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COMPLEXES OF ORGANOALUMINIUM COMPOUNDS WITH NITRILES STRUCTURE AND HEAT OF COMPLEX FORMATION

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The electron-acceptor properties of organoaluminium compounds due to an electron deficiency of the aluminium atom is the direct cause of their tendency to associate and form dimers, trimers, and even polymers. These compounds react with negative ions or neutral molecules having electron-donating properties, to yield ionized salts or complexes of the donor–acceptor type. It is the electron-acceptor properties, or the relative acidity, of the organoaluminium compounds that define their reactivity and *eo ipso* their usefulness in various syntheses.

In the present paper, the heat (Q_r) of the complexing reactions* of organoaluminium compounds with benzonitrile was investigated in order to estimate their relative acidity and establish the structure of the resulting complexes.

Several papers[1-3] have dealt with calorimetric measurements of the heat (Q_r) of formation of complexes of organoaluminium compounds, or aluminium halides, with electron donors but the heat of complex formation of organoaluminium compounds with nitriles has not so far been studied.

EXPERIMENTAL

1. *Reactants*

The organoaluminium compounds used were prepared by the methods already described[4,5]. The dialkyl and trialkyl derivatives were distilled before use. Organoaluminium compounds of type $RAlX_2$ were purified by crystallization from n-heptane. Benzonitrile (Xenon, Łódź, Poland) was dried over anhydrous magnesium sulphate in a nitrogen atmosphere, then distilled twice and stored over type-4A molecular sieves. Commercial-grade oxygen-free n-heptane was distilled from sodium in a nitrogen atmosphere and stored over type-4A molecular sieves.

2. *Apparatus*

The diathermic method was considered to be the most suitable method for calorimetric measurements.

The apparatus (Fig. 1) was designed to take into account certain specific properties of the organoaluminium compounds used. The calorimeter was thermostatted at 25° ±0.2°.

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* Q_r refers to the *actual*, *viz.*, dimeric, formula of the organoaluminium compound, whereas the heat of complex formation, Q_t, refers to the organoaluminium compound *monomer*.

3. *Method*

The reaction of complex formation was carried out in an aluminium test-tube (Fig. 1, (5)). A series of 5–6 experiments was carried out for each reactant molar ratio.

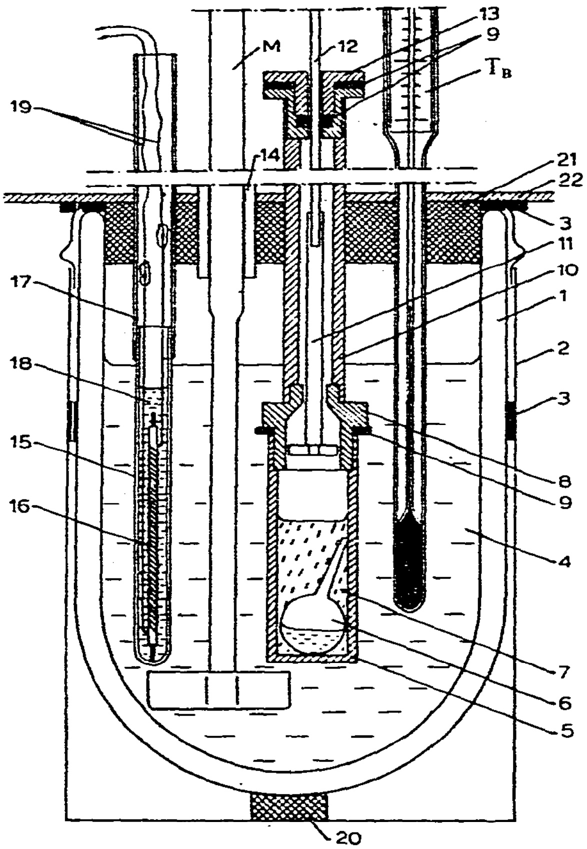


Fig. 1. The measuring calorimeter. (1), Dewar vessel; (2), Dewar vessel case; (3), expanded PVC spacer rings; (4), chlorobenzene as the calorimeter fluid; (5), aluminium test-tube; (6), glass ampoule with organoaluminium compound; (7), benzonitrile and n-heptane; (8), bung of the measuring test-tube; (9), gaskets; (10), test-tube mounting sleeve; (11, 12), stirrers; (13), packing gland; (14), gas-tight stirrer; (15), copper tube of the heater; (16, 17), heating element (10Ω); (18), transformer oil; (19), connecting leads; (20, 21), cork plugs; (22), mounting lid; (T_B), Beckmann thermometer (0°–5°).

