The Infrared Spectra of Alkylaluminum-Ether Complexes*[1]

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Because of experimental difficulties, the infrared spectra of alkylaluminum-ether complexes have never been reported except for Hoffmann's report dealing with the triethylaluminum - diethyl ether complex along with nine alkylaluminum compounds.[1] As the importance of compounds of this type is increasing from both theoretical and practical points of view, however, fifteen kinds of such complexes have now been prepared and a systematic study of their infrared spectra has been carried out.

Their spectra have been assigned in the 2000—350 cm^{-1} region, although some of them are tentative. Hoffmann's assignment of the infrared spectrum of the triethylaluminum - diethyl ether complex has been partly corrected. Special attention has been paid to two absorption bands corresponding to the C–O antisymmetric and the C–O symmetric stretching vibration of ether. These C–O bands shift to lower frequencies when ether forms an alkylaluminum complex; the magnitudes of the shifts caused by trimethylaluminum and triethylaluminum complex formation have been compared with each other. The magnitudes of the shifts caused by AlR_3-, AlR_2X- or $AlRX_2$- (R=methyl, or ethyl, X=halogen) diethyl ether complex formation have also been compared. The infrared spectra of five kinds of ethylaluminum ethoxide have also been measured.

Experimental

Preparation of Alkylaluminum-Ether Complexes. —Trialkylaluminums, dialkylaluminum halides and alkylaluminum dihalides, which were distilled just before use, were mixed with dimethyl ether, tetrahydrofuran, ethyl methyl ether and diethyl ether which had been dried and distilled just before use, in a molar ratio of 1 : 1, and distilled in vacuo. All manipulations were carried out under an atmosphere of purified nitrogen. Trimethylaluminum, dimethylaluminum chloride, and methylaluminum dichloride

TABLE I. ALKYLALUMINUM-ETHER COMPLEXES

Complex	B. p., °C (mmHg)	Al, %		Mol. wt.	
		Calcd.	Found*[1]	Calcd.*[2]	Found*[3]
$AlMe_3 \cdot Me_2O$*[4]	41.5 (10)	22.8	22.7	118.2	121.6
$AlMe_3 \cdot THF$	54.0—55.5 (2)	18.7	18.5	144.2	146.4
$AlMe_3 \cdot MeOEt$	55.5—56.5 (10)	20.4	20.0	132.2	134.4
$AlMe_3 \cdot Et_2O$	45.5—47.0 (4)	18.5	18.3	146.2	149.5
$AlMe_2Cl \cdot Me_2O$	85.5—87.0 (10.5)	19.5	19.8	138.6	151.7
$AlMe_2Cl \cdot Et_2O$	73.0—74.5 (2.5)	16.2	16.4	166.6	199.7
$AlMeCl_2 \cdot Et_2O$	123.0—125.0 (7)	14.4	14.5	187.0	226.3
$AlEt_3 \cdot Me_2O$	76.5—78.0 (3)	16.8	17.5	160.2	176.3
$AlEt_3 \cdot THF$	123.0—125.0 (9)	14.5	14.8	186.3	198.6
$AlEt_3 \cdot MeOEt$	82.0—83.5 (3.5)	15.5	16.1	174.3	185.2
$AlEt_3 \cdot Et_2O$	88.5—91.5 (3.5)	14.3	14.8	188.3	205.8
$AlEt_2Br \cdot Et_2O$	97.5—99.5 (2.5)	11.3	11.6	239.1	261.1
$AlEt_2Cl \cdot Et_2O$	92.0—93.0 (3.5)	13.9	14.2	194.7	202.9
$AlEtBr_2 \cdot Et_2O$	161.0—165.0 (15)	9.3	9.9	290.0	324.5
$AlEtCl_2 \cdot Et_2O$	122.0—130.0 (5.5)	13.4	13.9	201.1	213.2

*[1] Analysis was carried out by volumetric method (oxine complex salt method).

*[2] Molecular weights were calculated for monomeric forms.

*[3] Determined by measuring freezing point depression of benzene solution; values listed are mean values of several measurements.

*[4] Me=CH_3, Et=C_2H_5, THF=tetrahydrofuran; these abbreviations are used throughout Tables I—VII.

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*[1] Presented partly at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

[1] E. G. Hoffmann, *Z. Elektrochem.*, **64**, 616 (1960).

