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THERMOCHEMICAL INVESTIGATION OF SOME SELECTED SOLVATES OF CALIX[4]RESORCINARENE

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Abstract

Lipophilic calix[4]resorcinarene derived from lauryl aldehyde forms stable crystalline solvates with a range of organic solvents: acetone, 1,4-dioxane, methylethyl ketone, dimethylformamide, dimethylacetamide, N-methylpyrrolidinone, butyronitrile, methanol, 1,2-dimethoxybenzene and acetonitrile. The composition and thermal stability of these solvates was followed by thermogravimetric method, indicating a stoichiometry ranging from 1 to 3 (calixresorcinarene/solvent). The activation energy was evaluated for the selected solvates. Molecular modelling, using Hyperchem 5.0 software, was applied to the selected solvates.

Keywords: calix[4]resorcinarene, solvates, thermogravimetry

Introduction

Calixarenes are the class of macrocyclic molecular receptors derived from phenols and aldehydes [1], capable of forming well defined complexes with organic and inorganic cations, anions and neutral molecules. One of the characteristic features of calixresorcinarenes is their ability to form a range of solvates with solvent molecules upon crystallization. These solvates are particularly strong in many cases and thus the preparation of solvent-free host systems meets serious problems. Calix[4]resorcinarenes [2] form a great variety of solvates, as well as their derivatives, so-called cavitands, in which hydroxyl groups are linked by small bridging units, such as methylene, ethylene, silyl, etc. X-ray crystal structures of a wide range of cavitand solvates have been collected in a monograph [3] and in a recent paper by Cram and co-workers [4].

The complexing abilities of calixarenes depend strongly on the solvent. This dependence is due to the competitive binding of the solvent molecules by calixarenes, but also due to conformational equilibria of calixarenes in various

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solvents. The conformational equilibria can be followed conveniently by variable-temperature NMR spectroscopy [5], and the binding properties of calixarenes towards solvent molecules can be assigned by calorimetric and ther-

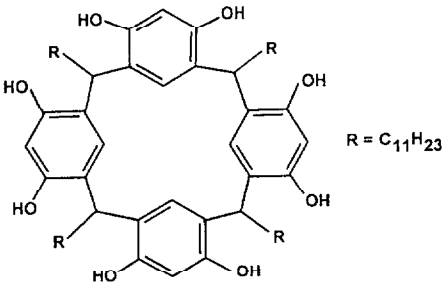

Fig. 1 Structural formula of calix[4]resorcinarene

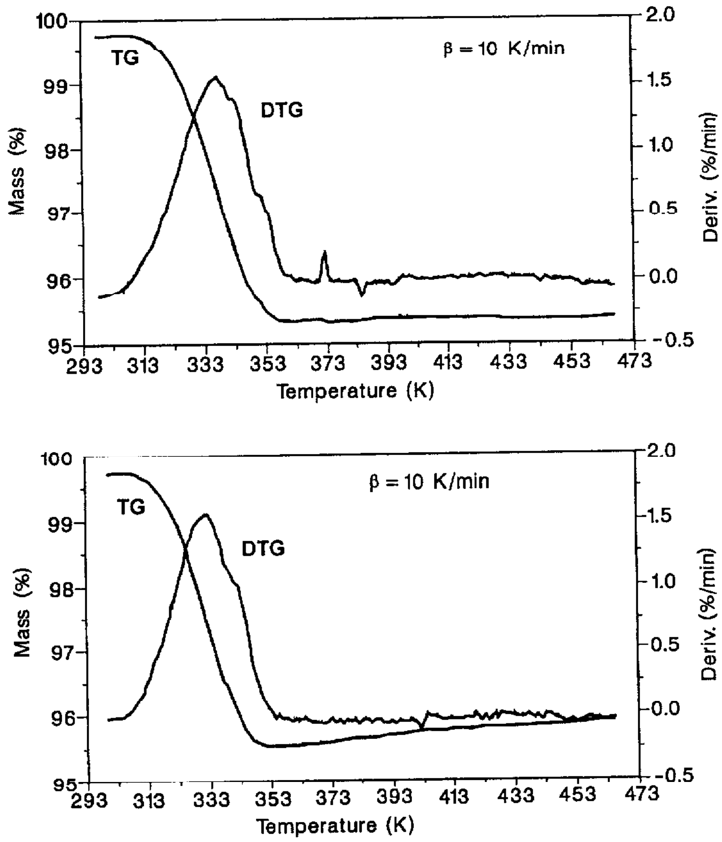

Fig. 2a TG and DTG curves of calix[4]resorcinarene solvates with acetonitrile (top) and methanol (bottom)

