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CALCIUM ALKOXYALANATES

I. SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION

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Summary

Soluble calcium alkoxyalanates, $Ca[AlH_{4-n}(OR)_n]_2$, in which n ranges from 1 to 3, generally complexed with tetrahydrofuran, have been obtained by partial alcoholysis of calcium alanate with various branched aliphatic alcohols and with 2-methoxyethanol in toluene. With a few exceptions X-ray powder diffraction patterns and infrared Al—H absorptions indicate that the calcium alkoxyalanates are individual molecular species.

Introduction

Although calcium alanate was synthesized several years ago [1], the chemistry of its derivatives in which the hydride hydrogens are partly replaced by different ligands has received little attention. Our previous results [2] showed that such substitution by imino groups gives compounds with well defined molecular structures. In contrast with calcium alanate, which is insoluble in solvents other than tetrahydrofuran and monoglyme [3], these compounds were found to be soluble in ether and aromatic hydrocarbons. In the context of our research on the application of aluminum hydride derivatives in polymerization catalysis [4] and the hydrogenation of organic compounds [5], our investigation has been extended to products obtained by partial alcoholysis of calcium alanate by aliphatic alcohols. This paper deals with some of the results.

Results and discussion

A. Reaction of $Ca(AlH_4)_2$ with alcohols

Calcium aluminum hydride, tetrahydrofuran and alcohols react exothermally

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at room temperature according to eq. 1, with formation of calcium alkoxyalanates (CAA):

$$Ca(AlH_4)_2 + 2n\ ROH \rightarrow \underset{(I)}{Ca[AlH_{4-n}(OR)_n]_2} + 2n\ H_2 \qquad n \leqslant 4 \tag{1}$$

The reaction is quite vigorous when either tetrahydrofuran solution or hydrocarbon suspensions of calcium alanate are used. However, the heat and hydrogen evolution can be controlled by the rate of addition of the alcohols to alanate. Various aliphatic alcohols have been used, viz., ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, i-amyl, cyclohexyl, 2-ethylhexyl alcohol and 2-methoxyethanol. The solubility of CAA in aromatic hydrocarbons depends on the size of the alkoxy radicals, their structure, and their number.

In particular:

i) The minimum value of n for obtaining well-soluble products is 1.

ii) For $n \geqslant 1$, except for i-$C_5H_{11}OH$ at $n = 1$, the branched alcohols studied and 2-methoxyethanol give soluble products of composition expected for reaction 1; these products are amorphous or crystalline powdery solids (Table 1). In contrast, linear alcohols give a mixture of soluble and insoluble material even at $n = 2$ (higher values have not been investigated).

Details of the results of the synthesis of calcium bis-, tris- and tetrakis(alkoxy)-alanates are shown in Tables 2, 3 and 4, respectively. The composition of products from branched alcohols and from $CH_3OCH_2CH_2OH$ generally agrees with the formation of CAA complexes with tetrahydrofuran; exceptionally, i-$C_5H_{11}OH$ at $n = 2$ and $CH_3OCH_2CH_2OH$ at $n = 1.5$ and 2 give compounds with no tetrahydrofuran. All these products are stable up to ca. 150°C, and are soluble in aromatic, hydrocarbons and ethereal solvents. They have received most of our attention up to now. The mixtures of soluble and insoluble material obtained from linear alcohols, and evidently arising from disproportionation, were not further characterized.

Derivatives from branched alcohols with lower hydride hydrogen content ($n = 2.5$ and 3 in I), as well as the corresponding completely substituted alkoxy

(continued on p. 6)

TABLE 1

PHYSICAL STATE [a] OF COMPOUNDS $Ca[AlH_{4-n}(OR)_n]_2 \cdot x$THF OBTAINED BY ALCOHOLYSIS OF CALCIUM ALANATE

R	$n = 1$		$n = 1.5$		$n = 2$		$n = 3$		$n = 4$	
	x	X-ray analysis	x	X-ray analysis	x	X-ray analysis	x	X-ray analysis	x	X-ray analysis
i-C_3H_7	1	A	1	A	1	A	1	A	0	XX
i-C_4H_9	1	XX	1	XX [b]	1	A	1	A	1	A
t-C_4H_9	1.5	A	2	A	1	XX	1	XX	1	XX
i-C_5H_{11}	—	—	—	—	0	A	—	—	—	—
C_6H_{11}	3	A	1	XX	1	XX	0	XX	1	XX
$CH_3OCH_2CH_2$	0.5	XX	0	XX	0	XX	0	XX	0	[c]

[a] Based on X-ray powder pattern: A = amorphous; XX = crystalline. [b] Slightly crystalline. [c] Sticky liquid.