TABLE II. OBSERVED FREQUENCIES OF METHYLALUMINUM-ETHER COMPLEXES IN cm^{-1} AND VIBRATION ASSIGNMENT

$AlMe_3 \cdot Me_2O$	$AlMe_3 \cdot THF$	$AlMe_3 \cdot MeOEt$	$AlMe_3 \cdot Et_2O$	$AlMe_2Cl \cdot Me_2O$	$AlMe_2Cl \cdot Et_2O$	$AlMeCl_2 \cdot Et_2O$	Assignment
	1476 vw	1474 m	1479 vw	1466 sh		1478 vw	CH_3 degenerate deformation CH_2 scissoring
1462 s	1459 m		1469 s	1456 s	1469 s	1467 s	
	1451 sh	1451 m	1448 m		1449 m	1448 m	
		1393 m	1393 s		1395 s	1395 s	CH_3-C symmetric deformation
	1372 w						
	1350 m						
	1319 vw	1312 w	1327 m		1328 m	1328 m	CH_2 wagging CH_2 twisting
	1294 vw		1282 m		1282 m	1280 m	
1250 w	1244 w	1255 vw	1254 vw	1252 m	1255 w	1256 vw	
1185 vs	1182 vs	1185 vs	1187 s	1194 s	1194 s	1201 s	CH_3 rocking
1153 m		1150 m	1151 s	1151 m	1150 s	1149 s	
		1091 m	1091 s		1092 s	1092 s	
	1040 vw						
1046 vs	1017 vs	1042 vs	1036 vs	1031 vs	1023 vs	1009 vs	C-O antisymmetric stretching
	958 w	966 s	996 m		993 vw	990 sh	C-C stretching
	919 m						
891 s	869 vs	833 s	898 s	882 s	893 s	884 s	C-O symmetric stretching
		800 m	834 m		834 w	833 m	CH_2 rocking
			781 m		774 w	771 s	
				854 vw			
				822 vw			
				769 vw			
710 s	707 s	708 s	706 s				Al-C degenerate stretching
622 m	616 m	625 m	624 m				
			576 vw				
525 m	519 m	525 m	526 m				Al-C symmetric stretching
		507 vw	506 vw				
473 m	455 vw	456 vw	462 w				Al-O stretching
				690 vs	685 vs		Al-C antisymmetric stretching
				582 s	580 s		Al-C symmetric stretching
				489 m	517 m		Al-O stretching Al-Cl stretching
					(488 w)		
				407 m	409 m		
						673 s	Al-C stretching
						534 m	Al-O stretching
						489 m	Al-Cl antisymmetric stretching
						408 m	Al-Cl symmetric stretching

were purchased from Texas Alkyls, Inc., and triethylaluminum, diethylaluminum chloride and ethylaluminum dichloride, from the Ethyl Co. Diethylaluminum bromide and ethylaluminum dibromide were prepared by the method of Grosse and Mavity.[2] Table I shows the boiling points, aluminum contents, and molecular weights of alkylaluminum-ether complexes prepared as above.[*2]

Preparation of Ethylaluminum Ethoxides. — Diethylaluminum ethoxide, and ethylaluminum diethoxide were prepared by the method of Grosse and Mavity.[2] Ethylethoxyaluminum chloride and ethylethoxyaluminum bromide were prepared by the reaction of ethylaluminum sesquihalide and aluminum triethoxide.[3] Ethylethoxyaluminum iodide was prepared by the reaction of diethyl aluminum iodide and anhydrous ethanol.[4] Table VI shows the boiling points, aluminum contents, and molecular weights of the ethylaluminum ethoxides thus obtained.

Measurements of the Infrared Spectra.—A Japan Spectroscopic Co. model DS-402G infrared spectrophotometer was used for the infrared absorption measurements. Thin liquid films of the samples were used in all cases. Freshly-distilled samples were injected in KRS-5 airtight cells in a glove box filled with purified nitrogen; this operation had to be performed as rapidly as possible, because even

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[2] A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

[*2] The authors are indebted to Mr. Takao Tsunoda and Mr. Makoto Iizuka of our laboratory for their help in the synthetical work, and to Mr. Hitoshi Shinkoda of our laboratory for his aluminum analysis.

[3] Brit. Pat. 858498 (1959).

[4] N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

in an atmosphere of carefully-purified nitrogen long exposure of samples brings about contamination with oxidation as a result of the trace amount of oxygen present. Absorption bands due to oxidized contaminants were discriminated by comparing the spectrum obtained with the spectrum obtained with the intentionally airoxidized samples. To make sure that samples did not react with window materials, the observed spectrum was compared with that taken by the polyethylene-sandwich method. No absorption band disappeared even if the polyethylene-sandwich method was applied, showing that no absorption bands due to reaction products with window materials could be detected at all.