mogravimetric methods. Thermal analysis of the solvate of *p*-isopropylcalix[4]arene with *p*-xylene has been recently published [6].

Experimental

All reagents of analytical grade were obtained from Fluka, Aldrich, or Merck, and used as received. The calix[4]resorcinarene (Fig. 1) was prepared by the method of Aoyama [7] from lauryl aldehyde and resorcinol, and dried at 100°C under a pressure of 0.1 Torr for 12 h. Crystallization was performed in the solvents listed in Table 1. It should also be noted that attempts to obtain solvates with toluene, chloroform, cyclohexane, methylene chloride and carbon tetrachloride failed, due to the gelation of the solvent upon addition of calix[4]resorcinarene. Solvates were dried in air at 20°C.

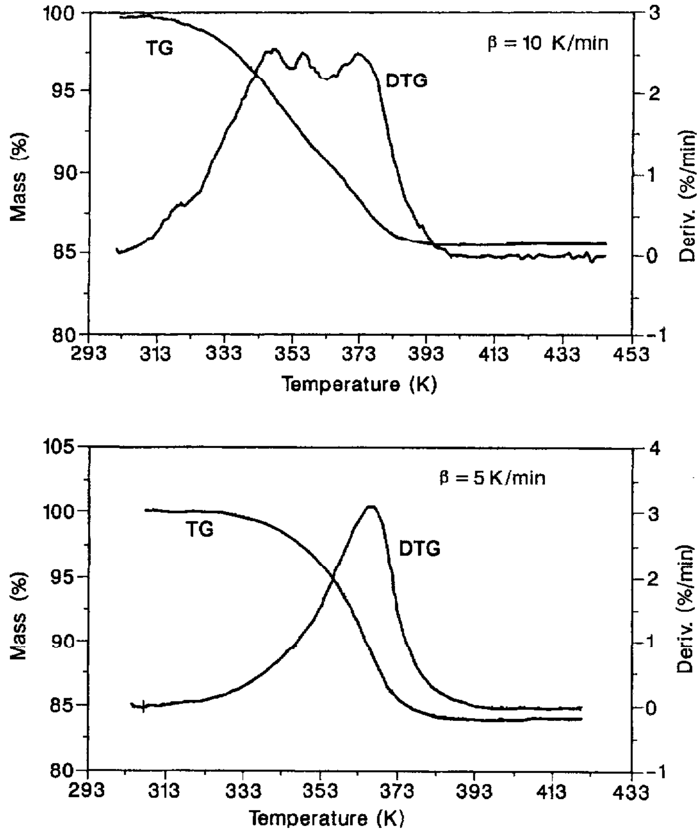

Fig. 2b TG and DTG curves of calix[4]resorcinarene solvates with acetone (top) and methylethylketone (bottom)