Solid organoaluminium compounds were placed, by means of a spatula, in a wide-necked tared glass ampoule inside a manipulator operated in a deoxygenated, dried nitrogen atmosphere. All ampoules in use for a given series of measurements were filled simultaneously.

Liquid organoaluminium compounds were injected into ampoules by means of a hypodermic syringe and the ampoules sealed.

After they had been withdrawn from the manipulator, the plugged or sealed ampoules were stored in a desiccator in a nitrogen atmosphere.

The other reactant, benzonitrile, was weighed (to within ±0.0005 g) in the test-tube (Fig. 1, (5)) just before measurement. The ampoule containing an organoaluminium compound was placed in the nitrogen-flushed test-tube with the weighed benzonitrile, and n-heptane (7 ml) added as solvent. The test-tube was placed in the calorimeter and thermostatted for 1 h at 25°. The ampoule containing the organoaluminium compound was then broken and the resulting mixture stirred for 5 min.

In each series of measurements, the reaction mixture was analyzed qualitatively for ketones[6].

RESULTS

The heat of complexing reactions of type R_nAlX_{3-n} compounds ($R=CH_3$, C_2H_5; $X=Cl$, Br, I; $n=0$, 1, 2) with benzonitrile was investigated using various reactant molar ratios.

The average molar heats (Q_r) of complexing reactions are listed in Table 1

TABLE 1

HEAT (Q_r, kcal/mole) OF COMPLEXING REACTION OF ORGANOALUMINIUM COMPOUNDS WITH BENZONITRILE

Organoaluminium compound	*OrgAl: C_6H_5CN molar ratio*		
	1:1	1:2	2:1
Me_3Al	15.28	17.11	17.92
Me_2AlCl	17.17	18.12	20.73
$MeAlCl_2$	20.68	21.60	22.60
Et_3Al	16.01[a]		
Et_2AlCl	16.28	15.97	15.62
$EtAlCl_2$	19.10	21.83	21.61
$MeAlBr_2$	24.40		
Me_2AlI	18.31		
$MeAlI_2$	20.72		

[a] A ketone was detected

for the molar ratios 1:1, 1:2 (benzonitrile in excess), and 2:1 (R_nAlX_{3-n} in excess). It can be seen that, passing from trialkyl- through dialkylhalo- to monoalkyldihaloaluminium compounds, Q_r increases for each reactant molar ratio. In any one organoaluminium–benzonitrile system, the heat varies only slightly with the molar ratio, the maximum difference being about 2 kcal.

The complexes obtained are solid compounds which can be crystallized from n-heptane. Also, they can further rearrange upon hydrolysis to yield ketones. The rearrangement reaction obviously, affects the thermal effect of the complexing reaction, and therefore, after the calorimetric measurement had been completed, the reaction mixture was analyzed for ketones. Slight amounts of a ketone were detected only in the triethylaluminium–benzonitrile reaction mixture. The heat of this complexing reaction is thus subject to some error.

DISCUSSION

The 1:1 reactions carried out at room temperature produced donor–acceptor type[7-10] complexes having the aluminium atom bound to nitrogen by its unshared electron pair:

$$2\,C_6H_5CN + (R_3Al)_2 \rightarrow 2\,C_6H_5CN \cdot AlR_3 \qquad (1)$$

The complexing reactions proceed rapidly and irreversibly with the production of considerable quantities of heat. The resulting complexes, mostly crystalline compounds, are stable at room temperature.

At room temperature the organoaluminium compounds investigated are associated and occur as dimers[11-14]. The corresponding equilibrium is represented by the following equation:

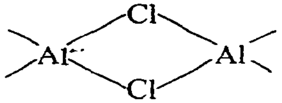
$$2\,R_3Al \rightleftharpoons (R_3Al)_2 - U_D \qquad (2)$$

where U_D is the heat of dissociation of the dimer.

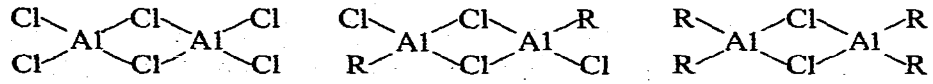
The heats of dissociation of: trimethylaluminium $(Me_3Al)_2$, 20.2 kcal/mole; aluminium chloride $(AlCl_3)_2$, 29.0 kcal/mole, and other aluminium halides[1] are given in the literature, but so far, no related investigations on other dimeric organoaluminium compounds have been published.

The heat of dissociation of dimeric trimethylaluminium is smaller than that of dimeric aluminium chloride. The decisive factor is the structure of the bridge in the dimer. In trimethylaluminium the aluminium atoms are linked by two carbon bridges, whereas in aluminium chloride they are joined by chlorine bridges. The chlorine bridge is more stable than the carbon bridge, because chlorine is the more electronegative element, possesses free electron pairs, is smaller in volume than the methyl group, etc.