Results and Discussion

Methylaluminum-Ether Complexes.—The observed frequencies of the infrared spectra of seven kinds of methylaluminum-ether complexes in the 2000—350 cm^{-1} region are shown in Table II. Figure 1 shows three typical spectra charts. As the spectrum of trimethylaluminum has no absorption band in the 1150—800 cm^{-1} region,[1] and that of dimethyl ether has two bands, 1094 and 920 cm^{-1} (C–O antisymmetric and symmetric stretching vibrations),[5] the absorption bands of the trimethylaluminum-dimethyl ether complex at 1046 and 891 cm^{-1} are assigned to the C–O antisymmetric and symmetric stretching vibrations respectively. These two C–O stretching bands are also easily found for the six other complexes. Table III shows the shifts of the C–O bands of dimethyl ether, tetrahydrofuran, ethyl methyl ether and diethyl ether upon trimethylaluminum-complex formation. The assignments of the other bands have been made by comparing the spectra of these seven complexes with one another.

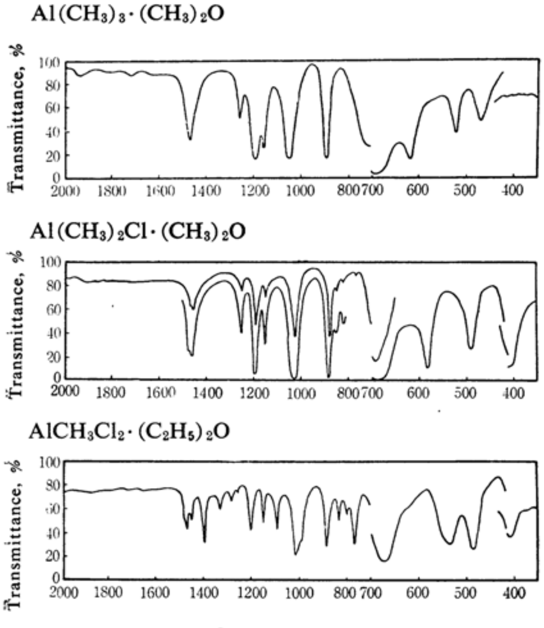

Fig. 1. Spectra of methylaluminum-ether complexes.

TABLE III. SHIFTS OF THE C–O VIBRATION BANDS OF ETHERS ON $AlMe_3$ COMPLEX FORMATION

	$\nu_{as}(CO)$ (cm^{-1})		$\nu_s(CO)$ (cm^{-1})	
	Ether*	Complex	Ether*	Complex
$AlMe_3\cdot Me_2O$	1094	1046	920	891
$AlMe_3\cdot THF$	1073	1017	913	869
$AlMe_3\cdot MeOEt$	1120	1042	925	833
$AlMe_3\cdot Et_2O$	1120	1036	926	898

* The values listed are taken from Mashiko's data in CCl_4 solution for Me_2O, MeOEt, and Et_2O.[5] For THF, the frequencies obtained by us in the pure liquid state are used.

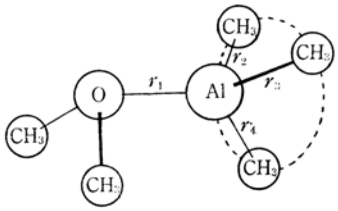

Fig. 2. Molecular model and internal coordinates of $Al(CH_3)_3\cdot(CH_3)_2O$.

The assignment in the KBr prism region is guided by a consideration of the molecular model $Al(CH_3)_3\cdot(CH_3)_2O$, as is illustrated in Fig. 2.[*3] On the assumption that the trimethylaluminum - dimethyl ether complex has the C_s symmetry only, the symmetry coordinates for each type of vibration in the model are as given in Table IV. Table IV also summarizes the symmetry coordinates for the dimethylaluminum chloride - dimethyl ether complex (in which r_4 represents the Al–Cl distance) and the methylaluminum dichloride - diethyl ether complex (in which r_3 and r_4 represent the two Al–Cl distances).

The assignments for the trimethylaluminum - dimethyl ether, - tetrahydrofuran, - ethyl

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[5] Y. Mashiko, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 470 (1958); Y. Mashiko, ibid., **80**, 593 (1959).

[*3] Bauer and his co-workers measured the bond lengths and the angles of the boron trifluoride - dimethyl ether complex. They found that all angles of $BF_3\cdot(CH_3)_2O$ are 109.5° and that the carbon atoms are staggered relative to the fluorine atoms. [S. H. Bauer, G. R. Finlay and A. W. Laubengayer, *J. Am. Chem. Soc.*, **67**, 339 (1945).]

Although the bond lengths and angles of $Al(CH_3)_3\cdot(CH_3)_2O$ have not been measured, it seems most probable in this case that we may assume a staggered conformation as in the case of $BF_3\cdot(CH_3)_2O$.