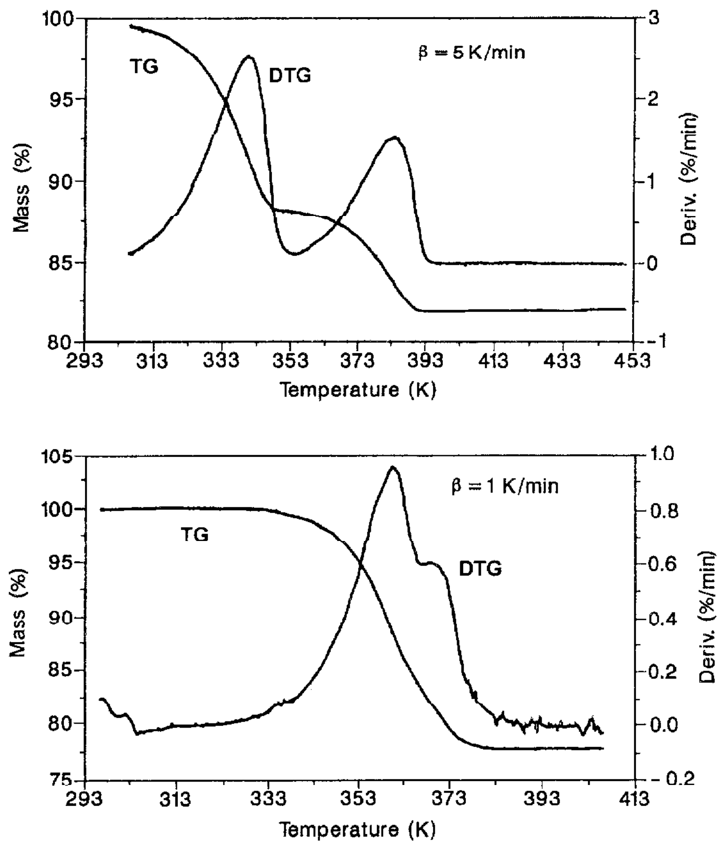

Fig. 2c TG and DTG curves of calix[4]resorcinarene solvates with 1,4-dioxane (top) and 1,2-dimethoxybenzene (bottom)

The thermal properties of the crystalline complexes were investigated using a DuPont TGA 951 thermogravimetric analyser. Calibration of the TGA cell was effected using a sample of calcium oxalate monohydrate under a blanket of flowing dry argon (100 ml min^{-1}) at a heating rate of 5 K min^{-1}. The accuracy of the mass measurements was 1%. The inflection temperature of the first transition (dehydration) corresponded to 426.9±1 K and the loss of bound water was equal to 12.5%. The TGA Standard Data Analysis Programme, Version 5.0 was used for mass loss determination, and the Decomposition Kinetics Data Analysis Programme, Version 4.0 for DuPont Thermal Analyst 2100 was used for the calculation of the activation energies of selected solvates [8]. Series of decomposition measurements of solvates were performed using various heating rates β=1, 2, 5, 10, 20 K min^{-1} for methanol, acetone, methylketone, 1,4-dioxane, and acetonitrile or β=0.5, 1, 2, 5, 10 K min^{-1} for 1,2-dimethoxybenzene.

Molecular modelling (MM+) of the selected solvates was performed using the HyperChem software version 5.0.

Results

Some selected thermogravimetric curves are shown in Fig. 2A-C, and the decomposition data for the solvates are presented in Table 1.

Table 1 Thermal behaviour of calix[4]resorcinarene complexes with some solvents

Solvent	*Bp.* of solv./ K	Mass loss/ %	Midpoint/ K**	C11*: solv. ratio	E_a/ J mol^{-1}
methanol	337–338	2.6	340	1:1	106.4
acetone	328–330	13.3	361.6	1:3	99.2
methylethylketone	352–353	15.8	372.6	1:3	82
1,4-dioxane	373–375	11.5	356	1:2	76
		6.3***	401***	1:1	78
1,2-dimethoxy-benzene	478–450	21.3	386.2	1:2	130
acetonitrile	352–354	4.0	360.9	1:1	156
butyronitrile	388–390	7.4	343.4	1:1	–
N,N-dimethyl-formamide	426–427	6.8	356.5	1:1	–
		9.4***	407.7***	1:2	–
N,N-dimethyl-acetamide	438–440	11.5	368.7	1:2	–
		11.8***	434.5***	1:2	–
1-methyl-2-pyrrolidinone	354/10 mm	9.4	484.9	1:1	–

* C11 – abbreviation for calix[4]resorcinarene
** β=10 K min^{-1}
*** Second stage of decomposition

