Journal of Organometallic Chemistry, 61 (1973) C8–C10

Preliminary communication

New complexes of organoaluminium compounds with esters

KAZIMIERZ B. STAROWIEYSKI, STANISŁAW PASYNKIEWICZ and ANDRZEJ SPORZYŃSKI
Institute of Organic Chemistry and Technology, Technical University (Politechnika), 00-662 Warsaw (Poland)

(Received September 9th, 1973)

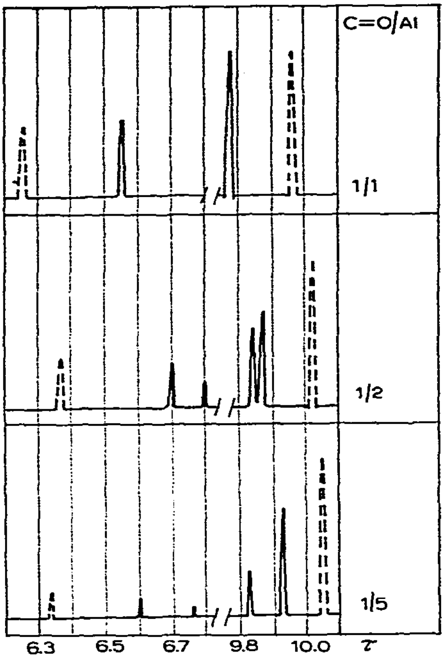
Organoaluminium compounds (OAC) form complexes with the majority of strong Lewis bases. Most of OAC form strong complexes of donor-acceptor type with nitriles[1] and *N*-substituted amides[2,3]. The complexes of those esters investigated with OAC are different from those with other strong electron donors. Besides the 1/1 complex, another complex containing a larger amount of OAC is also present in the solution.

The system studied was PhCOOMe with Me_2AlCl in aromatic solvents. Room- and low-temperature 100 MHz PMR studies, IR studies, cryoscopic measurements and calorimetric measurements of the heat of complex formation have been investigated.

The PMR spectra show that not only one complex is present in the system. At low temperature the peaks of $PhCOOC\underline{H}_3$ and $(C\underline{H}_3)_2AlCl$ in the mixture containing excess of OAC are split into doublets (Fig. 1). This occurs for C=O/Al molar ratios of 1/2, 1/5 and 1/10 and does not occur for the ratio 1/1 [*]. The intensities of the lines in these doublets are different for different molar ratios of the reagents. The IR spectra of complexes investigated show a characteristic shift of the C=O band towards the lower frequencies ($\Delta\nu \approx 80$–$90\ cm^{-1}$) and of the C—O—C band towards higher frequencies (bands 1280 and 1360 cm^{-1}). The C=O band in the complex is broad and its shape depends on the ratio of the reagents (Fig. 2). This peak consists of a main band and a shoulder. For the 1/1 ratio the frequency of the main band is about 1645 cm^{-1} and the shoulder about 1635 cm^{-1}; when there is an excess of OAC these figures are reversed. Cryoscopic measurements also have been carried out for the various molar ratios C=O/Al. The data obtained differ from those expected for the mixture of 1/1 complex and free OAC dimer (Table 1). These data also show that another complex besides the 1/1 is formed. The heats of complex formation of PhCOOMe with Me_2AlCl for 1/1 and 1/2 ratio were measured; the latter is about 10 kcal/mole greater, but a great dispersion of the results was observed, unlike for 1/1 ratio. PMR data exclude rearrangement reaction.

---

[*] C=O/Al means the ratio of the ester to the monomer of the OAC.



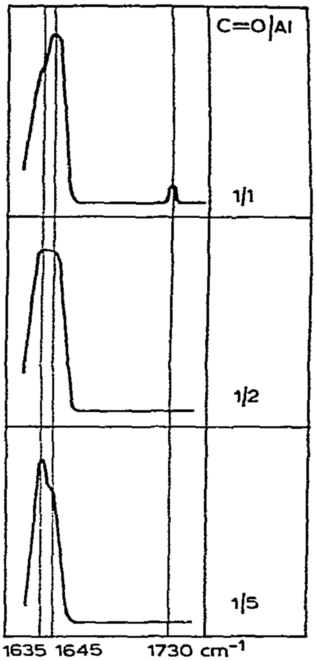


Fig.1. PMR spectra of $PhCOOMe/Me_2AlCl$ system at room and low temperature. - - - -20° ; —— −70°.

Fig.2. The shape of the complexed C=O group band in IR spectra.

TABLE 1

MOLECULAR WEIGHT DATA FOR THE SYSTEM $PhCOOMe/Me_2AlCl$ IN BENZENE

C=O/Al molar ratio	*Molecular weight*	
	Found	*Calcd. for the mixture of 1/1 complex and free OAC dimer*
1/1.04	246	228
1/1.34	257	222
1/1.61	253	218
1/2.02	245	214
1/3.09	235	206
1/7.45	205	195

The 1/1 complex is formed through the oxygen in the C=O group with a monomer of OAC. Another complex is also formed with the excess of OAC. It is suggested that the molar ratio of its components is 1/2 and it is formed through the oxygen of carbonyl group without or only partly with splitting of the chlorine bridge in OAC dimer.

REFERENCES

1 K. Starowieyski, S. Pasynkiewicz and M. Bolesławski, *J. Organometal. Chem.*, 10 (1967) 393.
2 S. Pasynkiewicz and Z. Buczkowski, *J. Organometal. Chem.*, 22 (1970) 525.
3 E. Herbeuval, J. Jozefonvicz, G. Roques and J. Neel, *C.R. Acad., Paris, Ser. C*, 275 (1972) 351.