TABLE 2

RESULTS OBTAINED IN THE SYNTHESIS OF CALCIUM BIS(ALKOXY)ALANATES FROM VARIOUS ALCOHOLS [a]

Run	$Ca(AlH_4)_2$ (mmol)	ROH (mmol)	Toluene (ml)	Time (h)	Chemical composition, Found (calcd.) [b]				
					Al (%)	Ca (%)	$H_{act.}$ [c]	Ca/Al (atomic ratio)	$H_{act.}$/Al (atomic ratio)
1	15.7	i-C_3H_7OH (31.4)	100	1	18.2 (18.6)	13.1 (13.8)	19.6 (20.8) [d]	0.48 (0.50)	2.91 (3.00)
2	20.0	i-C_4H_9OH (40.0)	100	2	18.3 (16.9)	13.2 (12.6)	19.7 (19.0) [d]	0.49 (0.50)	2.90 (3.00)
3	14.5	t-C_4H_9OH (29.0)	100	1	14.7 (15.4)	11.2 (11.4)	16.7 (17.3) [e]	0.51 (0.50)	3.07 (3.00)
4	15	i-$C_5H_{11}OH$ (30.0)	100	1	—	—	—	0.70	3.56
5	15	$C_6H_{11}OH$ (30.0)	100	1	11.0 (10.5)	8.0 (7.8)	11.4 (11.7) [f]	0.49 (0.50)	2.80 (3.00)
6	15.0	$CH_3OCH_2CH_2OH$ (30.9)	80	1	17.9 (18.8)	14.0 (14.0)	19.7 (21.1) [g]	0.53 (0.50)	2.97 (3.00)

[a] The drip rate of alcohols in toluene solution into stirred toluene suspension of $Ca(AlH_4)_2 \cdot 4$ THF was controlled so as to maintain the reaction temperature in the range 20°C (initial) to 40°C. [b] Analysis of soluble products. Except for runs 6 (ca. 75% yield) and 4, the yield was practically quantitative. [c] $H_{act.}$ indicates hydride hydrogen content as meq/g. [d] Calcd. for $Ca[AlH_3(OR)]_2 \cdot$ THF. [e] Calcd. for $Ca[AlH_3(OR)]_2 \cdot 1.5$ THF. [f] Calcd. for $Ca[AlH_3(OR)]_2 \cdot 3$ THF. [g] Calcd. for $Ca[AlH_3(OR)]_2 \cdot 0.5$ THF.

TABLE 3

RESULTS OBTAINED IN THE SYSTHESIS OF CALCIUM TRIS(ALKOXY)ALANATES FROM VARIOUS ALCOHOLS [a]

Run [b]	$Ca(AlH_4)_2$ (mmol)	ROH (mmol)	Toluene (ml)	Time (h)	Chemical composition. Found (calcd.)					Molecular weight [d]	Association degree [d]
					Al (%)	Ca (%)	$H_{act.}$ [c]	Ca/Al (atomic ratio)	$H_{act.}$/Al (atomic ratio)		
1	25.6	i-C_3H_7OH (76.8)	200	2	15.9 (15.5)	11.9 (11.5)	13.7 (14.5) [e]	0.50 (0.50)	2.32 (2.50)	n.d.	
2	10.6	n-C_4H_9OH (31.8)	100	5	—	—	—	0.79 (0.50)	2.86 (2.50)	—	
3	30	i-C_4H_9OH (90)	200	2	13.2 (13.8)	10.0 (10.3)	12.0 (12.9) [e]	0.51 (0.50)	2.43 (2.50)	700 (390.5) [e]	1.79
4	9.8	t-C_4H_9OH (29.4)	100	5	11.9 (11.7)	8.7 (8.7)	10.9 (10.9) [f]	0.49 (0.50)	2.47 (2.50)	395 (462.6) [f]	0.85
5	9.9	$C_6H_{11}OH$ (29.7)	100	5	9.8 (10.0)	7.5 (7.4)	9.1 (9.3) [e]	0.51 (0.50)	2.50 (2.50)	530 (540.7) [e]	0.98

