836. *Structural Chemistry of the Alkoxides. Part XI.*[1] *Branched-chain Alkoxides of Iron*(III).

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Ferric alkoxides $Fe(OR)_3$, where R = Pr^i, Bu^s, Bu^t, Pr^iMeCH, Pr^nMeCH, Et_2CH, $EtMe_2C$, Et_2MeC, Pr^nMe_2C, or Et_3C, have been prepared. Determinations of molecular weights and volatilities revealed the effect of chain branching of the alkyl group on the physicochemical properties. These results are compared with those on the corresponding aluminium derivatives and some interesting differences in behaviour are apparent.

Recently we reported[1] the preparation and properties of some primary alkoxides of iron(III). The normal alkoxides $Fe(OC_nH_{2n+1})_3$, where n = 1, 2, 3, 4, or 5, were all trimers in boiling benzene (cf. aluminium derivatives, which are tetramers[2]) whereas the *neo*-pentyloxide was dimeric; hence it was clear that a systematic investigation of the effect of chain branching would be interesting. The comparison between the alkoxides of aluminium and ferric iron is particularly so in connection with our stereochemical theory for the alkoxides because of the similarity in atomic size of these elements and their analogous stereochemistry. This should lead to a similarity in degrees of polymerisation for aluminium and ferric alkoxides with the same alkoxide groups.

Accordingly, branched-chain alkoxides of iron have been prepared either by alcohol interchange or by the reaction involving ferric chloride, the alcohol, and ammonia in benzene.

Table 1.

	M = Al[2]			M = Fe		
R in $M(OR)_3$	B. p./5·0 mm.	*M*	*n*	B. p./0·1 mm.	*M*	*n*
Bu^n	270°	962	3·9	171°	873	2·9
Bu^i	—	—	—	173	884·5	3·0
Bu^s	172	580	2·4	159	522	1·9
Bu^t	—	480	1·95	136	412	1·5

Ferric iso*Propoxide.*—This was a dark-brown crystalline solid which sublimed without decomposition at 149°/0·1 mm. and was dimeric in boiling benzene. By contrast aluminium *iso*propoxide, which is trimeric,[2] is considerably more volatile, b. p. 124°/5 mm.[2]

Isomeric Butoxides of Iron.—These were all obtained by alcohol interchange by use of ferric ethoxide[1] and the appropriate alcohol. All except the *tert.*-butoxide were also prepared by the ammonia method with ferric chloride. This method gave a hydrolysed product for *tert.*-butyl alcohol, but a pure product resulted when ferric chloride was replaced by the less reactive pyridinium salt $(C_5H_6N)_3Fe_2Cl_9$. Molecular weights (ebullioscopic in benzene), degree of polymerisation (n), and volatilities are shown in Table 1 which also contains results for some corresponding aluminium alkoxides.[2] The butoxides of iron and aluminium both exhibit the expected decrease in degree of polymerisation and increase in volatility with increased branching of the butyl group. However, the ferric butoxides are uniformly lower in degree of polymerisation than the corresponding aluminium compounds. In fact the *tert.*-butoxide of iron must contain a considerable proportion of monomer. Furthermore, although Mehrotra[2] has demonstrated that aluminium *tert.*-butoxide cannot be obtained by alcohol interchange owing to the formation of the stable mixed alkoxide $Al(OR)(OBu^t)_2$, we find that ferric *tert.*-butoxide can be obtained directly by alcohol interchange.

Isomeric Pentyloxides of Iron.—All these were prepared by alcohol interchange with ferric ethoxide. The derivatives of *n*-, *iso*-, or *sec.*-butylcarbinol (*n*-pentanol, *iso*pentanol,

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[1] Part X, Bradley, Multani, and Wardlaw, *J.*, 1958, 126.

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

or 2-methylbutanol) were also prepared from ferric chloride by the ammonia method. The *tert.*-amyloxide was also obtained by the ammonia method involving the pyridinium ferrichloride. The volatilities, molecular weights (ebullioscopic in benzene), and degrees of polymerisation are in Table 2.

These results show clearly how chain branching affects the degree of polymerisation and consequently the volatility of the isomeric pentyloxides. That this is essentially a steric effect due to the shielding exerted by the alkoxide groups is shown by the behaviour of the *neo*pentyloxide group which forms a derivative similar in physicochemical properties to the secondary pentyloxides. A comparison of the properties of aluminium and ferric pentyloxides is interesting. Although in the primary pentyloxides (and *neo*pentyloxide) the aluminium derivatives have higher degrees of polymerisation, yet in the secondary pentyloxides (and *neo*pentyloxide) the aluminium and iron alkoxides have the same degrees of polymerisation.

TABLE 2.

	M = Al [2]			M = Fe		
R in $M(OR)_3$	B. p./mm.	*M*	*n*	B. p./0·1 mm.	*M*	*n*
Bu^nCH_2 …………	255°/1·0	1152	4·0	178°	952	3·0
Bu^iCH_2 …………	195/0·1	1160	4·0	dec. 200	941	3·0
Bu^sCH_2 …………	~200/0·6	1194	4·1	178	951	3·0
Bu^tCH_2 …………	180/0·8	598	2·1	159	634	2·0
Et_2CH ……………	165/1·0	601	2·1	163	634	2·0
Pr^nMeCH ………	162/0·5	596	2·1	165	602	1·9
Pr^iMeCH ………	162/0·6	572	2·0	162	604	1·9
$EtMe_2C$ …………	—	—	—	131	476	1·5