TABLE IV. SYMMETRY COORDINATES

Complex	Coordinate	Description
$AlMe_3 \cdot Me_2O$	Δr_1	Al-O stretching
	$(\Delta r_2+\Delta r_3+\Delta r_4)/\sqrt{3}$	Al-C symmetric stretching
	$(2\Delta r_2-\Delta r_3-\Delta r_4)/\sqrt{6}$	Al-C degenerate stretching*
	$(\Delta r_3-\Delta r_4)/\sqrt{2}$	
$AlMe_2Cl \cdot Me_2O$	Δr_1	Al-O stretching
	$(\Delta r_2+\Delta r_3)/\sqrt{2}$	Al-C symmetric stretching
	$(\Delta r_2-\Delta r_3)/\sqrt{2}$	Al-C antisymmetric stretching
	Δr_4	Al-Cl stretching
$AlMeCl_2 \cdot Et_2O$	Δr_1	Al-O stretching
	Δr_2	Al-C stretching
	$(\Delta r_3+\Delta r_4)/\sqrt{2}$	Al-Cl symmetric stretching
	$(\Delta r_3-\Delta r_4)/\sqrt{2}$	Al-Cl antisymmetric stretching

* If only $AlMe_3 \cdot O$ part of the skeleton is taken into consideration, the symmetry is C_{3v} and these two coordinates must be doubly degenerate. When the two methyl groups are attached to the oxygen atom, the over all symmetry of the complex becomes C_s and these degenerate frequencies split into two. See also Ref. 6.

TABLE V. OBSERVED FREQUENCIES OF ETHYLALUMINUM-ETHER COMPLEXES IN cm^{-1} AND VIBRATION ASSIGNMENTS

$AlEt_3 \cdot Me_2O$	$AlEt_3 \cdot THF$	$AlEt_3 \cdot MeOEt$	$AlEt_3 \cdot Et_2O$	Assignment
1468 s		1468 s	1466 s	CH_3 degenerate deformation CH_2 scissoring (ether)
	1459 s			
1456 w	1452 sh	1454 s	1452 sh	
1436 sh				
1411 s	1411 s	1412 s	1409 s	CH_2 scissoring ($-CH_2-Al$)
		1393 s	1392 s	CH_3-C symmetric deformation
1375 w	1372 w	1374 w		
1339 vw	1350 w			
	1317 vw	1313 m	1326 m	CH_2 wagging (ether) CH_2 twisting (ether)
	1296 vw		1283 m	
1253 m	1244 vw	1254 vw		
1225 m	1224 w	1215 m	1223 m	CH_2 wagging ($-CH_2-Al$) CH_2 twisting ($-CH_2-Al$) CH_3 rocking
1188 s	1186 s	1187 s	1189 s	
1155 s		1151 s	1146 s	
	1120 vw			
		1091 s	1089 s	
	1040 vw			
1049 vs	1018 vs	1042 vs	1035 vs	C–O antisymmetric stretching
986 s	986 s	985 s	988 vs	C–C stretching
947 m	947 m	966 s	946 s	
		948 m		
918 sh	918 m	918 w	913 sh	
886 vs	865 vs	829 vs	894 s	C–O symmetric stretching
		800 m	835 m	CH_2 rocking (ether)
			774 s	
649 vs	647 vs	647 vs	648 vs	Al–C degenerate stretching
629 s	630 s	631 s	630 s	CH_2 rocking ($-CH_2-Al$)
597 w	599 sh	600 sh	600 w	Al–C degenerate stretching
496 w	494 w	511 m	510 w	Al–C symmetric stretching
472 w	455 vw	458 vw	457 w	Al–O stretching

TABLE V. (Continued)

$AlEt_2Br\cdot Et_2O$	$AlEt_2Cl\cdot Et_2O$	$AlEtBr_2\cdot Et_2O$	$AlEtCl_2\cdot Et_2O$	Assignment
1468 s	1468 s	1468 s	1469 s	CH_3 degenerate deformation
1449 w	1449 sh	1448 w	1450 m	CH_2 scissoring (ether)
1409 w	1410 w			CH_2 scissoring ($-CH_2-Al$)
1394 s	1394 s	1395 s	1396 s	CH_3-C symmetric deformation
1379 sh	1379 sh			
1362 vw		1362 vw		
1327 m	1328 m	1326 m	1329 w	CH_2 wagging (ether)
1282 m	1282 m	1280 w	1283 w	CH_2 twisting (ether)
1256 w	1255 w	1255 vw	1257 vw	
1223 w	1224 w	1222 vw	1224 vw	CH_2 wagging ($-CH_2-Al$)
1191 m	1190 m	1191 m	1193 m	CH_2 twisting ($-CH_2-Al$)
1149 m	1149 m	1149 m	1151 m	CH_3 rocking
1091 s	1091 s	1092 s	1092 s	
1021 vs	1027 vs	1006 vs	1010 vs	C-O antisymmetric stretching
992 s	991 s		990 vw	C-C stretching
952 m	951 m	958 vw	957 vw	
921 w	919 w	923 w	922 vw	
889 s	890 s	881 s	884 s	C-O symmetric stretching
832 m	831 s	832 m	833 m	
		(795 w)	(796 w)	CH_2 rocking (ether)
772 s	771 s	766 s	769 s	
650 vs				Al-C antisymmetric stretching
623 s				CH_2 rocking ($-CH_2-Al$)
593 sh				
553 s				Al-C symmetric stretching
516 w				
464 w				Al-O stretching
356 w				Al-Br stretching
	650 vs			Al-C antisymmetric stretching
	625 s			CH_2 rocking ($-CH_2-Al$)
	595 vw			
	556 m			Al-C symmetric stretching
	515 w			Al-O stretching
	406 m			Al-Cl stretching
			629 s	CH_2 rocking ($-CH_2-Al$)
			609 sh	Al-C stretching
			532 m	Al-O stretching
			502 s	Al-Cl antisymmetric stretching
			405 w	Al-Cl symmetric stretching

