INFRARED SPECTRA OF TETRAALKYLALUMINIUM COMPLEXES

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INTRODUCTION

The chemical behaviour of aluminium complexes is influenced to a considerable extent by the existence of a free unfilled orbital in the aluminium atom, due mostly to the sp^3 hybridization, which results in an almost tetrahedral structure for tetravalent aluminium orbitals. The presence of a low-energy orbital in aluminium leads in the case of tri-*n*-alkylaluminium compounds to their dimerization *via* electron-deficient bonds[1]; if the aluminium alkyls can accept an unshared electron pair of another molecule the formation of electron-donor co-ordination complexes takes place. One group of co-ordination complexes comprises a number of compounds in which aluminium co-ordinates with negatively-charged particles thus forming complex tetra-substituted anions with aluminium as the central atom. The compounds of the $MAlX_4$ and $MAlH_4$ types (M is an alkali metal, X a halogen) where ionic structures with AlX_4^- (ref. 2) and AlH_4^- anions are present, are included in this group. The compounds of the $MAlR_4$ type, which are studied in this paper, belong to the same group and it may be assumed that they will also have an ionic structure with AlR_4^- anions. This hypothesis is supported by the fact that complete series of mixed complexes containing both alkyls and halides[3,4,5] or hydrides, *e.g.*, $MAlR_nH_{4-n}$[6], have been prepared. Nevertheless, tetraalkyl complexes differ from others in their size, complexity and the electronegativity of the co-ordinated groups so that, *a priori*, the possible formation of other structures, *e.g.*, bridge structures, is not excluded. The aluminium tetraalkyl compounds were first prepared by Baker and Sisler[7] and Zakharkin and Gavrilenko[6] using the reaction of alkali-metal alkyls or pure alkali-metals with trialkylaluminium. Dickson and West[8] have recently used these compounds as alkylating agents, but up to the present no attention has been given to their structure. The only information regarding these compounds was published by Hein *et al.*[9], who found high electrical conductivities in solutions of alkali-metal alkyls in triethylaluminium even at a ratio of the components corresponding to the formation of the compound, $NaAl(C_2H_5)_4$. By evaluating the transfer numbers they concluded that the alkali-metal cations and complex anions were the conducting particles. In this paper, the infrared spectra of the tetraalkyl compounds are studied both in the crystal lattice and in ether solution in order to obtain information on their structure.

EXPERIMENTAL

$LiAl(C_2H_5)_4$ and $NaAl(C_2H_5)_4$ were prepared using the method of Zakharkin[6] by boiling triethylaluminium with Li or Na in benzene medium. The complexes were precipitated as white crystals after concentrating and cooling the solutions; the crystals were washed with heptane and dried *in vacuo*. $LiAl(CH_3)_4$ was prepared by boiling trimethylaluminium and Li in ethyl ether. After removing most of the ether by distillation, the white flocks obtained were washed with hexane and dried at an elevated temperature to remove ether completely[6]. $NaAl(CH_3)_4$ was prepared by boiling trimethylaluminium with Na in tetrahydrofuran (THF). The solid complex, $NaAl(CH_3)_4 \cdot THF$, obtained was decomposed *in vacuo* at a temperature near 100° and the white powder of $NaAl(CH_3)_4$ was sealed into ampoules. All operations connected with the preparation and separation of these compounds were carried out in a nitrogen atmosphere, as they react vigorously with oxygen and water.

Infrared spectra were measured with a UR-10 Zeiss spectrometer. Solid samples of complexes were prepared using Nujol techniques in a nitrogen atmosphere; ethyl ether solutions were measured in KBr cuvettes. The cuvettes were connected to an all-glass apparatus during their filling to exclude air.

RESULTS AND DISCUSSION

The infrared spectra of the substances in the region 400–1500 cm^{-1} are shown in Figs. 1 and 2; the wave numbers are given in Table 1.

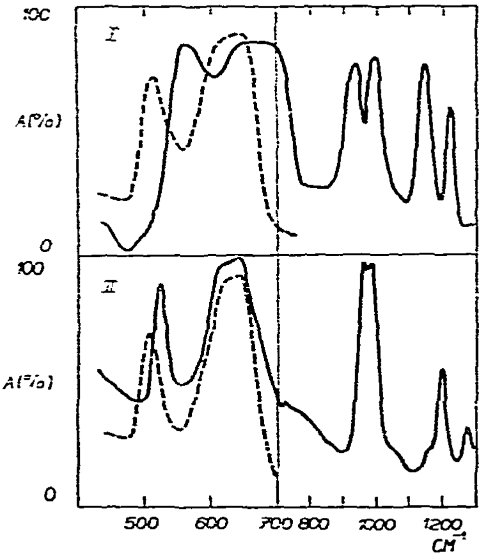


Fig. 1. Infrared spectra of: (I), $NaAl(C_2H_5)_4$; (II), $LiAl(C_2H_5)_4$. ——, Nujol mull; – – –, ethyl ether solution in 0.4 mm KBr cuvette.