[a] The drip rate of alcohols in toluene solution into stirred toluene suspension of $Ca(AlH_4)_2 \cdot 4\ THF$ was controlled so as to maintain the reaction temperature in the range 20°C (initial) to 40°C. [b] Analysis of soluble products. Except for run 2, the yield was practically quantitative. [c] $H_{act.}$ indicates hydride hydrogen content as meq/g. [d] Measured by ebulliometry in diethyl ether. [e] Calcd. *for* $CaAl_2H_5(OR)_3 \cdot THF$. [f] Calcd. *for* $CaAl_2H_5(OR)_3 \cdot 2\ THF$.

TABLE 4

RESULTS OBTAINED IN THE SYNTHESIS OF CALCIUM TETRAKIS(ALKOXY)ALANATES FROM VARIOUS ALCOHOLS [a]

Run [b]	$Ca(AlH_4)_2$ (mmol)	ROH (mmol)	Toluene (ml)	Time (h)	Chemical composition. Found (calcd.)					Molecular weight [d]	Association degree [d]
					Al (%)	Ca (%)	$H_{act.}$ [c]	Ca/Al (atomic ratio)	$H_{act.}$/Al (atomic ratio)		
1	21	n-C_3H_7OH (84)	180	5	—	—	—	0.79 (0.50)	2.33 (2.00)	—	
2	26.1	i-C_3H_7OH (104.4)	200	2	12.9 (13.3)	10.0 (9.9)	8.9 (9.9) [e]	0.52 (0.50)	1.86 (2.00)	420 (406.5) [e]	1.03
3	11.1	n-C_4H_9OH (44.4)	200	2	—	—	—	0.78 (0.50)	2.36 (2.00)	—	
4	36	i-C_4H_9OH (144.0)	200	2	11.4 (11.7)	8.6 (8.7)	7.9 (8.7) [e]	0.51 (0.50)	1.87 (2.00)	630 (462.6) [e]	1.36
5	23.5	t-C_4H_9OH (94)	150	6	11.2 (11.7)	8.1 (8.7)	8.6 (8.7) [e]	0.49 (0.50)	2.07 (2.00)	454 (462.6) [e]	0.98
6	27.2	i-$C_5H_{11}OH$ (108.8)	150	3	11.9 (12.1)	9.5 (9.0)	8.7 (9.0) [f]	0.54 (0.50)	1.97 (2.00)	n.d.	
7	26.5	$CH_3(CH_2)_3OH$ $(C_2H_5)CH_2OH$ (106)	180	2	—	—	—	0.51 (0.50)	1.82 (2.00)	—	
8	45.2	$C_6H_{11}OH$ (180.8)	280	6	9.5 (9.5)	7.0 (7.1)	7.1 (7.1) [e]	0.50 (0.50)	2.02 (2.00)	588 (566.8) [e]	1.04
9	57.7	$CH_3OCH_2CH_2OH$ (230.8)	230	2	13.4 (13.5)	9.5 (10.1)	9.8 (10.1) [f]	0.48 (0.50)	1.97 (2.00)	506 (398.4) [f]	1.27

[a] The drip rate of alcohols in toluene solution into stirred toluene suspensions of $Ca(AlH_4)_2 \cdot 4$ THF was controlled so as to maintain the reaction temperature in the range 20°C (initial) to 40°C. [b] Analysis of soluble products. Except for runs 6 (75% yield), 1 and 3, the yield was practically quantitative. [c] $H_{act.}$ indicates hydride hydrogen content as meq/g. [d] Measured by ebulliometry in diethyl ether. [e] Calcd. for $Ca[AlH_2(OR)_2]_2 \cdot$ THF. [f] Calcd. for $Ca[AlH_2(OR)_2]_2$.

compounds, were also prepared from $Ca(AlH_4)_2 \cdot 4$ THF in toluene, according to reaction 1, mainly in order to correlate their physicochemical properties with those of the compounds given in Tables 2—4. However, each is completely soluble in aromatic hydrocarbons and ethereal solvents.