methyl ether and - diethyl ether complexes are given straightforwardly in Table II, the band appearing at 473—455 cm^{-1} being assigned to the Al-O stretching mode.

The assignments for the methylaluminum dichloride -, the ethylaluminum dichloride - and the diethylaluminum bromide - diethyl ether complexes can also be given straightforwardly, as in Tables II and V (see also Fig. 3). The two Al-Cl vibrations appear at 489 and 408 cm^{-1} for the methylaluminum dichloride complex and at 502 and 405 cm^{-1} for the ethylaluminum dichloride complex. The Al-Br vibration appears at 356 cm^{-1} for the diethylaluminum bromide complex.[*4] The Al-O stretching vibrations are assigned for these molecules in Tables II and V. These assignments for the Al-O stretching vibrations are reasonable when we compare them with the B-O stretching vibration assigned by Begun, Fletcher and Palko.[6)],[*5]

The spectra in the KBr region of the dimethylaluminum chloride - dimethyl ether, the dimethylaluminum chloride - diethyl ether and

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[*4] We also measured the spectrum of the ethylaluminum dibromide - diethyl ether complex. It has 425 and 362 cm^{-1} bands, which are assigned to two Al-Br stretching bands.

6) G. M. Begun, W. H. Fletcher and A. A. Palko, *Spectrochim. Acta*, **18**, 655 (1962).

[*5] The difference between 670 cm^{-1} (the B-O stretching vibration) and 530—460 cm^{-1} (the Al-O stretching vibration) can be explained in terms of the difference between the masses of boron and aluminum atoms.

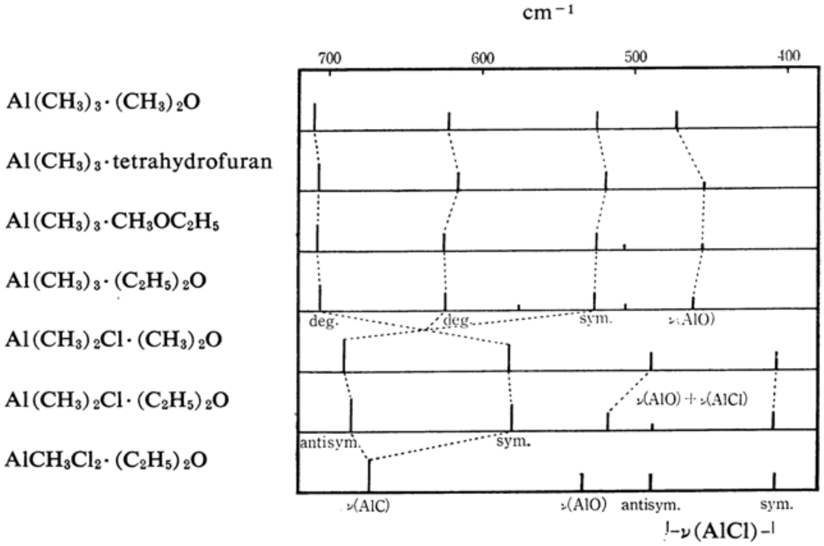


Fig. 3. The KBr region spectra of methylaluminum-ether complexes.

