

FREE RADICALS AS HOST MOLECULES

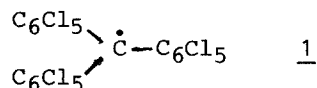
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ABSTRACT. Perchlorotriphenylmethyl radical (1) and some of its radical derivatives form inclusion compounds with cyclic molecules. Thermal stabilities and crystal studies of some clathrates of 1 are presented and discussed.

1. INTRODUCTION

The design of new host molecules is currently an object of increasing interest. The general structure features of many clathrands are molecular bulkiness and limited conformational flexibility¹. Molecular symmetry (specially three- or two-fold symmetry) also plays an important role in determining the inclusion ability of a host compound; providing a new principle for the design of novel host molecules².

Perchlorotriphenylmethyl radical (PTM, 1) is an exceptionally stable carbon free radical with a considerably bulky molecular geometry³. On the basis of space filling models it has been concluded that PTM radical has a propeller-like conformation (D₃ symmetry)^{3a}. It has also been suggested that such conformation must be very rigid (high enantiomerization barrier for the reversal of propeller helicity) due to the intramolecular congestion of the three pairs of voluminous ortho-chlorine atoms⁴. Those clathratogenic features encouraged us to start a systematic study of the inclusion properties of PTM radical, functionalized derivatives and other polychlorinated triarylmethyl radicals³.



2. CLATHRATES AND THERMAL STABILITIES

PTM radical forms beautiful crystalline inclusion compounds with benzene, fluorobenzene, chlorobenzene, toluene, 1,4-dioxane, tetrahydrofuran, cyclohexane and cyclohexene; the host guest ratio being 1:1 for most of them. Those compounds are stable towards vacuum drying at room temperature but on heating a release of the guest molecules takes place at different temperatures.

The thermal stability of some of the PTM inclusion compounds has been studied for the solid state declathration:



using DSC and TG techniques, under both non-isothermal and isothermal conditions.

The loss of the guest molecules corresponds to endothermic processes with low enthalpic values ($\Delta H_{\text{dec}} \sim 13\text{--}30 \text{ KJ mol}^{-1}$). The rate constants for such processes were evaluated for each compound at several temperatures, by fitting isothermal TG curves to different kinetic physical mechanisms of solid state reactions (diffusion, nucleation, growth, nucleation-growth and homogeneous)⁵. The kinetic parameters (K_0 , E_a) were calculated from an Arrhenius plot of the rate constants. The declathration physical mechanisms were assigned on the basis of agreement between these calculated kinetic parameter and those determined from non-isothermal TG curves by mean of Coats-Redfern method.

On the basis of both thermodynamic and kinetic parameters and the assigned physical mechanisms two types of thermal behaviour can be differentiated. One preferred for smaller guests (C_6H_6 and $\text{C}_6\text{H}_5\text{F}$; $\Delta H_{\text{dec}} \approx 15 \text{ KJ mol}^{-1}$, $E_a > 100 \text{ KJ mol}^{-1}$ and Growth mechanism) and the other for the larger ones ($\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{Br}$ and $\text{C}_4\text{H}_8\text{O}_2$; $\Delta H_{\text{dec}} \approx 30 \text{ KJ mol}^{-1}$, $E_a < 100 \text{ KJ mol}^{-1}$ and Nucleation-Growth mechanism).

3. CRYSTAL STRUCTURES

The crystals of the inclusion compounds belong to the triclinic system, $P\bar{1}$ space group, with two PTM molecules and two molecules of guests in the unit cells. In $\text{PTM} \cdot 1\text{C}_6\text{H}_6$ the host molecules adopt a non-symmetrical propeller conformation with fixed benzene molecules accommodated in channels.

The packing of six neighbour host molecules through their coplanar phenyl groups (apparently a π - π -type interaction) create the channels where the guests are located. This structural arrangement is similar to that observed for the xylene clathrate of tris(1,8-naphthalenedioxy)cyclotriphosphazene⁶ and differs substantially from those observed in most of the families of hosts with trigonal symmetry (triphenylmethane, tri-*o*-thymotide, cyclotrimeratrylene, hexahosts and perhydrotriphenylene)².

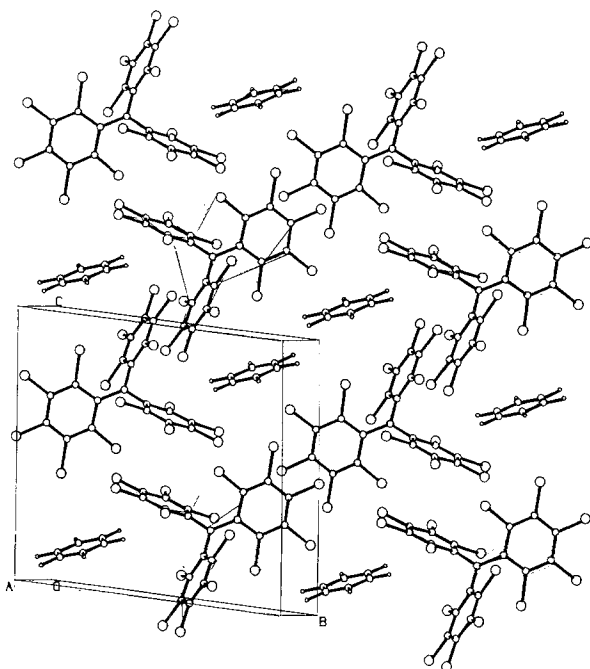


Figure. Packing in the $\text{PTM}\cdot\text{1C}_6\text{H}_6$ clathrate

4. CONCLUDING REMARKS

Other polychlorinated triphenylmethyl radicals also present similar inclusion properties even with linear hydrocarbons. The introduction of functional groups (hydroxyl, phosphonium, etc) at the para position(s) of PTM radical permits to engineer new clathrate hosts with improved thermal stabilities, due to the higher energies of host-host interactions (hydrogen bonding, ionic). The PTM radical may be considered only as a first representative of a series of host compounds having radical character and therefore providing a stable paramagnetic contour with possible useful applications (radical intermediates, polymerizations).

REFERENCES

1. F. Vögtle, H-G.Löhr, J. Franke, D. Worsch, Angew. Chem. Int. Ed. Engl. 24 (1986) 727.
2. D.D. Mac Nicol, in J.L. Atwood, J.E. Davies, D.D. Mac Nicol (Eds): Inclusion Compounds. Vol. 2, Academic Press, London 1984, P. 123-168.

3. a) M. Ballester, J. Riera, J. Castañer, C. Badía, J.M. Monsó, J. Am. Chem. Soc. 93 (1971) 2215. b) M. Ballester, J. Riera, J. Castañer, A. Rodríguez, C. Rovira, J. Veciana. J. Org. Chem. 47 (1982) 4498. c) M. Ballester, J. Veciana, J. Riera, J. Castañer, C. Rovira, O. Armet. J. Org. Chem. 51 (1986) 2472.
4. K.S. Hayes, M. Nagumo, J.F. Blount, K. Mislow, J. Am. Chem. Soc. 102 (1980) 2773.
5. D.H. Bamford, Ed. Compr. Chem. Kinet. (1980) Chapter 3, p. 22.
6. H.R. Allcock, M. Teeter-Stein, E.C. Bissell, J. Am. Chem. Soc. 96 (1974) 4795.