B. Physicochemical characterization

Among the possible substituted derivatives from alanates of Group IA and IIA metals, only alkali metal alkoxyalanates have received much attention in recent years, and this was directed towards their use in stoichiometric hydrogenation of organic molecules [6]. Little attention has been given to establishing their chemical structures.

Some years ago, X-ray and IR measurements were reported [7] which led to the general conclusion that solid products obtained from the partial alcoholysis of lithium, sodium, potassium and caesium alanates by methyl, ethyl, i-propyl and t-butyl alcohols consist of mixtures of the starting alanate $MAlH_4$ and the completely substituted $MAl(OR)_4$; in solution complexes between these two compounds were assumed to exist. However, alkali tris(t-butoxy)alanates, $MAlH(O{-}t{-}C_4H_9)_3$, are individual molecular species. Further studies of the intensity of ν(Al—H) stretching vibration bands (1900—1600 cm^{-1}) have revealed [8] that the usual preparations of $NaAlH_2(OCH_2CH_2OCH_3)_2$ by alcoholysis of $NaAlH_4$ do not give a single product, but rather an equilibrium mixture whose additional components are $NaAlH_4$, $NaAlH(OCH_2CH_2OCH_3)_3$ and possibly $NaAl(OCH_2CH_2OCH_3)_4$.

Even for the simpler alkoxyalanes $[AlH_{3-n}(OR)_n]_x$ ($R = CH_3, C_2H_5, i\text{-}C_3H_7, n\text{-}C_4H_9$; $n = 1, 2, 3; x \geqslant 2$), Nöth and Suchy [9] found that the stability of monoalkoxyalanes towards disproportionation into AlH_3 and $(RO)_2AlH$ decreases as the carbon chain of the alkyl group becomes more and more branched at the α-C atom, while the stability of dialkoxyalanes increases in the reverse order. These findings suggested a study of the chemical individuality of the CAA obtained from branched alcohols. Although crystals of CAA derived from t-butanol or cyclohexanol can be readily obtained by crystallization of tetrahydrofuran or dioxane solutions, our attempts to obtain single crystals for X-ray determinations were unsuccessful. Thus we turned to indirect physicochemical data of solid products and their solutions.

B.1. X-Ray powder analysis. Approximately half of the samples analyzed show crystalline phases (Table 1). Details of the powder patterns together with those of $Ca(AlH_4)_2 \cdot x$ THF ($x = 1, 4$) are listed in Table 5. It is important to note that the X-ray patterns of the alkoxy derivatives show that no calcium alanate complexes are present. Moreover, derivatives of the same alcohol at different degrees of alcoholysis differ essentially from one another. Although the results are not conclusive, they support the existence of solid CAA as individual compounds. In two cases however, viz. $Ca[AlH_{4-n}(O{-}t{-}C_4H_9)_n]_2 \cdot$ THF ($n = 2$, 3) and $Ca[AlH_{4-n}(OCH_2CH_2OCH_3)_n]_2$ ($n = 1, 1.5$), analytically different compounds from the same alcohol show very similar X-ray patterns, which casts some doubt with regard on their individuality even though there is no other evidence for disproportionation or decomposition.