TABLE VI. ETHYLALUMINUM ETHOXIDES

Ethoxide	B. p., °C (mmHg)	Al, %		Mol. wt.	
		Calcd.	Found*1	Calcd.*2	Found*3
AlEt₂OEt	59.0 (1.5)	20.7	20.4	260.3 (2)	278.7
AlEt(OEt)₂	155.0—165.0 (3)	18.5	19.0	438.5 (3)	450.4
AlEt(OEt)Cl	96.0—97.0 (4.5)	19.8	19.7	409.7 (3)	395.9
AlEt(OEt)Br	130.0 (7)	14.9	15.0	362.0 (2)	374.5
AlEt(OEt)I	120.0—122.0 (4)	11.8	11.8	456.0 (2)	471.8

*1 Method of analysis is the same as in Table I.

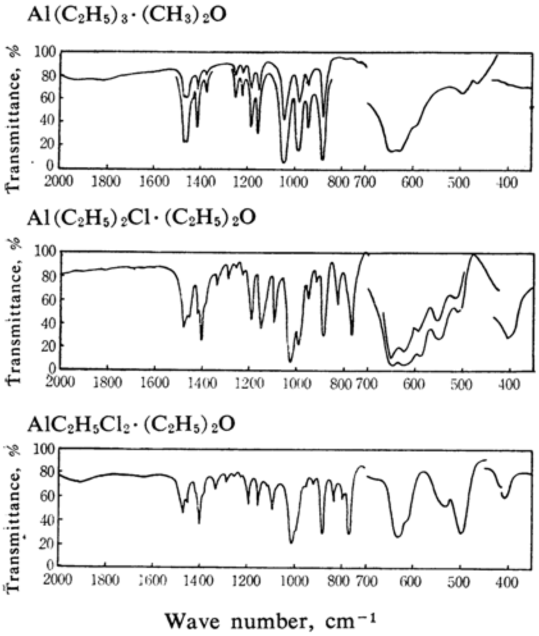
*2 Molecular weights were calculated by assuming degree of polymerization as shown in parentheses.

*3 Experimental method is the same as in Table I. AlEt(OEt)Cl isomerized from dimeric to trimeric form in a few days and AlEt(OEt)Br in a few months (see footnote in Appendix). The data listed for these two compounds come from measurements at the time one week after they had been synthesized.

the diethylaluminum chloride-diethyl ether complexes, given in Tables II and V, are somewhat complex. They have two bands in this region, 489 and 407 cm^{-1} for the dimethylaluminum chloride-dimethyl ether, 517 and 409 cm^{-1} for the dimethylaluminum chloride-diethyl ether, and 515 and 406 cm^{-1} for the diethylaluminum chloride-diethyl ether complex. These bands can only be understood in terms of the strong coupling between the Al–O stretching and the Al–Cl stretching vibrations. As has been mentioned above, the Al–O stretching vibration of the trimethylaluminum complex appears near 460 cm^{-1}, while that of the methylaluminum dichloride complex appears near 534 cm^{-1}. These two facts suggest that the A–O stretching bands of the dimethylaluminum chloride complex appear in the region between 470 and 500 cm^{-1}. In this region the Al–Cl stretching vibration is also expected to appear. Therefore, it is very probable that these two bands are coupled with each other and appear as two bands, as has been postulated above.

Ethylaluminum-Ether Complexes.—The observed frequencies of the infrared spectra of eight kinds of ethylaluminum-ether complexes in the 2000—350 cm^{-1} region are shown in Table V. Figure 4 shows three typical spectra charts. The assignments are almost self-evident if one uses the results of the assignments of methylaluminum-ether complexes.

Hoffmann assigned the absorption band near 770 cm^{-1} of the triethylaluminum-diethyl ether complex to the C–O symmetric stretching vibration.¹⁾ The above assignment for the C–O symmetric stretching band of the trimethylaluminum-dimethyl ether complex, however, suggests that the band at 894 cm^{-1} originates from the C–O symmetric stretching. Since only the diethyl ether complexes of


$Al(C_2H_5)_3 \cdot (CH_3)_2O$

$Al(C_2H_5)_2Cl \cdot (C_2H_5)_2O$

$AlC_2H_5Cl_2 \cdot (C_2H_5)_2O$

Fig. 4. Spectra of ethylaluminum-ether complexes.

alkylaluminums show an absorption band near 770 cm^{-1}, while the dimethyl ether, tetrahydrofuran and ethyl methyl ether complexes do not, this band is assigned to the CH_2 rocking vibration of diethyl ether, as is shown in Tables II and V.

In the KBr prism region, the CH_2 rocking band of the CH_2 group adjacent to the aluminum atom appears near 630 cm^{-1} and the spectra of ethylaluminum-ether complexes become more complicated than those of methylaluminum-ether complexes.[1] The spectrum of the ethylaluminum dibromide-diethyl ether complex in the 710—350 cm^{-1} region is not simple and no adequate assignment has been made.