Again, although Mehrotra [2] found that aluminium *tert.*-amyloxide could not be obtained by alcohol interchange we were able to prepare the ferric derivative by this method and it is clear that the latter has an important proportion of monomer. This led us to explore the possibilities of making a completely monomeric ferric alkoxide by using even larger branched alkyl groups. The ferric derivatives of 3-methylpentan-3-ol, 2-methylpentan-2-ol, and 3-ethylpentan-3-ol were obtained by alcohol interchange on the ethoxide and all were monomeric in boiling benzene. They were dark red liquids boiling at 137°/0·1, 135°/0·1, and 132°/0·1 mm. respectively. To summarise all the available data on aluminium and ferric alkoxides, it seems that in general the aluminium derivative has a higher degree of polymerisation than the corresponding ferric compound. It is tempting to explain this in terms of stronger intermolecular bonding in the aluminium alkoxides but this would cause them to be less volatile than ferric alkoxides, which is contrary to the facts. However, it must be remembered that Mehrotra found " ageing " effects with the aluminium alkoxides and this might vitiate a comparison of their degrees of polymerisation with those of ferric compounds.

EXPERIMENTAL

Apparatus and techniques were similar to those described previously.[1]

Tripyridiniumiron Enneachloride.—A solution of ferric chloride (5·6 g.) in ethyl alcohol (150 c.c.) was saturated with dry hydrogen chloride. Pyridine (7·8 g.) was then added and the solution again saturated with hydrogen chloride. After removal of alcoholic hydrogen chloride under reduced pressure the residue was heated at 120°/0·5 mm. until no more pyridinium chloride was evolved. A yellow-green *solid* remained on cooling [Found: Fe, 16·3; Cl, 46·8. $(C_5H_6N)_3Fe_2Cl_9$ requires Fe, 16·6; Cl 47·5%].

Ferric iso*Propoxide.*—*iso*Propyl alcohol (58·6 g.) was added dropwise to the frozen (*ca.* – 10°) mixture of ferric chloride (11 g.) and benzene (200 g.) with continued cooling. Ammonia was passed in slowly in excess and after storage for 12 hr. at room temperature the volatile components were evaporated off under reduced pressure. The residue of ammonium chloride and ferric *iso*propoxide was extracted with benzene (*ca.* 150 g.) and the *ferric* iso*propoxide* obtained as a dark brown crystalline solid (3·5 g.) after evaporation of the benzene [Found: Fe, 24·2; Pr^iO, 75·6. $Fe(OPr^i)_3$ requires Fe, 24·0; Pr^iO, 76·0%].

Ferric tert.*-Butoxide.*—Pyridiniumferric chloride (15 g.) was suspended in a cold (*ca.* 5°) mixture of benzene (200 g.) and *tert.*-butyl alcohol (50 g.). Ammonia was passed in and the *ferric* tert.*-butoxide* isolated as in the previous experiment. A brown solid (3·4 g.) was obtained. [Found: Fe, 20·2. $Fe(OBu^t)_3$ requires Fe, 20·3%].

Preparation of Other Ferric Alkoxides.—Ferric *alkoxides* were prepared either by the two foregoing methods or by alcohol interchange on ferric ethoxide.[1] The essential data are in Table 3.

TABLE 3.

R in $Fe(OR)_3$	Taken *	C_6H_6 (g.)	ROH (g.)	$Fe(OR)_3$ (g.)	Fe (%) Found	Fe (%) Calc.
Bu^s	5·0 [a]	150	29	2·5	20·1	20·3
Pr^iMeCH	5·0 [c]	80	40·5	8·0	17·4	17·6
Pr^nMeCH	5·0 [c]	80	50	8·1	17·3	17·6
$EtMe_2C$	20·8 [b]	200	50	4·8	17·4	17·6
,, ...	3·0 [c]	100	15·5	4·8	17·5	17·6
Et_2MeC	3·0 [c]	100	12·0	5·6	15·5	15·6
Et_3C	2·8 [c]	100	10·0	4·3	13·6	13·7

* Weight (g.) of (*a*) Fe_2Cl_6, (*b*) $(C_5H_6N)_3Fe_2Cl_9$, or (*c*) $Fe(OEt)_3$.

TABLE 4.

R in $Fe(OR)_3$	*m* (g.)	C_6H_6 (g.)	$\Delta T/m$ (°/g.)	*M* Found	*M* Calc.
Pr^i	0·0213—0·1986	18·0	0·351	466 [a]	232·8
Bu^s	0·0423—0·2226	18·0	0·314	522 [b]	278·4
Et_2CH	0·0481—0·2986	16·3	0·284	634	316·8
Pr^nMeCH	0·0438—0·2831	17·0	0·273	602	316·8
Pr^iMeCH	0·0724—0·3623	18·4	0·252	604	316·8
Me_3C	0·0413—0·2788	16·9	0·422	412	278·4
$EtMe_2C$	0·0410—0·1866	18·3	0·338	476	316·8
Et_2MeC	0·0362—0·1941	16·0	0·513	359	358·8
Pr^nMe_2C	0·0521—0·3621	17·5	0·468	360	358·8
Et_3C	0·0411—0·1882	18·25	0·402	402 [c]	400·8

Found by " internal calibration " method [1] (*a*) *M* = 462, (*b*) *M* = 529, (*c*) *M* = 399.

Molecular Weights.—Measurements were carried out with techniques previously described[3] (Table 4).

One of us (R. K. M.) thanks the Hans Raj College (Delhi University) for study leave.

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[3] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977; Bradley, Wardlaw, and Whitley, *J.*, 1956, 5.