The heats of dissociation of methylaluminium dichloride $(MeAlCl_2)_2$ dimethylaluminium chloride $(Me_2AlCl)_2$, and aluminium chloride $(AlCl_3)_2$ should be approximately the same. All these compounds dimerize to form the chlorine bridge



Onishi and Shimanouchi[15] have shown that the chlorine bridges in aluminium chloride and dimethylaluminium chloride have identical structures. In these compounds the Cl–Al–Cl angle is 90°, and the length of the Al–Cl bond 2.31 Å; also, the substituent–aluminium–substituent angles are identical (120°). It is only the bond lengths between the aluminium atom and the external substituent that differ: Al–CH_3 (2.06 Å) and Al–Cl (2.00 Å). Since the chlorine bridge in various organoaluminium compounds has the same structure, its stability (heat of dissociation) should also be identical. This may be deduced from considerations of the effect of external substituents on the structure and stability of the chlorine bridge. Whether they are electron-accepting or electron-donating, the various symmetrical substituents have been found to affect neither the structure nor the stability of the bridge. In aluminium chloride, methylaluminium dichloride and dimethylaluminium chloride, the external substituents are in symmetrical positions and their heats of dissociation may be assumed to be approximately equal:



trans- and *cis*-configurations

If the small heats of crystallization and dissolution of the complex are neglected, the heat of complex formation, Q_t may be treated as a sum of the heats of complexing reaction, Q_r, and of dimer dissociation, U_D.

$$Q_t = Q_r - 0.5\ U_D \tag{3}$$

The Q_t-data calculated from eqn. (3) are given in Table 2. For the given electron donor (benzonitrile), the heat of complex formation should be related to the electron-accepting (acid strength) properties of an organoaluminium compound. Since the acid strength of an organoaluminium compound depends on the number of chlorine atoms combined directly with the aluminium atom, the stability of the complexes should increase in the following order:

TABLE 2

HEAT (Q_t, kcal/mole) OF FORMATION OF COMPLEXES OF ORGANOALUMINIUM COMPOUNDS WITH BENZONITRILE

Organoaluminium compound	Q_t
Me_3Al	25.4
Me_2AlCl	31.7
$MeAlCl_2$	35.2
$MeAlBr_2$	37.8
Me_2AlI	29.5
$MeAlI_2$	31.9

$$R_3Al < R_2AlX < RAlX_2$$

where X = Cl, Br, I.

These suppositions have been entirely supposted by the experimental data. In fact, the heats of complexing reaction (Table 1) and of complex formation (Table 2) follow this sequence.

As already shown, in the IR spectra the shift of the band characteristic of the triple bond C≡N in nitriles, is related to the nature of the organoaluminium compound with which a given nitrile reacts to yield a complex of the donor–acceptor type. The higher the relative acidity, the higher the $\Delta\nu(C{\equiv}N)$ shift measured in cm^{-1}.

Since the heat of complex formation is also related to the acid strength of the organoaluminium compound, *i.e.*, increases as the acid strength is increased (Table 2), it should be related also to the $\Delta\nu(C{\equiv}N)$ shift.

If $\Delta\nu_1$ and $\Delta\nu_2$ represent the C≡N band shifts (in cm^{-1}) of two nitriles ($\Delta\nu = \nu(C{\equiv}N)_k - \nu(C{\equiv}N)_w$, where $\nu(C{\equiv}N)_k$ and $\nu(C{\equiv}N)_w$ are the C≡N band frequencies for the complex and the pure nitrile, respectively) and Q_{t_1} and Q_{t_2} are the heats of complex formation of the two nitriles:

$$\Delta\nu_1/\Delta\nu_2 = Q_{t_1}/Q_{t_2} \tag{4}$$

The heat of complex formation is difficult to measure, whereas the C≡N band shift is easily determined.

With $\Delta\nu_1$, Q_{t_1} and $\Delta\nu_2$ known, it is possible to calculate from eqn. (4) the heat of complex formation, Q_{t_2}, required

$$Q_{t_2} = Q_{t_1}(\Delta\nu_2/\Delta\nu_1) \tag{5}$$

In order to verify eqn. (5), the heats of formation of various complexes were calculated and compared with those measured calorimetrically (Table 3). The results obtained and those calculated from eqn. (5) are consistent and agree within the limits of error of calorimetric measurement.