Shifts of the C-O Antisymmetric and Symmetric Stretching Bands of Ether on Forming Complex.—Both the C-O antisymmetric stretching (near 1100 cm^{-1}) and the symmetric stretching vibration bands (near 920 cm^{-1}) of ether shift to lower frequencies when a complex is formed either with trimethylaluminum (Tables II and III) or with triethylaluminum (Table V). For trimethylaluminum and triethylaluminum, the magnitudes of the shifts are almost the same. These facts suggest that, in the alkylaluminum-ether complex, the C-O bonds of ether are somewhat weaker than those in the free ether molecule because an unshared pair of electrons of the oxygen atom co-ordinates to the aluminum atom.

If we compare the magnitudes of the shifts of the C-O antisymmetric and symmetric stretching bands of diethyl ether caused by the complex formation with trimethylaluminum, dimethylaluminum chloride and methylaluminum dichloride, the shifts become larger in this order. As regards the magnitudes of the shifts of these two bands of diethyl ether caused by the complex formation with triethylaluminum, diethylaluminum halide and ethylaluminum dihalide, the shifts become larger in this order. Figure 5 shows the shifts of the C-O stretching bands in eight kinds of diethyl ether complexes. From this figure, the following two conclusions can be drawn.

i) The electron-accepting tendency of alkylaluminum becomes larger in the order of $AlR_3 < AlR_2X < AlRX_2$ (R=methyl or ethyl, X=halogen).

ii) The electron-accepting tendencies of $Al(CH_3)_nX_{3-n}$ and $Al(C_2H_5)_nX_{3-n}$ (n=1, 2, 3) are almost the same.

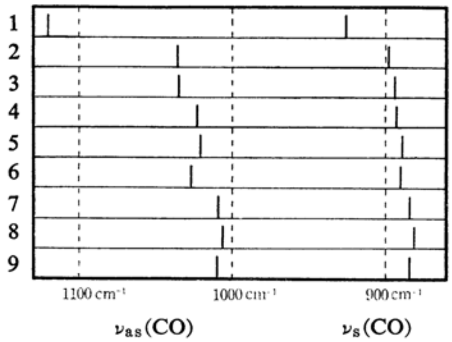


Fig. 5. Shifts of the absorption bands of CO antisymmetric and symmetric stretching vibration of ether on complex formation.

1 $(C_2H_5)_2O$
2 $Al(CH_3)_3 \cdot (C_2H_5)_2O$
3 $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$
4 $Al(CH_3)_2Cl \cdot (C_2H_5)_2O$
5 $Al(C_2H_5)_2Br \cdot (C_2H_5)_2O$
6 $Al(C_2H_5)_2Cl \cdot (C_2H_5)_2O$
7 $AlCH_3Cl_2 \cdot (C_2H_5)_2O$
8 $AlC_2H_5Br_2 \cdot (C_2H_5)_2O$
9 $AlC_2H_5Cl_2 \cdot (C_2H_5)_2O$

As has been mentioned previously, the Al-O stretching vibration bands of trialkylaluminum-diethyl ether and alkylaluminum dihalide-diethyl ether complexes appear near 460 and 534 cm^{-1} respectively. This fact suggests that the Al-O co-ordination bond in alkylaluminum dihalide-diethyl ether complexes is stronger than that in trialkylaluminum-diethyl ether complexes. This interpretation corresponds closely with the above two conclusions, i) and ii).

Lehmkuhl has reported, in comparing the thermal stabilities of complex salts, that the tendency of ethylaluminum compounds to form a $K^+[Al(C_2H_5)_3Cl]^-$-type complex salt with alkali halides increases in the order of triethylaluminum < diethylaluminum chloride < ethylaluminum dichloride.[7] It is of interest that the electron-accepting tendencies of alkylaluminum compounds obtained by the thermal and the infrared spectroscopic methods give the same order: trialkylaluminum < dialkylaluminum halide < alkylaluminum dihalide.

Summary

Fifteen samples of alkylaluminum-ether complexes (alkyl=methyl or ethyl) have been prepared, and their infrared spectra have been measured in the 2000—350 cm^{-1} region. Most of the absorption bands in this region have been assigned. In the KBr prism region, the assignments of the absorption bands of the trimethylaluminum - dimethyl ether complex have been made on the assumption that this complex has the C_s symmetry only. The absorption bands of these complexes have been found to shift to lower frequencies in the C-O antisymmetric and symmetric streching vibrations in the order of trialkylaluminum-ether < dialkylaluminum halide - ether < alkylaluminum dihalide - ether complexes. The infrared spectra of five samples of ethylaluminum ethoxides have also been measured in the 2000—350 cm^{-1} region.

