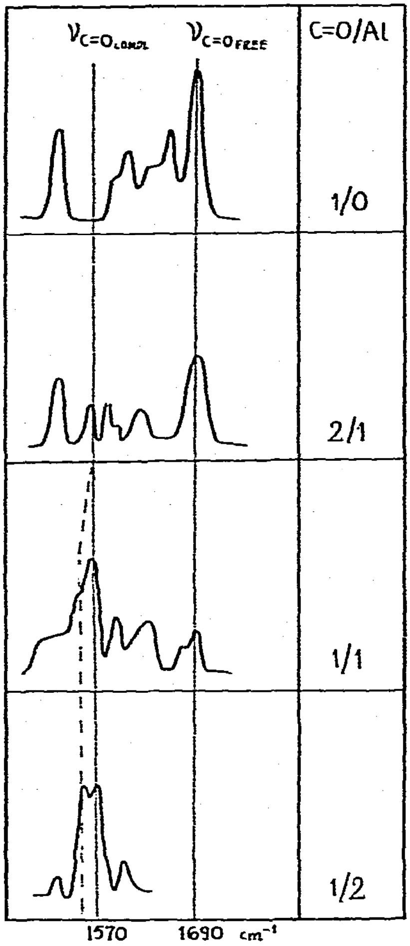


Fig. 1. ν(C=O) region of IR spectra of the system PhCOMe/AlCl$_3$ in benzene.

TABLE 1

MOLECULAR WEIGHT DATA, DIPOLE MOMENTS AND MOLAR CONDUCTANCES FOR THE SYSTEM PhCOMe/AlCl$_3$ IN BENZENE

C=O/Al molar ratio	Molecular weight (M) found (calcd.)	ΔM	Dipole moment (D)	Molar conductance ($\Omega^{-1} \cdot cm^2 \cdot mole^{-1}$)
1/1	256 (253)	+3	8.0	0.28
1/2	351 (387) [a]	—36	10.2	0.76
Ketone			3.0	

[a] Calculated for 1/2 complex; a value calculated for the mixture of 1/1 complex and (AlCl$_3$)$_2$ is 260.

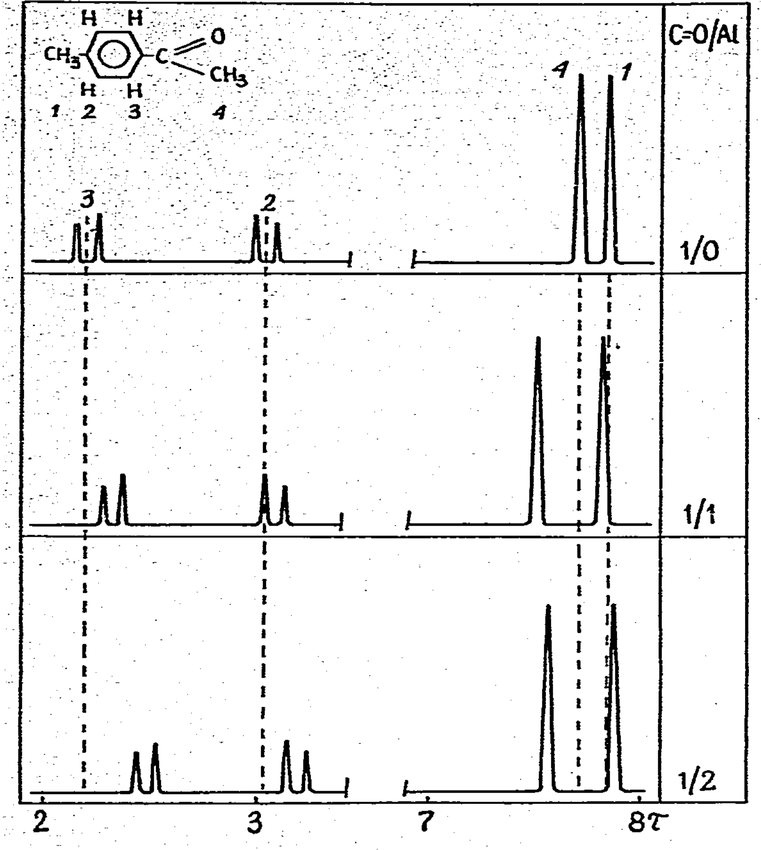


Fig. 2. PMR spectra of the system p-$MeC_6H_4COMe/AlCl_3$ in C_6D_6.

field for the 1/1 complex. A larger shift towards higher field is observed for the 1/2 mixture. This shift is greater for the protons in *ortho*-position (relative to the acetyl group). The signal of protons in $C\underline{H}_3C{=}O$ group shifts downfield for the 1/1 complex, and appears for 1/2 ratio between the signal of the 1/1 complex and that of the free ketone. Similar spectra have been obtained for non-substituted ketones, but the system of aromatic proton signals was complex.

