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TRITYL HYDROXYPENTACHLOROANTIMONATE

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Abstract—Trityl hydroxypentachloroantimonate has been prepared and characterized by comparing its m.p., IR, NMR and UV spectra with that of trityl hexachloroantimonate.

THE usual method of preparing carbonium ions in solution or in certain instances stable salts is to react certain organic halides with an antimony pentahalide.⁽¹⁾ On the basis of some earlier observations, we decided it should be possible to obtain a mixed ligand anion trityl salt by the reaction of trityl alcohol with antimony pentachloride. This report concerns the preparation and characterization of trityl hydroxypentachloroantimonate which, to our knowledge, has not been reported previously. A trityl salt with a hetero ligand polar anion should be of importance in ionic reaction studies in which the anion is involved in the mechanistic path the reaction might follow.

RESULTS AND DISCUSSION

Trityl hydroxypentachloroantimonate (PC) is bright orange in contrast with trityl hexachloroantimonate (HC) which, prepared in a similar manner, is a canary yellow coloured solid.

Chemical analysis. The calculated percent carbon and hydrogen for the PC compound is 40·78 and 2·89. Microanalysis laboratory reports 39·83 and 3·00.

Melting point. Both the HC and PC compounds lack sharp m.p. The decomposition range, however, is quite different for the two compounds.

HC compound: On a Kofler microheating stage apparatus the first evidence for decomposition occurred at 220°C. The field of view became lightly misty with a yellowish hue. As the temperature increased, the solid particles of sample became liquid droplets and by 230°C a large part of the sample which had been through the liquid state remained only as a greyish residue.

PC compound: In the range 220–230°C no evidence of change occurred. As the temperature increased above 240°C the orange colour of the sample slowly changed to an orange brown colour which, at yet higher temperatures, changed to a brown colour. At 290°C the globules of sample were intact and there was still no evidence for complete decomposition (i.e., residue).

IR Spectra. Spectra of triphenylmethanol, HC and PC as nujol mulls and in analar 1,2 dichloroethane were compared. Absorption peaks of the solution spectra of particular interest to the characterization of the PC compound are those associated with the —OH stretch in the 3500 cm^{-1}(2) region and the C—O stretch in the 1150 cm^{-1} region.(2)

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[1] N. C. Deno, *Chem. and Eng. News* Oct. 5, p. 88 (1964).

[2] L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules* p. 83. J. Wiley, London (1954); W. Brugel, *An Introduction to Infra Red Spectroscopy* (Translated by A.R. and A. J. D. Katritzky) p. 337. Methuen and Co., London (1962).

The triphenyl methanol solution spectrum contained a sharp peak at 3515 cm^{-1} which was not present in the solution spectrum of the HC compound but was evident in the solution spectrum of the PC compound as a broad band over the range 3530 cm^{-1} to 3030 cm^{-1}. The C—O stretching frequency absorption in the solution spectrum of triphenyl methanol appeared at 1160 cm^{-1} as a medium sized sharp peak. This peak, as might be expected, was not evident in the spectra of the PC or HC compounds. Pertinent absorption regions are shown in Fig. 1. A comparison of the nujol mull spectra resulted in the same observations. The spectra of the PC and HC compounds either in nujol or 1,2 dichloroethane were identical in all other respects.

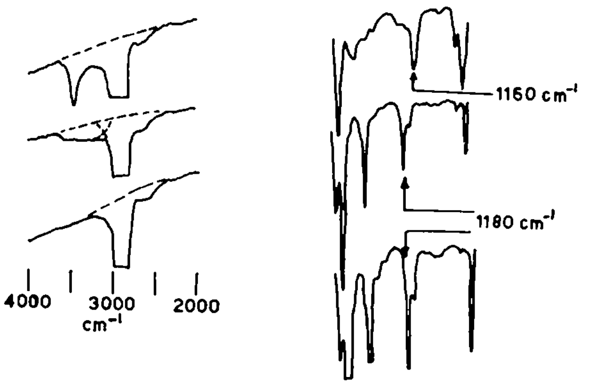

FIG. 1. IR absorption peaks in the region of the —OH and —C—O stretching frequencies. From top to bottom of Fig.; trityl methanol trityl hydroxypentachloroantimonate and trityl hexachloroantimonate in 1,2 dichloroethane.

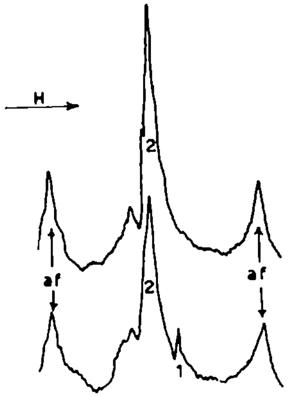

FIG. 2. PMR evidence for the proton in the anion hydroxypentachloroantimonate.