TABLE 3

COMPARISON OF OBSERVED AND CALCULATED HEATS OF COMPLEX FORMATION (kcal/mole)

Reference complex	Q_{t_1} *exptl.*	$\Delta\nu_1$ *(cm^{-1})*	*Complex examined*	$\Delta\nu_2$ *(cm^{-1})*	Q_{t_2} *from eqn.* (5)	Q_{t_2} *exptl.*
$PhCN \cdot AlMeCl_2$	35.2	58			24.9	
$PhCN \cdot AlMe_2Cl$	31.7	52	$PhCN \cdot AlMe_3$	41	25.0	25.4
$PhCH_2CN \cdot AlMeCl_2$	39.5	63			25.8	
$PhCN \cdot AlMe_3$	25.4	41			32.2	
$PhCN \cdot AlMeCl_2$	35.2	58	$PhCN \cdot AlMe_2Cl$	52	31.6	31.7
$PhCH_2CN \cdot AlMeCl_2$	39.5	63			32.6	
$PhCN \cdot AlMe_3$	25.4	41			36.0	
$PhCN \cdot AlMe_2Cl$	31.7	52	$PhCN \cdot AlMeCl_2$	58	35.3	35.2
$PhCH_2CN \cdot AlMeCl_2$	39.5	63			36.3	
$PhCN \cdot AlMe_3$	25.4	41			36.6	
$PhCN \cdot AlMe_2Cl$	31.7	52	$PhCN \cdot AlCl_3$	59	36.0	
$PhCN \cdot AlMeCl_2$	35.2	58			35.8	
$PhCN \cdot AlMe_3$	25.4	41			39.1	
$PhCN \cdot AlMe_2Cl$	31.7	52	$PhCH_2CN \cdot AlMeCl_2$	63	38.5	39.5
$PhCN \cdot AlMeCl_2$	35.2	58			38.2	

A knowledge of the heat of complexing reaction at various reactant molar ratios, gives some indication of the structure of the complexes. The hypothetical complexes of organoaluminium compounds with benzonitrile for various reactant molar ratios are given in Table 4.

As shown before, the 1 : 1 reaction at room temperature affords a stable complex of structure I.

Since the heat of complexing reaction is practically invariant with the reactant molar ratio (Table 1), formulae IV, V and VI are ruled out because they should differ considerably from complex I in heat of complexing reaction.

However, the complexing reaction heat data are insufficient to decide the structure of complex III, because reaction (6) produced as much heat as reaction (7):

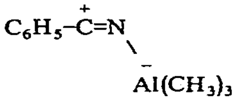
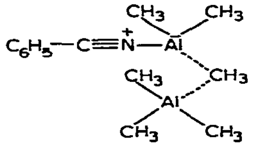
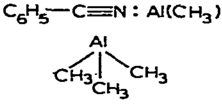
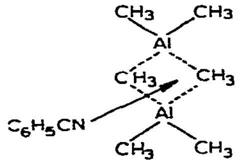
$$C_6H_5CN + (Me_3Al)_2 \rightarrow C_6H_5CN \cdot 2\,AlMe_3 \tag{6}$$

$$C_6H_5CN + (Me_3Al)_2 \rightarrow C_6H_5CN \cdot AlMe_3 + 0.5\,(Me_3Al)_2 \tag{7}$$

In reaction (6), one Al–CH_3 bridge bond is ruptured in one mole of the dimer; in reaction (7), two such bonds are ruptured, but only in half the mole of the dimer.

TABLE 4

STRUCTURE OF HYPOTHETICAL COMPLEXES OF TRIMETHYLALUMINIUM WITH BENZONITRILE AT ROOM TEMPERATURE

Ratio of *$(CH_3)_3Al$ to benzonitrile*			
1:1	I $C_6H_5\text{-}C{\equiv}\overset{+}{N}\text{-}\overset{-}{Al}(CH_3)_3$ *sp*	II  $C_6H_5\text{-}\overset{+}{C}{=}N\text{-}\overset{-}{Al}(CH_3)_3$	
2:1	III 	IV 	V 
1:2	VI 2 $C_6H_5CN\cdot Al(CH_3)_3$		

Therefore, the over-all number of bridge bonds ruptured in the dimer of the organoaluminium compound and the number of the resulting complex N–Al bonds are equal in both cases.

SUMMARY

The heats of complexing reaction of organoaluminium compounds of type R_nAlX_{3-n} ($R=CH_3$, C_2H_5; $X=Cl$, Br, I; $n=0$, 1, 2) with benzonitrile have been measured.

The heats of complex formation were calculated and a relationship between the heat and the $\Delta\nu(C{\equiv}N)$ band shift is given.

As with $\Delta\nu(C{\equiv}N)$, the heat of complex formation may be a measure of the relative acid strength of organoaluminium compounds.

The structure of the resulting complexes has been discussed in terms of the heat of complexing reaction data measured at various reactant mole ratios.

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