The structures of these compounds may be interpreted in three ways which take into consideration the different possible deformations of the tetrahedral anion.

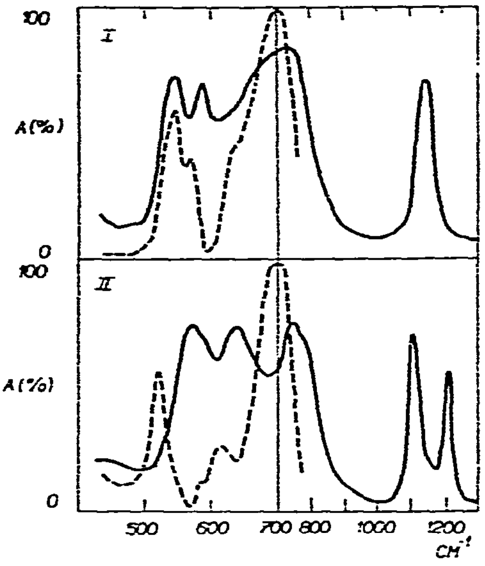
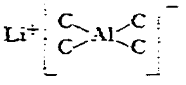
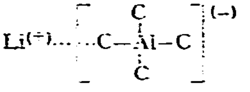
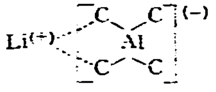


Fig. 2. Infrared spectra of: (I), $NaAl(CH_3)_4$; (II), $LiAl(CH_3)_4$. ——, Nujol mull; – – –, ethyl ether solution in 0.4 mm KBr cuvette.


(I)


(II)


(III)

A weak bond Li···C is assumed in structures (II) and (III), which may deform the tetrahedral structure to a less symmetrical one. The high electrical conductivities measured[9] do not agree with the normal bridge electron-deficient bond Li···C···AlC_3 and, as it will appear later, neither does the relative simplicity of the spectrum in the region 400–700 cm^{-1}. This skeleton would constitute a rare case of a strong electron-deficient bond between two metals of different electronegativities and it should exhibit four absorption bands in the region mentioned. Structure (I) assumes a tetrahedral anion, which may give rise to one valence vibration of the skeleton, $\nu_1(F_2)$, in the infrared spectrum. Structure (II) should have C_{3v} symmetry and three valence vibrations of the skeleton $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(E)$, which would appear in the infrared spectrum. Structure (III) should have C_{2v} symmetry with two valence vibrations $\nu_1(B_1)$, $\nu_2(B_2)$, which are expected to coincide with $\nu_3(A_1)$ and $\nu_4(A_2)$. The criterion for the analysis of the infrared spectra will be first of all the number of absorption bands in the region of valence vibrations of structures (I)–(III), which should be found in the range 400–800 cm^{-1} (*cf.* trimethyl- and triethylaluminium spectra in ref. 10). A very strong CH_3-rocking vibration band of the methyl derivative, and a very strong CH_2-rocking vibration band of the ethyl derivatives may be expected in the regions slightly above and below 700 cm^{-1}, respectively. In the region above 800 cm^{-1} C–C and C–H vibrations of methyl and ethyl groups will then appear, and these are affected only slightly by the nature of the neighbouring metal (see infrared spectra of the tetramethyl and tetraethyl derivatives of the elements of Group IV A in refs. 11, 12). Measurements in the region above 800 cm^{-1} were made only on samples

TABLE I

INFRARED SPECTRA OF TETRAALKYLALUMINIUM COMPLEXES IN NUJOL MULL AND ETHYL ETHER SOLUTIONS

Assignment and symmetry group		$LiAl(C_2H_5)_4$		$NaAl(C_2H_5)_4$		$LiAl(CH_3)_4$		$NaAl(CH_3)_4$	
T_d	C_{2v}	*nujol*	*ether soln.*	*nujol*	*ether soln.*	*nujol*	*ether soln.*	*nujol*	*ether soln.*
ν_1 (F_2)		526 *s*	508 *s*	565 *vs*	512 *s*		525 *s*		546 *s*
	ν_1 (B_1)					575 *s*		550 *s*	
	ν_2 (B_2)					636 *s*		594 *s*	
CH_2-rocking		615 *sh*	640 *vs, b*	665 *vs, b*	640 *vs, b*				
		640 *vs*					585 *w*		570 *m*
							620 *m*		630 *sh, w*
CH_3-rocking		—		920 *sh, w*		748 *vs, b*	708 *vs, b*	680 *sh*	710 *vs, b*
						770 *sh*		755 *vs, b*	
C-C-stretching		960 *s*		936 *s*					
CH_2-twisting		985 *s*		990 *s*					
CH_2-wagging		1194 *m*		1147 *s*					
		1277 *w*		1220 *m*					
CH-bending		—		1426 *m*		1110 *s*		1140 *s*	
						1210 *s*			

Alkyl vibrations are assigned according to ref. 12.

prepared by the Nujol techniques; in ether solution this region was covered with very strong ether bands.

