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Crystal Structure of Benzoyl Chloride–Antimony Pentachloride

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Friedel–Crafts and related reactions have recently been reviewed in a series of books edited by Olah.[1] Structural indications of the intermediate complexes by infrared studies have been reported:[2] complexes have been shown to exist as donor–acceptor compounds and acylium salts, or mixtures. According to infrared spectroscopy, the $PhCOCl,SbCl_5$ compound contains only a small amount of the ionic oxocarbonium form and is a donor–acceptor complex.[3] In order to confirm this result we have established the geometrical structure of $PhCOCl,SbCl_5$.

The benzoyl chloride–antimony pentachloride complex was prepared from pure reagents, using carbon tetrachloride as the reaction medium.[4] Needle-shaped colourless crystals were obtained by recrystallization from carbon tetrachloride.

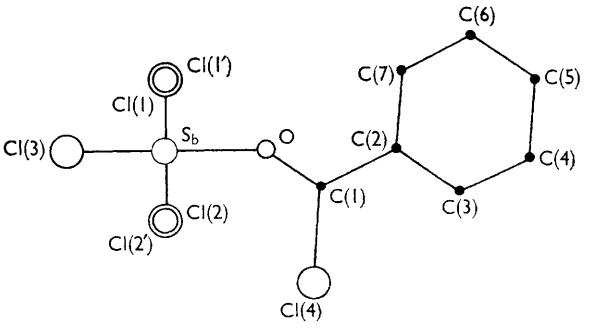
Oscillation photographs, rotation-retigraph and precession photographs established lattice type and space group extinctions; the crystals are monoclinic, with space group $P2_1/m$, and $a = 10{\cdot}46_0$, $b = 7{\cdot}12_9$, $c = 9{\cdot}07_8$Å, $\beta = 103°24'$, $Z = 2$. The intensity data were recorded on multiple equi-inclination Weissenberg photographs about b ($k = 0, \ldots, 6$) utilizing Zr-filtered Mo-K_α radiation. The positional parameters of the antimony atom in the special positions $x\ \frac{1}{4}\ z$ and $\bar{x}\ \frac{3}{4}\ \bar{z}$ were obtained from the Patterson projection P(u, w).

A three-dimensional Fourier synthesis was computed using only those structure factors whose phase angles seemed to be determined by the antimony-atom contribution. This synthesis gave the positions of all the chlorine atoms. Several more Fourier syntheses gave the positions of the remaining atoms.

Refinement of positional and isotropic thermal parameters by least squares and difference synthesis calculations have led to a discrepancy index, R, of 11·3% for 575 non-zero reflexions.

The adduct is composed of a $SbCl_5$ group co-ordinated with the oxygen of the benzoyl group. The adduct has symmetry m. The benzoyl chloride part, the Sb atom, and one Cl atom are all in the symmetry plane; two chlorine atoms are above and another two below the plane.

The Figure shows the molecule projected on the symmetry plane. The co-ordination around antimony is essentially octahedral and the deformations are due to the steric effect of the oxygen



Figure

atom; at present the Sb–Cl bond lengths are 2·29 ± 0·02 Å and the Sb–O bond length is 2·20 Å. All distances in the benzoyl group are normal; the mean distance of the six "benzene" distances is $1{\cdot}38_6$ Å. The molecules are located in layers which are separated by $b/2$ (3·56 Å) from each other. The packing of the molecules is largely governed by chlorine contacts.

This work will be continued using anisotropic temperature factors and locating hydrogen atoms.

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[1] G. A. Olah, "Friedel–Crafts and related reactions", Interscience, New York, 1963.
[2] B. P. Susz and J. J. Wuhrmann, *Helv. Chim. Acta*, **1957**, **40**, 722, 971; D. Cook, *Canad. J. Chem.*, 1959, **37**, 48; D. Cassimatis, P. Gagnaux, and B. P. Susz, *Helv. Chim. Acta*, 1960, **43**, 424; B. P. Susz and D. Cassimatis, *ibid.*, 1961, **44**, 396.
[3] G. A. Olah, S. J. Kuhn, W. S. Tolgyesy, and E. B. Baker, *J. Amer. Chem. Soc.*, 1962, **84**, 2733.
[4] H. Meerwein and H. Maier-Hüser, *J. prakt. Chem.*, **1932**, **134**, 68.