B.2. IR analysis. It is well known [10] that the infrared spectra of aluminum hydride derivatives show strong Al—H stretching vibration bands in the range

TABLE 5

X-RAY POWDER DIFFRACTION PATTERNS (*d* SPACINGS, Å)

a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*l*	*m*	*n*
6.42vw	8.50ms	10.40vs	9.61s	14.49	12.11s	11.41s	11.79s	11.79vs	10.40vs	8.84w	8.84vs
5.79s	7.28ms	8.67w	7.76vs	12.81m	10.40vs	10.05vs	10.28vs	10.40vs	9.21m	7.37vs	7.76w
5.07w	6.56m	7.37s	6.07vs	11.41mw	9.36vs	8.80m	8.98m	9.31vs	8.23vs	6.28w	6.26vs
4.72m	5.91m	6.73m	4.79s	9.93s	8.01s	8.23m	6.32w	8.27ms	6.73w	5.28m	5.39w
4.60m	4.86mw	5.40vm	4.55m	9.02vs	7.37m	7.37m	5.05w	7.53m	6.13s	4.33m	4.93w
4.21mw	4.62w	5.14m	4.11s	8.04vs	6.28m	6.56m	4.71w	6.81m	5.57vw	4.13w	4.56w
3.95mw	4.44w	4.73w	3.90m	8.01s	5.61m	6.28m	4.33s	6.00m	5.08m	3.75vw	4.35w
3.69m	4.23s	4.52w	3.61m	6.56m	4.99s	5.72m	4.04mw	5.28s	4.57vw	3.34ms	4.13m
3.51m	3.90m	4.37w	3.20w	6.15w	4.76vs	5.21m	3.85mw	4.90vs	4.33s	2.83w	3.92s
3.41ms	3.72w	4.20m	3.04m	5.89w	4.44m	4.95s	3.06w	4.55s	4.11s	2.64mw	3.71m
3.29ms	3.42w	3.99w	2.94m	5.44mw	4.16vw	4.57m	2.95w	4.30vs	3.85m	2.49mw	3.56w
3.17ms	3.28m	3.63ms	2.82w	5.13vw	3.88s	4.32ms	2.82vw	4.09s	3.66w	2.36w	3.39m
3.04w	3.17w	3.28m	2.69w	4.82m	3.66m	4.02ms	2.72vw	3.84m	3.51w	2.25vw	3.13s
2.90s	3.01m	3.17w	2.54vw	4.56s	3.37vw	3.75w	2.63vw	3.71m	3.35vw	2.07w	2.92m
2.80s	2.88w		2.47m	4.25m	3.26w	3.49mw		3.52m	3.24s		2.81vw
2.64vw	2.77m		2.40w	4.10m	3.11m	2.88vw		3.37w	3.08m		2.71w
2.54w	2.64m		2.30w	3.89m	2.93w	2.73w		3.27w	2.82m		2.50w
1.99m	2.52w		2.21m	3.72w	2.76w	2.64vw		3.11m	2.65m		2.46vw
	2.45vw		2.12w	3.51m	2.67w	2.56vw		3.00m	2.55vw		2.39w
	2.35w		2.04w	3.28mw	2.58w			2.87w	2.47vw		2.25w
	2.29vw		1.96w					2.76w	2.41w		2.14w
			1.93w					2.66m	2.33vw		2.06w
			1.87w					2.57vw	2.28m		2.01vw
			1.81w					2.49m	2.19vw		1.94vw
								2.39w	2.08w		1.89vw
								2.29mw	1.94w		1.85vw
									1.86w		1.80vw
									1.81w		1.76w
									1.76w		1.70vw

[a] $Ca(AlH_4)_2 \cdot THF$. [b] $Ca(AlH_4)_2 \cdot 4\ THF$. [c] $Ca(AlH_3O\text{-}i\text{-}C_4H_9)_2 \cdot THF$; [d] $Ca[AlH(O\text{-}t\text{-}C_4H_9)_3]_2 \cdot THF$; [e] $Ca[Al(O\text{-}t\text{-}C_4H_9)_4]_2 \cdot THF$; [f] $Ca[AlH_{2.5}(O\text{-}c\text{-}C_6H_{11})_{1.5}]_2 \cdot THF$; [g] $Ca[AlH_2(O\text{-}c\text{-}C_6H_{11})_2]_2 \cdot THF$; [h] $Ca[AlH(O\text{-}c\text{-}C_6H_{11})_3]_2$; [i] $Ca[Al(O\text{-}c\text{-}C_6H_{11})_4]_2 \cdot THF$; [l] $Ca[AlH_{2.5}(OCH_2CH_2OCH_3)_{1.5}]_2$; [m] $Ca[AlH_2(OCH_2CH_2OCH_3)_2]_2$; [n] $Ca[AlH(OCH_2CH_2OCH_3)_3]_2$.