$LiAl(C_2H_5)_4$

There are essentially two strong bands in the spectra obtained both in ether solution and Nujol mull in the region of the skeletal valence vibrations considered (Fig. 1). The band at 640 cm^{-1} is very broad and is situated in the region where CH_2-rocking vibrations are expected so that it may be ascribed to this vibration. CH_2-rocking vibrations may be found in most aluminium ethyl derivatives in the same region: triethylaluminium and diethylaluminium halides at 625 cm^{-1}, $LiAl(C_2H_5)Cl_3$ at 625 cm^{-1} and diethylaluminium fluoride at 615 cm^{-1} (ref. 13). Absorption bands of CH_2-rocking vibration are usually very broad and even in substances with a regular structure, *e.g.*, in $(C_2H_5)_4Sn$ and $(C_2H_5)_4Pb$ this vibration may be revealed by very strong broad bands which are split into two maxima (667, 680 cm^{-1} and 674, 656 cm^{-1})[12]. The maximum of this band in $LiAl(C_2H_5)_4$ is found at the same wave number in the Nujol mull and ether solution spectra. The band shoulder which is found in the Nujol mull at 615 cm^{-1} is probably due to the CH_2-rocking vibration which is influenced by the crystal lattice arrangement, as it does not appear in the solution. Strong absorption bands at 526 cm^{-1} and 508 cm^{-1} in the solid complex and in ether solution, respectively, may be assigned unambiguously to the $\nu_1(F_2)$ vibration of the tetrahedral anion (structure I). The lower frequency of this vibration in the ether solution may be explained by the complex solvation in the solvent. Absorption bands of the ethyl group which are characteristic for most aluminium ethyls and are situated at 932 cm^{-1}, 962 cm^{-1}, 998 cm^{-1}, 1200 cm^{-1} and 1232 cm^{-1} (refs. 10, 13), are rather displaced in the infrared spectrum of solid $LiAl(C_2H_5)_4$. It is clear, however, that the ethyl groups are sterically affected or their regular structure is perturbed in some way. It is interesting that the ethyl-group bands remain at the wave numbers given above in similar complexes of the $MAlX_3C_2H_5$-type[4].

$NaAl(C_2H_5)_4$

The infrared spectra of $NaAl(C_2H_5)_4$ and $LiAl(C_2H_5)_4$ solutions are rather similar to each other with respect to frequencies and intensities of the $\nu_1(F_2)$ valence vibration bands and CH_2-rocking vibrations (Fig. 1), so that there is no doubt that the structure of both complexes in the solution is similar. In the Nujol mull of $NaAl(C_2H_5)_4$, however, both bands are shifted to considerably higher frequencies at 565 cm^{-1} and 665 cm^{-1}. This implies that the Al–C bonds in the lattice are much stronger and also more covalent. Further information on the state of the ethyl groups may be obtained from the spectral range above 800 cm^{-1}. A very strong band at 1147 cm^{-1} is probably due to the same vibration as those which appear in $(C_2H_5)_4Sn$ at 1191 cm^{-1} and in $(C_2H_5)_4Pb$ at 1155 cm^{-1} as very strong bands and was assigned to the CH_2-wagging vibration[12]. The other part of the spectrum is also rather similar to the $(C_2H_5)_4Pb$ spectrum, which suggest rather persuasively that $Al(C_2H_5)_4^-$ anions have an accurate tetrahedral structure in their sodium salt which is not deformed by the Na^+ ion field. In the case of $LiAl(C_2H_5)_4$, the anions evidently have the tetrahedral structure as there is only one skeletal band at 526 cm^{-1} but the ethyl-group vibrations are probably affected by regularly arranged Li^+ ions which can approach closer to an ethyl group owing to their small effective radii.