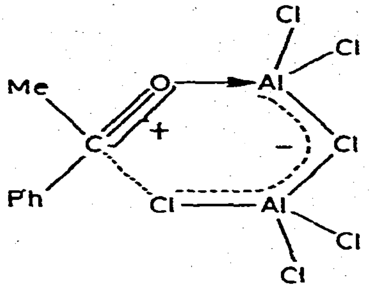
Discussion

In the IR spectra the shape of the complexed $\nu(C{=}O)$ band demonstrates that two complexes exist in solution. Equilibrium of complex formation depends on the ratio of the reagents:

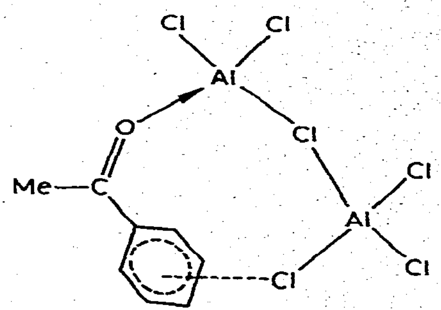
$$2\ PhCOMe \cdot AlCl_3 \rightleftharpoons PhCOMe \cdot 2AlCl_3 + PhCOMe$$

$$PhCOMe \cdot AlCl_3 + AlCl_3 \rightleftharpoons PhCOMe \cdot 2AlCl_3$$

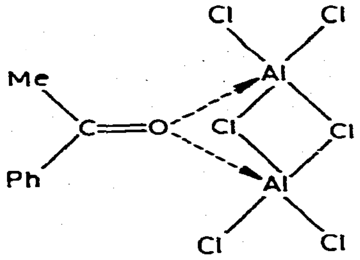
Only a 1/1 complex is formed with excess of ketone. For a 1/1 reagent ratio another complex is formed, containing more than one molecule of $AlCl_3$, and the amount increase as the aluminium chloride/ketone ratio is increased. The molecular weight data also show that in addition to the 1/1 complex, another is formed for 1/2 ratio of reagents. The dipole moments suggest the complexes are covalent, and the larger value for the 1/2 ratio confirms that the solubility of $AlCl_3$ in the solution of ketone is not caused by physical dissolving in the 1/1 complex solution (physical dissolving would diminish dipole moment relative to the 1/1 ratio solution because $(AlCl_3)_2$ has no dipole moment). Conductance data show that both 1/1 and 1/2 complexes are non-ionic. On the basis of solubility of aluminium chloride and molecular weight data one can propose the ratio of reagents for the complex with excess of aluminium chloride equal to 1/2. The following structures can be proposed for this complex:



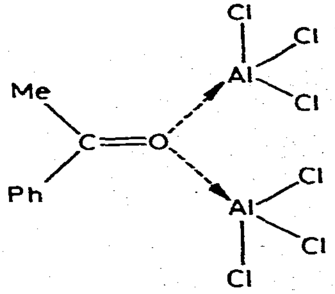
(I)



(II)



(III)



(IV)

Structure I is in best agreement with PMR results. The chemical shift of acetyl protons for 1/2 ratio shows an increase of electron density on the carbonyl atom, relative to the 1/1 complex. The upfield chemical shift of ring protons could be caused by decrease of conjugation between aromatic ring and carbonyl group. The formation of complex II, with interaction between chlorine and aromatic ring, should cause an increase of ring current and a downfield shift of the signals of ring protons, which is not observed, so this structure can be excluded. Structure III should give a bigger shift of acetyl protons for the 1/2 than for the 1/1 complex. The formation of such a complex should also not have so big an influence on the chemical shift of ring protons, so this structure also can be excluded. Structure IV is hardly possible energetically. So structure I is most probable for 1/2 complex.

Experimental

Materials

Aluminium trichloride (BDH, Laboratory Reagent, England) was purified by sublimation in vacuum through a layer of aluminium turnings. Acetophenone (Sojuzchimexport, USSR) was dried over 4A molecular sieves and distilled under nitrogen. *p*-Methylacetophenone was obtained from toluene and acetyl chloride. Benzene and deuterobenzene were dried over sodium, distilled under nitrogen and stored over Na—K alloy.

Technique

Complexes were prepared under nitrogen. A known amount of aluminium chloride was placed in a flask, and suitable amounts of benzene and ketone were added. During these operations the flask was cooled and a solution was stirred with magnetic stirrer.

The IR spectra of about 3% benzene solutions of the compounds were recorded on a Zeiss UR-10 spectrophotometer using a liquid cell of 0.10 mm thickness, adapted for filling under nitrogen. The PMR spectra were recorded on a JEOL 100 MHz spectrometer, using sealed tubes. The molecular weights were measured cryoscopically in benzene, using a standard freezing point depression apparatus modified to work under nitrogen. Dipole moment measurements were run on Dipolmeter DM-01 apparatus. The conductance was measured on Merazet apparatus.

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