1900—1600 cm^{-1}, which give information about the environment of the aluminum atoms bonded to hydride hydrogens. Table 6 lists infrared ν(Al—H) absorptions in Nujol and in tetrahydrofuran observed for calcium-alkoxyalanates $Ca[AlH_{4-n}(OR)_n]_2 \cdot x$ THF with different values of n derived from various alcohols. It can be seen that:

i) For $n = 1.5$ and 2 (other values of n were not studied in Nujol), the same compound shows different absorptions in Nujol and in tetrahydrofuran. However, the absorptions of $Ca[AlH_2(OCH_2CH_2OCH_3)_2]_2$ are the same in both cases.

ii) For equal values of n, the IR spectra are very similar in THF in the range of Al—H absorptions, independent of the nature of R. For $n = 1$ they are characterized by a principal band at ca. 1740—1710 cm^{-1}, with a shoulder at ca. 1780—1750 cm^{-1}; other minor absorptions may be seen at lower frequencies. For $n = 1.5$ the intensity of the shoulder increases, while absorptions at frequencies lower than the principal band almost disappear. For $n = 2$ the two absorptions at 1790—1755 cm^{-1} and ca. 1745—1710 cm^{-1} are of comparable intensity; there is no evidence for other ν(Al—H) absorptions.

As n increases further, the intensity of the second absorption decreases, until for $n = 3$ only one absorption is observed at ca. 1790—1760 cm^{-1}. These changes of the IR Al—H absorptions with variation of the value of n are shown more clearly in Fig. 1.

TABLE 6

INFRARED ν(Al—H) (cm^{-1}) ABSORPTIONS OF $Ca[AlH_{4-n}(OR)_n]_2 \cdot x$THF [a] COMPOUNDS IN NUJOL OR TETRAHYDROFURAN [b]

R	Nujol		Tetrahydrofuran				
	$n = 1.5$	$n = 2$	$n = 1$	$n = 1.5$	$n = 2$	$n = 2.5$	$n = 3$
$i\text{-}C_3H_7$	1776 * 1745(sh) 1695—1585	1780 1750 *	1760(sh) 1720 * 1687(sh) 1605(sh)	1755 1715 * 1600(sh)	1758 1715	1757 * 1713	1757
$i\text{-}C_4H_9$	1858(sh) 1787 1751 * 1695—1610	1857 1785(sh) 1751 *	1780(sh) 1742 * 1622	1775 1740 *	1774 1740	1765 1725	1774
$t\text{-}C_4H_9$	1770 1736 1695—1610	1779 * 1732(sh) 1680—1585	1754(sh) 1713 *	1756 1714 *	1755 1710	1756 * 1712	1758
$i\text{-}C_5H_{11}$		1748			1773 1732		1780
C_6H_{11}	1838 1770 1729 *	1842 1736 * 1716	1780(sh) 1740 * 1625(sh)	1785 1740 *	1790 1745	1790 * 1748	1790
$CH_3(CH_2)_3CH\text{-}(C_2H_5)CH_2$		1859 1789 1759 * 1695—1550			1770 1730		
$CH_3OCH_2CH_2$		1767 1715	1755(sh) 1715 *		1770 1725		1773

[a] For the values of x see Table 1. [b] Asterisks indicate considerably stronger bands.

