

ON THE STOICHEIOMETRY OF ALUMINIUM ALKYL-ESTER COMPLEXES

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Summary

Three techniques (IR, ^1H NMR spectroscopy and cryoscopy) have been used in an attempt to detect the 1/2 complex previously suggested to be formed upon reaction of an ester with a trialkylaluminium. No evidence for such a complex was observed.

The wide variety of applications of trialkylaluminiums has led to many theoretical and experimental studies of the properties and reactivities of such compounds. Their Lewis acid character towards a large number of electron donors has been examined [1].

A problem often encountered is whether Lewis bases can complex with more than one aluminium centre. For nitriles stoichiometries other than 1/1 were reasonably excluded by IR spectroscopy [2], whereas for alkylpyridines the heat of reaction increases with the increasing initial alkylaluminium concentration up to twice that of the base [3]. In the case of geminal organodialuminium compounds, tertiary amines (including pyridine) form complexes with either one or two aluminium centers depending on their steric properties [4], while ketones are reported to give rise to only 1/1 stoichiometry [5].

The behaviour of alkylaluminiums in the presence of esters has aroused considerable interest because of the widespread applications of esters in the high yield Ziegler-Natta catalysis, where they are often added to catalysts in order to improve polymer stereoregularity [6]. However, experiments designed to solve the general problem of the stoichiometries of the complexes formed by esters and alkylaluminiums produced only contradictory results.

The 1/1 complexes are well known, thermally-stable, adducts, which undergo addition and reduction reactions at the carbonyl carbon atom only to a very slight extent even at 150°C [7,8]. When triethylaluminium is present in excess, its

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nucleophilic behaviour can be readily observed in the reaction with methyl methacrylate, suggesting the existence of a 1/2 ester/aluminium complex [9]. For the couple $\text{PhCOOCH}_3/(\text{CH}_3)_2\text{AlCl}$ a 1/2 complex in aromatic solvents was also postulated [10,11], on basis of the observation that excess of the organoaluminium greatly accelerates nucleophilic attack at the ester and of various experimental results. A cyclic six-membered structure was proposed for such a 1/2 complex. These suggestions were accepted in a recent paper [12].

The question of ester coordination can be better explored by using triisobutylaluminium (TBA) and methyl *p*-toluate (MT) as the reactants because: (a) TBA is monomeric in hydrocarbons, ruling out interference by other equilibria; (b) the couple TBA/MT is rather inert toward undesired reactions involving nucleophilic attack by TBA on MT, even with an excess of TBA. This system thus involves only complex formation, unlike systems previously examined [9–13]. Cryoscopy, IR and ^1H NMR spectroscopy were used, solutions in saturated hydrocarbons being used throughout.

Experimental

All manipulations were carried out under prepurified nitrogen. Solvents and reagents were purified by standard procedures. TBA was analyzed as described in ref. 14.

IR spectra were recorded with a Perkin–Elmer 125 spectrometer. ^1H NMR spectra were recorded with a Bruker WH-90 spectrometer, C_6D_6 (3%) being added as an internal lock. For the cryoscopic measurements the Beckman method was used.

Results and discussion

IR spectra (Fig. 1)

The carbonyl stretching wavenumber undergoes a marked shift on formation of the 1/1 complex (free ester: 1734 cm^{-1} ; 1/1 complex 1662 cm^{-1}), in accord with data for similar systems [8]. No further change is observed, however, on adding more TBA (up to an MT/TBA molar ratio of 1/3); even the rather complex $\nu(\text{CO})$ peak shape is retained.

^1H NMR spectra (see Table 1)

The ^1H NMR spectra were recorded in cycloheptane (δ 1.67 ppm, singlet), at -10°C in order to further slow down nucleophilic attack by TBA. With a 1/1 ratio of the reactants significant, though small, differences are observed for the ester alkoxy protons and the TBA methylene protons ($\Delta\delta$'s are ~ 0.2 ppm in both cases); the directions of the shifts are as expected for an electron pair donation from MT to TBA (downfield for the former, upfield for the latter). On adding TBA up to three times the quantity of MT, only one absorption is significantly affected, the methylene proton signals progressively moving towards these for free TBA. This continuous variation can be reasonably explained in terms of a fast exchange between free and complexed TBA molecules.

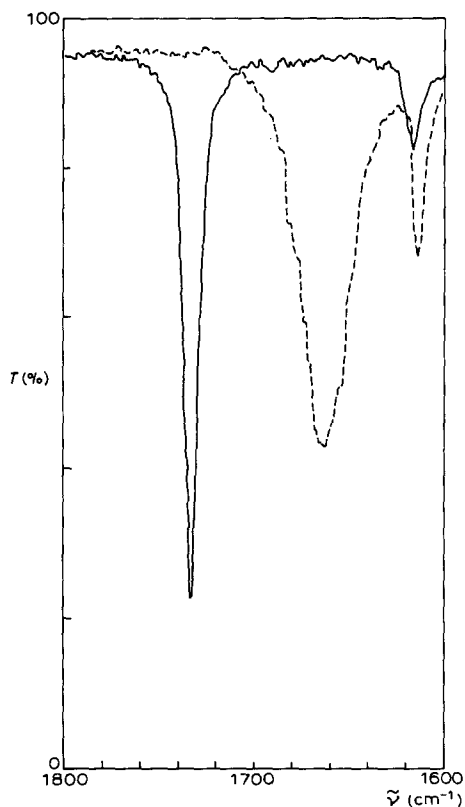


Fig. 1. The COOR region of the IR spectra of MT/TBA mixtures. Room temperature; solvent: n-heptane. MT concentration: 0.033 *M*. —: MT alone; - - - - -: MT/TBA molar ratios of 1 to 1/3.