The stoichiometry of solvation was estimated on the basis of the mass loss, and ranged from 1:1 to 1:3 stoichiometry. As shown by the thermal curves, it was difficult to resolve each particular step of the solvent liberation. For 1,4-dioxane, DMF and DMA two independent stages were confirmed – first the loss of two molecules of the solvent, followed by the loss of the third one for the dioxane solvate, one molecule followed by two molecules for the DMF solvate, and 2 molecules followed by two molecules of DMA. The character of TG and DTG curves suggested a complex pattern of desolvation – most probably, apparent stages are strongly biased, thus the calculated energies of activation may have a qualitative meaning. The dependence of logβ *vs.* T^{-1} for different fractional extents of reaction (α) for the selected solvates did not display linearity – this confirmed the complexity of the decomposition processes even in cases where the

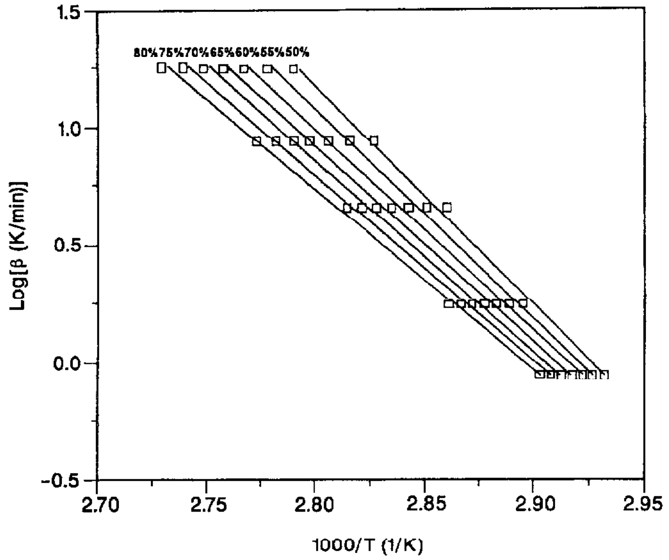

Fig. 3 The dependence of logβ *vs.* T^{-1} for the desolvatation of calix[4]resorcinarene in acetonitrile for different fractional extents of reaction, α

stoichiometry was 1:1, for example, calix[4]resorcinarene – methanol and calix[4]resorcinarene – acetonitrile solvates (Fig. 3). Most probably, the complexes of 2:2 (or x:x) are formed, as in the case of the calix[4]arene-*p*-xylene complex [6], and in the first stage the loss of the first molecule occurs, followed by the second molecule, but the processes are overlapping.

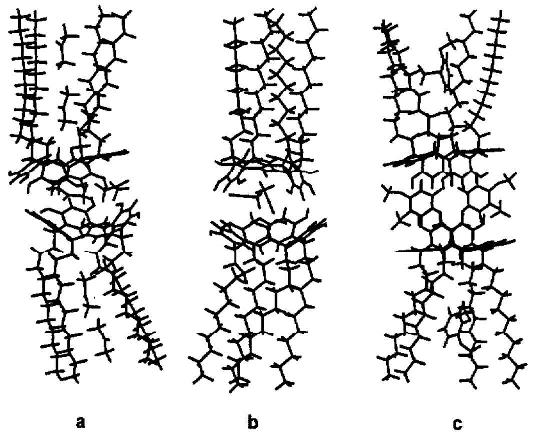

Fig. 4 Modelled structures of calix[4]resorcinarene solvates with acetone (a), acetonitrile (b) and 1,2-dimethoxybenzene (c)

Taking into account the estimated stoichiometry of the solvates and the crystallographic data [6, 10], as well as papers of Stirling related to self-assembly of amphiphilic calix[4]resorcinarenes [11], molecular modelling has been performed for the selected solvates with the calix[4]resorcinarene. Three of the modelled structures are shown in Fig. 4.

It turned out that for the given stoichiometry the most stable structures are obtained – they are much more stable than uncomplexed calix[4]resorcinarene. This points to the fact that the calix[4]resorcinarene will form solvates, and the preparation of the crystalline complexes with polyfunctional molecules may be difficult due to the competition with the solvent molecules, unless their binding strength with calix[4]resorcinarene is much higher than the solvation energy of the calix[4]arene. Complex formation between calix[4]resorcinarene and the guest molecules can be observed in the solution, but it is difficult to obtain the crystals for the reason mentioned above.

The calculated activation energies for the decomposition of solvates suggested that for the crystallization of complexes better results can be achieved in methylethylketone, acetone and methanol.

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