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Appendix

Ethylaluminum Ethoxides. — These compounds were studied as model substances of partly-oxidized ethylaluminum derivatives. The infrared spectra of five kinds of ethylaluminum ethoxides in the 2000—350 cm^{-1} region are shown in Table VII. Figure 6 shows three typical spectra charts. The infrared spectrum of ethylaluminum diethoxide is reported to have been studied by Schomburg, but his result is not easily accesible.[8] The spectrum of ethylethoxyaluminum chloride has been reported by

TABLE VII. OBSERVED FREQUENCIES OF ETHYLALUMINUM ETHOXIDES 1 N cm^{-1}

$AlEt_2OEt$	$AlEt(OEt)_2$	$AlEt(OEt)Cl$	$AlEt(OEt)Br$	$AlEt(OEt)I$
1482 w	1484 w	1480 s	1480 s	1481 w
1462 sh	1463 sh	1465 vw	1466 vw	1464 sh
1451 s	1449 s	1447 s	1450 s	1451 m
1409 m	1409 w	1407 vw	1407 sh	1406 vw
1394 s	1391 s	1393 s	1395 s	1397 s
1374 vw	1373 vw	1372 vw	1374 vw	1380 vw
1288 m	1285 w	1299 m	1298 m	1291 w
1254 w	1253 vw	1265 w	1256 w	1256 sh
1222 w	1223 w	1222 w	1224 w	1219 vw
1193 s	1193 s	1201 m	1200 m	1196 m
1163 m	1163 s	1167 s	1166 s	1165 m
1100 s	1101 s	1094 s	1097 s	1100 s
1058 vs	1060 vs	1041 m	1042 vs	1035 vs
985 s	986 s	997 s	995 s	991 m
948 m	951 m	960 vw	959 w	955 w
914 w	918 sh	926 w	923 w	921 m
894 s	895 s	896 w	895 s	895 s
		851 s	848 s	846 w
806 s	806 m	809 vw	811 vw	
		675 s	671 s	674 s
652 vs	633 vs	641 s	627 s	620 s
			598 w	591 w
		555 vw		
481 w	523 sh	527 m	519 m	514 m
	431 w	447 m	442 w	430 w
				387 w
			355 w	

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[7] H. Lehmkuhl, *Angew. Chem.*, 75, 1090 (1963).

[8] G. Schomburg, Dissertation, Technische Hochschule Aachen (1956).

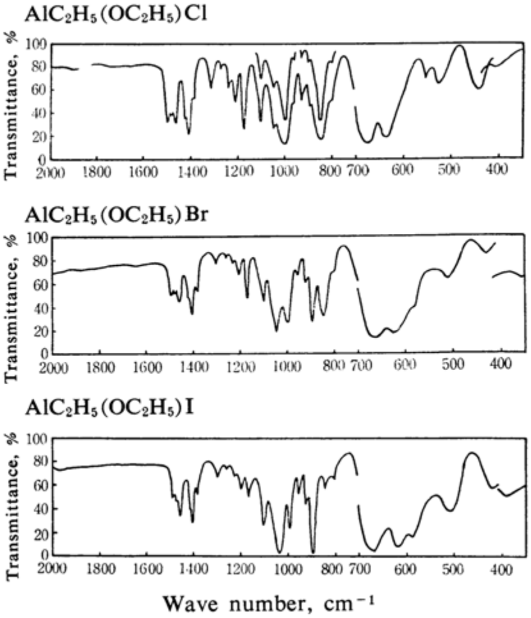

Fig. 6. Spectra of ethylaluminum ethoxides.

Scherer and Seydel ;[9] a comparison of our spectrum with theirs shows a good qualitative agreement.* The spectra of diethylaluminum ethoxide, ethylethoxyaluminum bromide and ethylethoxyaluminum iodide have not been published as yet. All five spectra show very strong bands near 1050 cm^{-1}; these bands may be due to the C–O stretching vibration band. The assignments of other bands are also still uncertain.

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9) H. Scherer and G. Seydel, *Angew. Chem.*, **75**, 846 (1963).

* Scherer and Seydel found that ethylethoxyaluminum chloride was dimeric just after it was synthesized, but that it isomerized to the trimeric form in a few days; they also reported a corresponding change in the infrared spectrum (intensity changes of four bands at 9.6, 10.0, 11.14 and 11.7 μ). The present authors recognized the same phenomenon. Our spectrum in this paper corresponds to that obtained by the measurement of an aged sample. In our laboratory it was found that ethylethoxyaluminum bromide and ethylethoxyaluminum iodide behaved analogously (isomerization from the dimeric to the trimeric form with a corresponding change in the infrared spectrum - intensity changes of four bands at 9.6, 10.05, 11.2 and 11.8 μ for ethylethoxyaluminum bromide - though the isomerization was much slower and the change of spectrum was less striking than in the case of ethylethoxyaluminum chloride).