

Fast Proton Exchange and Unimolecular Formation of Ion-Molecule Complexes: The Fragmentation of Protonated Tri- and Tetrabenzylmethane

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INTRODUCTION

The intramolecular proton transfer between protonated and neutral benzene rings is an extremely fast reaction, in contrast to the corresponding intermolecular process (Kuck, 1986, 1985). For example, 16 and 21 protons are equilibrated within some microseconds in protonated tribenzylmethane ($[1+H]^+$) and tetrabenzyl methane ($[2+H]^+$), respectively. Another intriguing feature of these protonated oligophenyl alkanes is the predominant (1) or exclusive (2) loss of *two* molecules of benzene, even from long-lived, metastable ions (Kuck, 1983). In a search for an eventual interrelation between the fast proton exchange and the unusual fragmentation behavior some homologs of 1 with less symmetrically branched alkane moieties have been investigated, and the structure of the fragment ions $[M+H-2C_6H_6]^+$ from $[1+H]^+$ and $[2+H]^+$ have been determined. The results corroborate the hypothesis that the origin of the simultaneous loss of two benzene molecules might be an *entropic stabilization* of arenium ions owing to their fast-moving protons, as suggested recently for mononuclear arenium ions (Mason, 1987; Fernandez, 1987).

EXPERIMENTAL

The fragmentation of the unlabelled ions was measured by MIKE spectrometry. The H^+/D^+ exchange in the deuterium labelled $[M+H]^+$ ions was determined by B/E linked scan spectrometry to achieve good mass resolution (*cf.* Kuck, 1983), using a double-focussing instrument (Vacuum Generators ZAB-2F). The $[M+H-2C_6H_6]^+$ fragment ions from $[1+H]^+$ and $[2+H]^+$ were compared by CID(He) with other $C_{10}H_{11}^+$ and $C_{17}H_{17}^+$ ions, respectively, generated by CI(*i*- C_4H_{10}) from 1- and 2-tetralol, 1-methyl-1- and 2-methyl-2-indanol, 2-hydroxymethylindan ($[M+H-H_2O]^+$), dialin, 1- and 2-methylindene ($[M+H]^+$), and 2-benzylindan ($[M+H-C_6H_6]^+$), as well as from 1- and 2-benzyl-1-tetralol, 2-benzyl-2-tetralol ($[M+H-H_2O]^+$), the corresponding olefins, 2,2'-spirobiindan ($[M+H]^+$), and 2,2-dibenzylindan ($[M+H-C_6H_6]^+$).

RESULTS

The abundance ratios $r_a = [M+H-2C_6H_6]^+ / [M+H-C_6H_6]^+$ for protonated tris-(ω -phenyl-alkyl)-methanes $[1+H]^+$ and $[3+H]^+$ to $[6+H]^+$ (Table 1) are smallest for homologs with different aliphatic chains, protonated tris-(β -phenethyl)-methane $[5+H]^+$ representing a relative maximum. Thus, r_a depends on the symmetry of the alkane moiety rather than on the proximity of the benzene rings. Nevertheless, the interannular proton exchange is very fast in all cases and independent of the alkane moiety, as shown by the random loss of benzene isotopomers from the deuterated analogs $[3a+H]^+$, $[4a+H]^+$ (Table 2) and $[1a+H]^+$, $[2a+H]^+$ (Table 3). The MIKE and CID spectra of ions $[1+H-2C_6H_6]^+$ and of the $C_{10}H_{11}^+$ reference ions (m/z 131) show no significant differences, suggesting that (possibly intercon-

verting) tetralyl or methylindanyl ions are formed along with the two C_6H_6 molecules. Likewise, ions $[2+H-2C_6H_6]^+$ and the $C_{17}H_{17}^+$ reference ions (m/z 221) show very similar MIKE and CID spectra, except for protonated 2,2'-spirobiindan, which, as a specific feature, yields abundant fragments $C_8H_9^+$ (m/z 105). Hence fragment ions $[2+H-2C_6H_6]^+$ are "simple" tertiary carbenium ions (probably benzyltetralyl type structures) rather than a protonated arene, viz. $[2,2'\text{-spirobiindan}+H]^+$. In contrast, the first C_6H_6 molecule from ions $[1+H]^+$ and $[2+H]^+$ is formed along with arenium type fragment ions, viz. $[2\text{-benzylindan}+H]^+$ and $[2,2\text{-dibenzylindan}+H]^+$, respectively, as shown independently by the fast interannular proton exchange in the latter two ions. The first C_6H_6 molecule sticks to these primary ions $[1+H-C_6H_6]^+$ and $[2+H-C_6H_6]^+$ because of their fast-moving protons, forming a proton-bound pair of arenes ($[\text{Arene}\cdot H^+\cdot C_6H_6]$). The mobile protons may stabilize these ion-molecule complexes, $[M+H-C_6H_6]^+\cdot C_6H_6$, and retard the elimination of the neutral fragment. The formation of the second C_6H_6 molecule requires a 1,2-C shift (Wagner-Meerwein rearrangement) of the benzene-solvated arenium ion to generate, within the ion-molecule complex, the final tertiary $C_{10}H_{11}^+$ or $C_{17}H_{17}^+$ ions with all protons now being immobilized at the carbon framework. Thus, the two benzene molecules are eliminated simultaneously because of mobile protons being present only in the primary ionic fragment of the intermediate ion-molecule complexes.

TABLE 1. Fragmentation of metastable $[M+H]^+$ ions of tris-(ω -phenylalkyl)-methanes $[C_6H_5(CH_2)_x C_6H_5(CH_2)_y C_6H_5(CH_2)_z]CH$, 1 and 3-6, and of tetrabenzylmethane, 2

Ion	x	y	z	r_a	Ion	x	y	z	r_a
$[1+H]^+$	1	1	1	4.4	$[5+H]^+$	2	2	2	0.14
$[3+H]^+$	2	1	1	0.006	$[6+H]^+$	4	2	2	0.12
$[4+H]^+$	2	2	1	0.012	$[2+H]^+$	-	-	-	≥ 60 .

TABLE 2. Loss of benzene isotopomers from $[ph-d_n]$ -labelled $[M+H]^+$ ions

Ion	Labelled group	C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5
$[3a+H]^+$	$C_6D_5(CH_2)_2$	7.9	29.9	38.8	19.0	3.7	0.7
$[4a+H]^+$	$C_6D_5CH_2$	8.4	28.8	39.2	19.0	4.1	0.5
calc'd for 11H/5D equilibr'n		5.8	28.9	41.2	20.6	3.4	0.1

TABLE 3. Loss of two benzene isotopomers from $[ph-d_5]$ -labelled $[M+H]^+$ ions

Ion	Lab'd group	' $C_{12}H_{12}$ '	' $C_{12}H_{11}D$ '	' $C_{12}H_{10}D_2$ '	' $C_{12}H_9D_3$ '	' $C_{12}H_8D_4$ '	' $C_{12}H_7D_5$ '
$[1a+H]^+$	one $C_6D_5CH_2$	0.0	0.8	8.7	32.8	42.4	15.3
calc'd for 11H/5D equil'n		-	0.3	6.0	30.2	45.3	18.1
$[2a+H]^+$	one $C_6D_5CH_2$	1.5	10.7	29.2	36.5	19.1	3.1
calc'd for 16H/5D equil'n		0.6	7.4	27.2	38.9	21.9	3.9

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