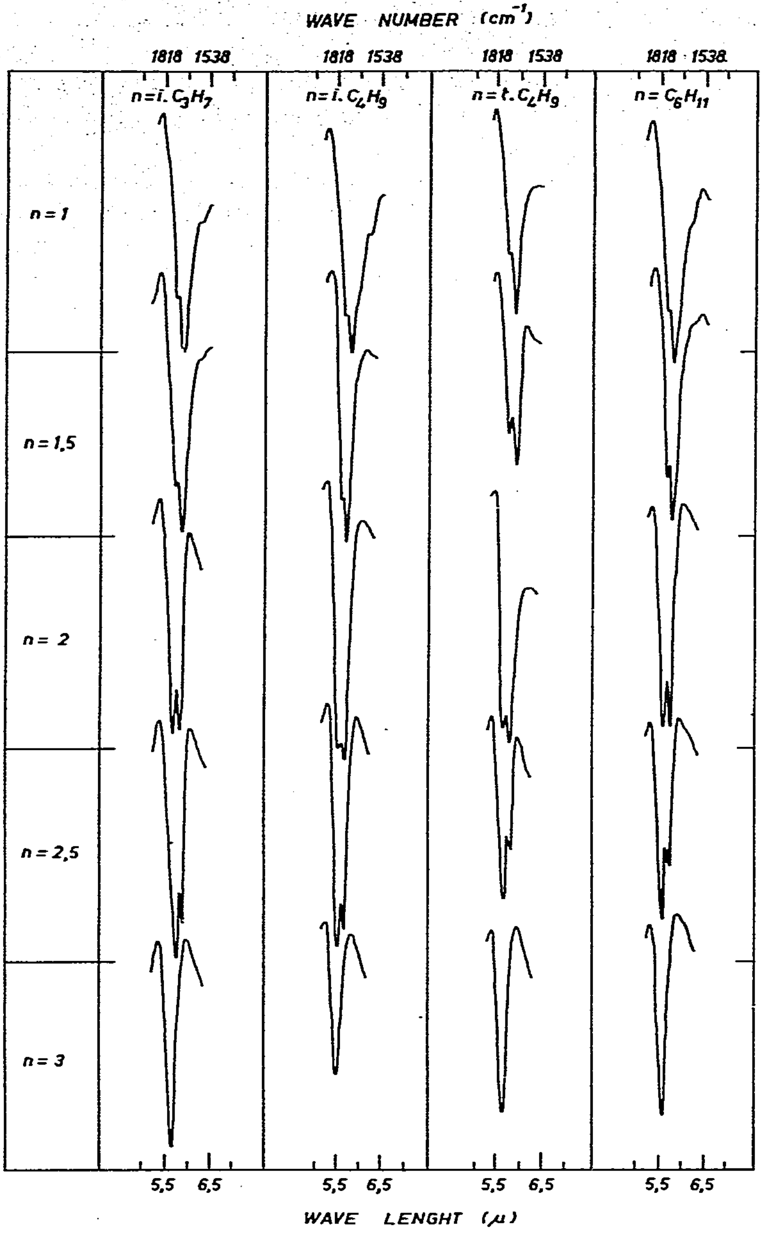


Fig. 1. Infrared ν(Al—H) (cm^{-1}) absorptions of $Ca[AlH_{4-n}(OR)_n]_2$ in tetrahydrofuran.

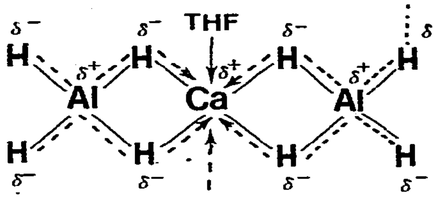
In our opinion these results support the following conclusions:

i) Up to $n = 2.5$, individual CAA contain Al—H bonds with different electronic densities.

ii) The different absorptions in Nujol indicate different molecular rearrangements for different tris- or tetrakis(alkoxy)alanates. The tendency of calcium to hexacoordination, as found for other substituted calcium alanate compounds [2], could be responsible for various inter and/or intramolecular Ca—OR—AlH bridges, depending, for example, on the steric requirements of the alkoxy radical.

iii) In THF, for the same *n*, different CAA have the same molecular rearrangement despite the steric features of the alkoxy radicals, because of the contribution of solvent molecules to hexacoordination of the calcium atom.

