$Fe(OR)_3$ (g.)	Found	Calc.
Me	10·45	120	50·0	6·8 *	37·1	37·5
Pr^n	7·8	150	50·0	4·0	23·9	24·0
Bu^n	11·2	200	50·4	4·7	20·2	20·3
Bu^i	8·0	200	50·0	4·0	20·2	20·3
n-C_5H_{11}	8·0	140	40·0	2·9	17·4	17·6
$Me_2CH{\cdot}CH_2{\cdot}CH_2$	12·5	175	50·0	5·6	17·4	17·6
$MeEtCH{\cdot}CH_2$	11·0	200	39·0	4·9	17·5	17·6

* Found: MeO, 62·6. $Fe(OMe)_3$ requires MeO, 62·5%.

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[6] Sidgwick, " The Chemical Elements and Their Compounds," Oxford, 1950, Vol. 1, p. xxix.

[7] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4204.

[8] Bradley, Halim, and Wardlaw, *J.*, 1950, **3451**.

Preparation of Alkoxides by Alcohol Interchange.—The details of the preparation of ferric *n*-propoxide illustrate the method. Ferric ethoxide (5 g.) was dissolved in benzene (80 g.) and *n*-propyl alcohol (35 g.) and the solution was fractionally distilled. The ethyl alcohol liberated in the reaction was removed as the benzene–alcohol azeotrope and the solution was then evaporated to dryness under reduced pressure. *Ferric* n-*propoxide* (6·08 g.) was obtained as a brown solid [Found: Fe, 23·9. $Fe(OPr)_3$ requires Fe, 24·0%]. The details of the other preparations are given in Table 3. The technique used was that described for the *n*-propoxide except that for ferric methoxide the fractionation procedure was omitted and the mixture of methyl and ethyl alcohols was evaporated off under reduced pressure. The product was repeatedly treated with fresh methyl alcohol until interchange was complete.

TABLE 3.

R in $Fe(OR)_3$	C_6H_6 (g.)	$Fe(OEt)_3$ (g.)	ROH (g.)	$Fe(OR)_3$ (g.)	Fe (%) Found	Calc.
Me	—	5·0	(50 + 50 + 50 + 50)	3·8 *	37·3	37·5
Pr^n	100	4·2	75	5·1	24·2	24·0
Bu^n	80	3·0	58·5	4·2	20·2	20·3
Bu^i	100	3·5	45	4·4	20·2	20·3
Am^n	80	4·9	50	8·1	17·8	17·6

* Found: MeO, 62·7. $Fe(OMe)_3$ requires MeO, 62·5%.

Molecular Weights.—Ebullioscopic measurements were carried out in the all-glass apparatus previously described.[9] The results given in Table 4 were obtained by the earlier method [7] involving the use of a calibration constant for the apparatus. When the ferric alkoxides differed considerably from aluminium alkoxides in molecular complexity some molecular weights were also determined by the more accurate "internal calibration" method.[10] These results are given in Table 5.

TABLE 4.

R in $Fe(OR)_3$	Range of *m* (g.)	Wt. of C_6H_6 (g.)	$\Delta T/m$ (°/g.)	*M*	R in $Fe(OR)_3$	Range of *m* (g.)	Wt. of C_6H_6 (g.)	$\Delta T/m$ (°/g.)	*M*
Me	0·0423—0·2834	18·20	0·351	446·0	Bu^t	0·0476—0·3242	17·92	0·199	824·5
Et	0·0481—0·3110	17·80	0·291	569·5	n-C_5H_{11}	0·0599—0·4612	17·81	0·174	951·0
Pr^n	0·0511—0·2944	18·62	0·226	698·5	$Me_3C{\cdot}CH_2$	0·0349—0·3862	18·00	0·258	634·0
Bu^n	0·0467—0·3146	18·52	0·199	797·0					

TABLE 5.

	Alkoxide		Fluorene		
R in $Fe(OR)_3$	Range of *m* (g.)	$\Delta T/m$ (°/g.)	Range of *m* (g.)	$\Delta T/m$ (°/g.)	*M*
Et	0·0481—0·3110	0·291	0·0031—0·0255	1·002	572
Pr^n	0·0511—0·2944	0·226	0·0046—0·0526	0·954	701
Bu^n	0·0423—0·3060	0·204	0·0216—0·0651	0·985	806

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[9] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.
[10] Bradley, Wardlaw, and Whitley, *J.*, 1956, 5.