$LiAl(CH_3)_4$

The situation is not so simple with methyl derivatives as it is in the case of ethyl compounds. First, a very strong and broad band at 725 cm^{-1} appeared in the spectrum of $LiAl(CH_3)_4$ ether solution, which may be assigned to the CH_3-rocking vibration [in $(CH_3)_4Pb$ at 765 cm^{-1}, in $(CH_3)_4Sn$ at 770 cm^{-1}][12]. This corresponds to a very broad band with a maximum at 748 cm^{-1} and a shoulder at 770 cm^{-1} in the spectrum of the complex in Nujol mull. Furthermore, two strong bands which are certainly associated with Al–C bond vibrations were found at 575 cm^{-1} and 636 cm^{-1}. In the region above 800 cm^{-1}, two approximately equally strong bands of the C–H symmetrical deformation vibration at 1100 cm^{-1} and 1210 cm^{-1} are found [one band in $(CH_3)_4Sn$ at 1198 cm^{-1} and one band in $(CH_3)_4Pb$ at 1148 cm^{-1}][12]. The discovery of these two approximately equally strong bands, the two Al–C valence vibration bands and the split CH_3-rocking bands leads to the conclusion that the two pairs of Al–C bonds in the deformed tetrahedral anion are different. The model of structure (III) where weak interactions of Li^+ with two CH_3 groups probably lead to small changes of the force constants of Al–C bonds only, would agree with the conception of this anion. The relatively high splitting of symmetrical C–H deformation vibrations is caused by the non-bonded interaction of CH_3 groups[14]. In the infrared spectrum of the ether solution, in addition to the band at 725 cm^{-1} already identified, three other bands are found; the strongest, being situated at 525 cm^{-1}, probably corresponds to the Al–C valence vibration of a regular tetrahedron. The frequency difference [approximately 20 cm^{-1} when $\nu_1(F_2)$ vibrations of $Al(C_2H_5)_4^-$ and $Al(CH_3)_4^-$ are compared] is approximately the same as that between tetraethyl- and tetramethyltin derivatives. The origin of the other two bands of weak and medium intensities at 585 cm^{-1} and 620 cm^{-1}, respectively, cannot be explained satisfactorily. By taking the spectra of different samples and finally of the partially oxidized sample it was checked that these bands do not belong to any oxidation or hydrolysis products. The strongest band in structure (II), where three skeleton vibration bands are expected, should be due to the $\nu_3(E)$ vibration with the highest frequency. In the spectrum of the $LiAl(CH_3)_4$ ether solution, however, the bands at 585 cm^{-1} and 620 cm^{-1} are too weak to be Al–C bond vibrations. It seems likely that most molecules are arranged tetrahedrally with the corresponding band at 525 cm^{-1}. The bands at 585 cm^{-1} and 620 cm^{-1} should belong in this case either to molecules with symmetry defects or should originate in ether complexes with the methyl aluminium complex. Ethyl ether is bound very strongly in methyl complexes, it is released only *in vacuo* at an elevated temperature. Ether residues are revealed in the infrared spectrum by a band at 1028 cm^{-1} which represents a shift by approximately 100 cm^{-1} to a lower wave number with regard to free ether. Ether is far more weakly bound in ethyl derivatives so that the bands corresponding to 585 cm^{-1} and 620 cm^{-1} may not appear in their ether solutions.

$NaAl(CH_3)_4$

The infrared spectrum of the $NaAl(CH_3)_4$ ether solution is similar to that of $LiAl(CH_3)_4$ solution, except for the higher wave number of the strong band at 546 cm^{-1} which suggests a greater Al–C bond strength in the sodium complex. The infrared spectra of the two complexes are more different in Nujol mull. The pair of Al–C valence vibration bands are situated in the sodium complex at 550 cm^{-1} and 594 cm^{-1}, *i.e.*, at lower wave numbers and the δ_{sym}-C-H band is single and is situated at 1140 cm^{-1}. The presence of two Al-C valence vibration bands requires the C_{2v} symmetry of the anion, *i.e.*, structure (III). The differences in the band wave numbers, however, are not so high in the sodium complex as in the lithium complex (*i.e.* 44 cm^{-1} *vs.* 61 cm^{-1}), the δ_{sym}-C-H vibrations are not affected by this difference. A comparison of the $NaAl(CH_3)_4$ spectrum with that of $LiAl(CH_3)_4$ in an ether solution shows that the solvated anion of the sodium complex is firmer [a higher wave number of the $\nu_1(F_2)$ band] whereas the same complex in the solid state has attenuated Al–C bonds most likely due to the stronger effect of sodium cations.

SUMMARY

Infrared spectra of a number of complexes of the type $MAlR_4$ ($M = Li, Na$; $R = CH_3, C_2H_5$) have been measured in ethyl ether solutions as well as in the solid state. The complexes form tetrahedral AlR_4^- anions, the structure of which, however, may be deformed by the arrangement of the crystal lattice, or by the co-ordination of solvent molecules which takes place in the solutions. Regular tetrahedral anions are formed in the $NaAl(C_2H_5)_4$ crystal lattice and most likely also in ether solutions of both ethyl derivatives. The skeleton of the anion of the solid lithium complex is also tetrahedral, but the ethyl group vibrations are influenced considerably by the packing of Li^+ cations. The anions of methyl complexes are deformed in the solid state to the C_{2v} symmetry; in ether solution they are probably of tetrahedral structure.

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