PMR spectra The PMR spectra of HC and PC compounds in methyl cyanide showed that the same peaks which were found in the spectrum of the HC compound were found in the spectrum of the PC compound in addition to the peak labelled 1 (Fig. 2). This peak is assigned to the proton of the hydroxypentachloro anion. Spectra of the triphenyl methanol and the solvent methyl cyanide were also determined. All spectra were calibrated and τ values calculated. The protons on the trityl cation were found to absorb at 2·37 τ while the protons of the trityl alcohol absorb at 2·77 τ.

The alcohol proton of trityl alcohol absorbed at 5·70 τ while the proton of the —OH function on the antimonate absorbs at 2·73 τ. The calibrated τ value for the protons of the solvent was determined as 8·13 τ which compares favourably with the literature value of 8·10 τ.(3)

For convenient comparison the τ values are set out in Fig. 3. All spectra were determined at 40 megacycles.

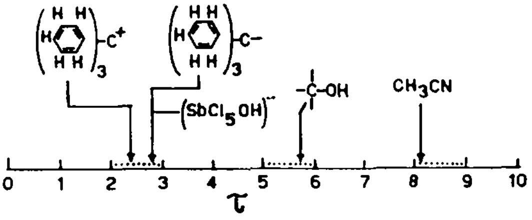

FIG. 3. Relative positions of τ values for protons of various compounds. The internal reference was tetramethylsilane.

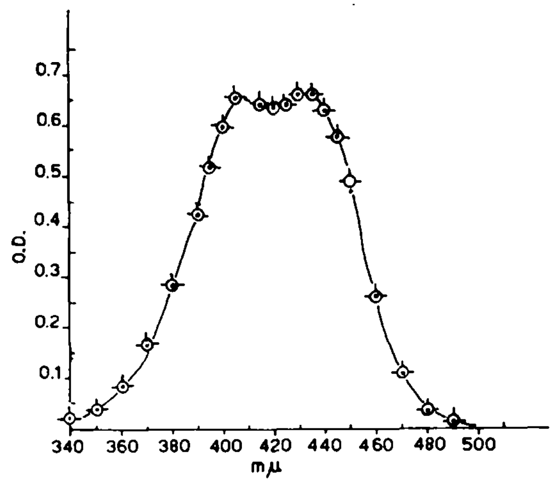

FIG. 4. UV spectrum of trityl hydroxypentachloroantimonate —○— immediately after preparation —⦶— 1 hr and —●— 24 hr after preparation.

UV spectroscopy. The UV spectrum of the PC compound is reproduced in Fig. 4. The absorption spectrum shows a maximum at 408 and 431 mμ. These values are nearly identical to those of the HC compound in the same solvent. The molar extinction coefficient ε at 431 mμ is calculated to be 32,600. Also in Fig. 4 are included the spectra taken after the sample solution had stood for 1 hr and 24 hr. It is evident that the stability of the PC compound in methylene dichloride under high vacuum anhydrous conditions is very good.

CONCLUSION

The greater relative stability of the PC compound to that of the HC compound, as indicated by m.p. behaviour, shows that two different compounds are being compared.

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[3] Tables compiled by G. V. D. Tiers of Central Research Department, Minnesota Mining and Mfg. Co., St. Paul, Minnesota, U.S.A.

The greater stability of the PC compound also indicates that in the solid state this compound has greater ionic or polar character. That the PC compound contains an —OH function but not the C—O linkage is made evident by the IR evidence. This, in turn, allows the conclusion that the —OH function must have been removed in tact from the trityl alcohol and exists elsewhere in the molecule as the —OH moiety. With the exception of the above IR absorptions, the invariance of the rest of the spectra of the PC and HC compounds further supports the conclusion that the PC compound is a carbonium ion salt. The protons of the cation of the PC compound resonate at the same frequency as those of the cation of the HC compound. This means, of course, that a solution of PC give the trityl carbonium ion, but of greater importance it means that the —OH function has been completely removed from the trityl methanol. The different τ value for the proton of the —OH function in the PC compound from that in the trityl methanol is indicative that this function is bonded or complexed differently from that of the alcohol function. Further evidence that the PC compound is a carbonium ion salt has been obtained from the UV spectrum of the PC compound in methylene dichloride. It is nearly identical to that of the HC compound. The same two maxima are obtained in the region of 410 and 430 mμ. The almost identical value of the molar extinction coefficient obtained indicates that the PC compound produces in solution carbonium ions in quantity comparable to that of the HC compound.

EXPERIMENTAL

Equimolar CCl_4 solutions of freshly vacuum distilled $SbCl_5$ and freshly purified trityl MeOH mixed under anhydrous conditions in a dry box gave a reddish-orange solid. The solid was isolated in the dry box and further dried on a high vacuum line.

Acknowledgement—The author is indebted to Mr. S. Walker for obtaining the PMR spectra on a Varian 4300B spectrometer.