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THE PENTAMETHYLBENZYL-CARBONIUM ION AS A STRONG ELECTROPHILIC AGENT IN PROTON ACIDS. REACTIONS WITH HYDROGEN, ALKANES AND AROMATIC HYDROCARBONS

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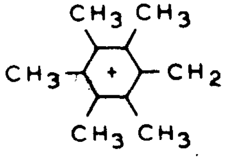
The pentamethylbenzyl-carbonium ion (PMB^+) has been prepared by several methods, e.g. by dissolving pentamethylbenzylchloride in strong proton acids (e.g. sulphuric acid, hydrogen fluoride) or by warming a solution of hexamethylbenzene in sulphuric acid (H_o = -10.0)[1].

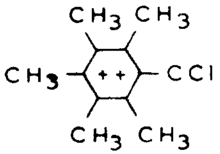


At room temperature hexamethylbenzene (p_K = -8.41 at 15°C)[2] in sulphuric acid (H_o = -10.0) is protonated and as such rather stable, although after a few days conversion to PMB^+ occurs. If, however, this solution is added to an excess (1 : 3 $^v/_v$) of phosphoric acid containing phosphorpentoxide PMB^+ is formed immediately.

A solution of PMB^+ in sulphuric acid has a purple-red colour (λ in mμ : 520 (1900); 330 (14300): 265 (6100); 240 (9000); 220 (8500)). The reactivity of this solution appears when alkanes, hydrogen, benzene or other aromatic compounds are added. The colour then changes from purple-red into bright yellow, indicating the formation of protonated hexamethylbenzene (λ in $m\mu$: 395(9000); 280 (5600)).

The acidity of the solution is essential for these reactions. If it is lowered (e.g. by adding phosphoric acid) the reaction rates decrease. This may be connected with the basicity of the leuco compound which is formed. Further evidence follows from the reactivity of PMB^+ in which one methyl group is replaced by $-CH_2NH_3^+$ *). Although the inductive effect associated with the $-NH_3^+$ group is expected to increase the electrophilic behaviour of the ion, the reaction rates are decreased. On the other hand the basicity of the leuco compound formed by e.g. H^- addition runs parallel to the reactivity: hexamethylbenzene in sulphuric acid ($H_0 = -10.0$) is completely protonated whereas pentamethylbenzylammonium is not protonated.

This picture is consistent with the observation that Hart's ion[4] in strongly acidic solvents is stable towards hydrocarbons:



The reactions with alkanes or hydrogen in sulphuric acid solutions can be carried out at room temperature. With methane or hydrogen the reaction rate is low, with iso-octane it is high.

The reactions with aromatic hydrocarbons are disturbed by sulfonations. The more so as these aromatics had to be substituted with $-OCH_3$ or $-CH_2NH_3^+$ groups to increase the solubility. At -20°C.

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*) This ion has been prepared by photo-oxidation of pentamethylbenzylamine in a glass of phosphoric acid containing phosphorpentoxide ($H_0 = -4.40$) at -70°C.[3] When this product is dissolved in sulphuric acid at room temperature it is stable.

however, the rate of the sulfonating reaction decreases, resulting in a fast reaction between the aromatic molecule and PMB^+.

It may be of interest to note that on warming up the reaction mixture from -20°C to room temperature the intensity of the absorption maximum of the end-product in sulphuric acid at 395 mμ decreases. Comparative experiments with pentamethylbenzene suggest that the decreased intensity at 395 mμ is due to intra-methyl migration.

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1 M.J. Jorgenson and D.R. Hartter, J. Amer. Chem. Soc. **85**, 878 (1963).

2 E.M. Arnett and R.D. Bushick, J. Amer. Chem. Soc. **86**, 1564 (1964).

3 To be published.

4 H. Hart and R.W. Fish, J. Amer. Chem. Soc. **80**, 5894 (1958).