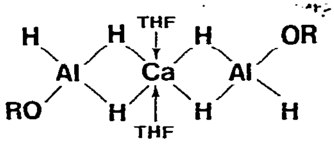
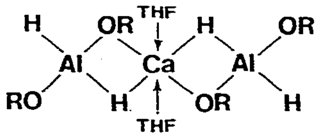
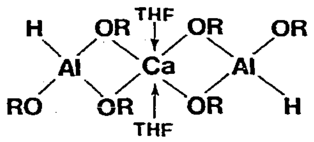
The infrared spectrum in Nujol of calcium alanate monotetrahydrofuranate [11] shows two ν(Al—H) absorptions at 1742 and at 1800 cm^{-1} corresponding to the internal and external hydride hydrogens in II. Therefore, the principal ν(Al—H) absorptions at lower and at higher frequency for different CAA may be quite reasonably assigned to Ca—H—Al bridges and to terminal Al—H bonds, respectively. The absorptions near 1600 cm^{-1} in less substituted derivatives can be attributed to Al—H—Al bonds [10]. On this basis the structures of Table 7 are suggested for CAA from branched aliphatic alcohols, as *n* increases, the



(II)

TABLE 7

SUGGESTED MOLECULAR STRUCTURES FOR $Ca[AlH_{4-n}(OR)_n]_2$ IN TETRAHYDROFURAN

Compound	Infrared absorption ν(Al—H) in THF (cm^{-1})	Suggested structure
$Ca[AlH_3(OR)]_2$	ca. 1780—1750 ca. 1740—1710	
$Ca[AlH_2(OR)_2]_2$	ca. 1790—1755 ca. 1745—1710	
$Ca[AlH(OR)_3]_2$	ca. 1790—1760	

decrease of the Al—H absorption at lower frequency (Fig. 1) would correspond to the disappearance of Al—H—Ca bonds. Possibly because of complexation of calcium atoms by O—CH_3 groups, calcium tetrakis(2-methoxyethoxy)alanates may have the same structure in Nujol and THF.

Experimental

Reagents and solvents

$Ca(AlH_4)_2$ was prepared, as previously described [12], by published methods [1]. Commercially supplied pure alcohols were dried over molecular sieves and/or over CaH_2 and distilled. All solvents were purified and dried by standard methods, and all the syntheses and physicochemical characterizations were performed under nitrogen.

Chemical analyses and physicochemical measurements

The chemical analyses of aluminum and calcium were performed on solutions obtained by decomposition of weighed samples with diluted aqueous acid solutions. The aluminum content was determined by the EDTA-$ZnSO_4$ method. After complexation of aluminum with triethanolamine, direct titration by EDTA at $pH > 12$ gave the calcium content. The hydride hydrogen content was determined by the measurement of hydrogen liberated upon decomposition of a weighed sample with small amounts of n-octyl alcohol and then with aqueous 50% H_2SO_4 in a flask directly connected to the gas volumetric apparatus.

X-ray powder diffraction data were obtained on a Philips X-ray unit using a 114.6 mm Debye camera with nickel-filtered Cu $K_{\bar{\alpha}}$ radiation ($\lambda = 1.5418$ Å). Samples were sealed in 0.5 mm capillaries under dry nitrogen and exposed to X-ray radiation for a mean time of 6 h. d spacings were evaluated from the 4θ (Cu $K_{\bar{\alpha}}$) measured by using an optical device, and line intensities were estimated visually.

IR spectra were recorded on a Perkin-Elmer model 157 spectrometer.

Syntheses of calcium alkoxyalanates

In addition to the data of Tables 2—4, a typical preparation is described in detail.

Calcium tetrakis(i-propoxy)alanate tetrahydrofuran. A solution of i-propyl-alcohol (104.4 mmol) in toluene (50 ml) was added dropwise to a stirred suspension of $Ca(AlH_4)_2 \cdot 4$ THF (26.1 mmol) in toluene (150 ml). An exothermic reaction started accompanied by hydrogen evolution as soon as the addition had begun. The temperature was kept below 40°C by controlling the rate of addition of the alcohol. The mixture was stirred for another 2 h, then filtered to remove traces of an insoluble material, and the solvent was removed in vacuo. The solid white residue was dried at room temperature (ca. 4 h) under vacuum (1×10^{-2} Torr) and analyzed. (Found: Al, 12.9; Ca, 10.0%; $H_{act.}$ 8.9 meq/g. $C_{16}H_{40}Al_2CaO_5$ calcd.: Al, 13.3; Ca, 9.9%; $H_{act.}$ 9.9 meq/g). The yield was quantitative.

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