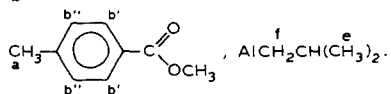
TABLE 1

¹H NMR SPECTRA OF MT/TBA MIXTURES IN CYCLOHEPTANE AT -10°C

Sample ^a (molar ratio)	δ (ppm), multiplicity and attribution ^b of the peaks					
MT alone	7.65, d, b''	6.89, d, b'	3.62, s, c	2.22, s, a		
TBA alone					0.86, d, e	0.33, d, f
MT/TBA (1/1)	7.75, d, b''	6.95, d, b'	3.85, s, c	2.28, s, a	0.90, d, e	0.083, d, f
MT/TBA (1/2)	7.76, d, b''	6.98, d, b'	3.84, s, c	2.28, s, a	0.92, d, e	0.183, d, f
MT/TBA (1/3)	7.79, d, b''	7.01, d, b'	3.86, s, c	2.28, s, a	0.915, d, e	0.241, d, f

^a Concentration of the sole or minor constituent 0.67 *M*.

^b



Cryoscopic measurements (see Fig. 2)

Addition of TBA to cyclohexane causes the expected freezing point depression (see thermogram A). As expected addition of one equivalent of MT to the solution

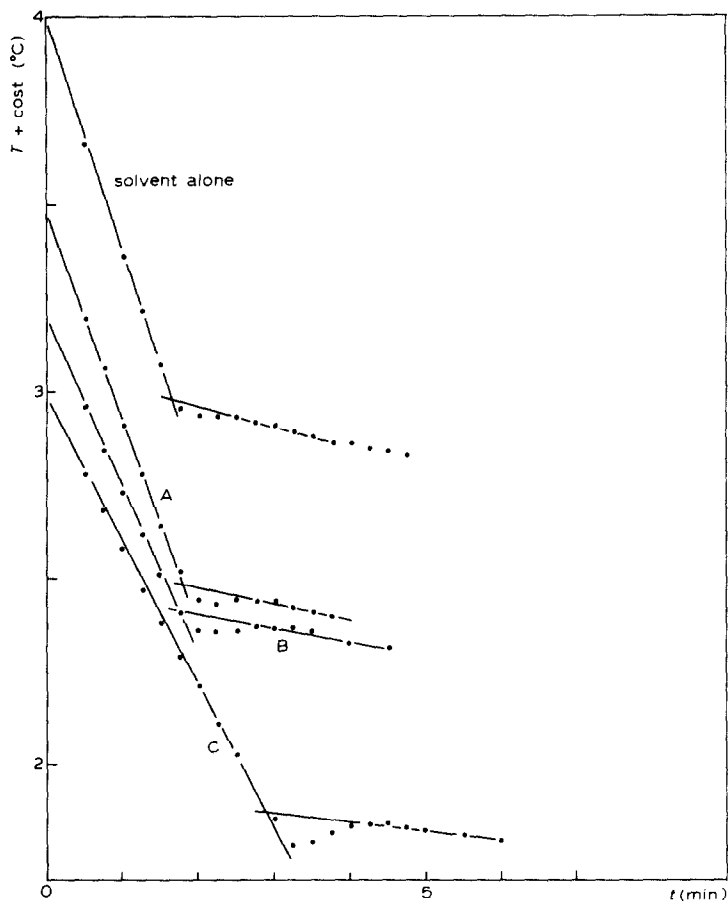


Fig. 2. Cryoscopic measurements in cyclohexane. A: 20 cm³ of solvent + 0.074 g of TBA 95% (remainder: ROAIR₂; HAIR₂ absent); M.W. found 205, calcd. 199. B: A + 0.053 g of MT (MT/TBA molar ratio 1); M.W. found 306, calcd. 341. C: B + 0.074 g of TBA 95% (MT/TBA molar ratio $\frac{1}{2}$); M.W. found 261, calcd. 270.

does not affect significantly the freezing point, because the number of dissolved molecules remains the same (1/1 association; see thermogram B). When another equivalent of TBA is added, the number of dissolved molecules doubles, as shown by a double ΔT_{cr} (see thermogram C); significant formation of a 1/2 complex between MT and TBA would lead to a smaller ΔT_{cr} .

Conclusions

The results rule out the presence of significant amounts of a MT · 2TBA complex. The presence of traces of such a species when excess TBA is added to MT cannot be excluded.

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