

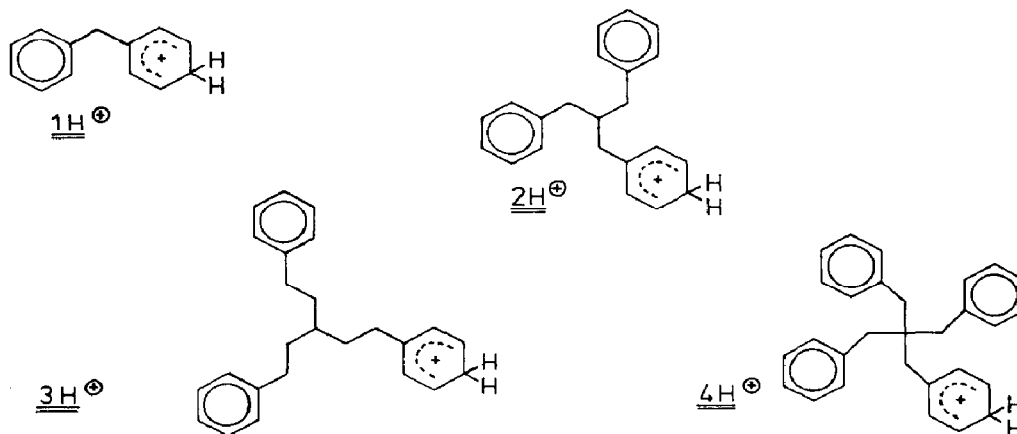
RING-TO-RING PROTON EXCHANGE IN DI- AND OLIGOPHENYL ALKANES
 UPON GAS PHASE PROTONOLYSIS

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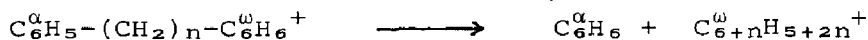
ABSTRACT

Protonolysis of diphenylmethane (1) and three oligophenyl alkanes (2 to 4) has been studied by chemical ionization mass spectrometry of some deuterium-labelled analogues. $1H^+$ ions reveal that intra-ring proton equilibration is complete within 10 μ s whereas inter-ring proton exchange is slow. $2H^+$, $3H^+$, and $4H^+$ ions, additionally, undergo complete inter-ring proton equilibration involving all of the 16 or 21 protons at the aromatic rings. A surprising double C_6H_6 elimination is found to occur in $2H^+$, $3H^+$, and $4H^+$ ions, suggesting that C_6H_6 acts as a 'solvent' of $[MH - C_6H_6]^+$ and $[MH - 2C_6H_6]^+$ ions prior to final fragmentation.

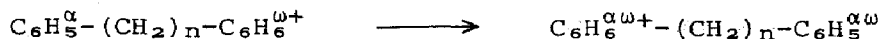


INTRODUCTION

Protonolysis of alkyl benzenes is a well-known reaction in both liquid and gaseous media. In the absence of any solvent acid this reaction can be effected by an arenium ion (e.g., $alkyl-C_6H_6^+$) if a neutral and a protonated benzene ring are present in the same molecular species, i.e.,



($1 \leq n \leq 20$, refs 1, 2). Protonolysis is accompanied by randomization of the eleven protons at the aromatic nuclei within $\sim 10 \mu$ s, even if $n = 20$ (ref. 2), i.e.,



In order to discriminate between intra-ring and ring-to-ring proton exchange and to understand the nature of the proton-transferring intermediates, diphenylmethane (1) and three symmetrical oligo-(ω -phenylalkyl) methanes (2 to 4) have been studied by CI-MS combined with deuterium labelling.

METHODS

All measurements were performed using a ZAB-2F double focussing mass spectrometer (Vacuum Generators) with a combined EI/CI ion source (reagent gas: *i*-butane, 99,96 %, Matheson; nom. source pressure 5 - 20 · 10⁻⁵ Torr; source temp. 200 °C; electron energy 100 V; emission 0,5 mA; accelerating voltages 6 and 8 kV). - The synthesis of the compounds will be described in a following paper. Isotopic purities were ≥97 % for all of the labelled compounds except 2b, which was a mixture of d₂ (67 %), d₁ (17 %), and d₃ (16 %) isotopomers with the label being partially distributed over all of the aliphatic positions.

RESULTS AND DISCUSSION

Diphenyl methane (1)

Contrary to its higher homologues, 1H⁺ is the only protonated 1, ω -diphenylalkane which does not undergo complete ring-to-ring proton exchange ([11 H]^{ar}) within ~10 μ s (refs 2, 3). This follows from the MIKE spectra of 1aH⁺, 1bH⁺, and 1cH⁺ (Table 1). This may be due to both steric and thermochemical reasons: As compared to, e.g., protonated 1,2-diphenylethane the activation energy for ring-to-ring proton transfer should increase, but energy requirements for protonolysis of the C ^{α} -C ^{i} bonds should decrease since a C₇H₇⁺ ion can be formed. Thus the rate constants for isomerization and fragmentation become similar which is reflected further by the isotope effects for these reactions.

TABLE 1

MIKE spectra of labelled 1H⁺ ions.

<u>MH⁺</u> / posn of label	Loss [%] of					
	C ₆ H ₆	C ₆ H ₅ D	C ₆ H ₄ D ₂	C ₆ H ₃ D ₃	C ₆ H ₂ D ₄	C ₆ HD ₅
<u>1aH⁺</u> 1,2,3,4,5-d ₅	18.8	12.1	1.2	1.0	11.8	55.1
<u>1bH⁺</u> 3,4,5-d ₃	32.0	7.5	7.2	53.4		
<u>1cH⁺</u> 2,4,6-d ₃	32.5	8.0	7.5	52.0		
<u>1dH⁺</u> α, α -d ₂	97.5	2.5	0.0			
Statistical for [6H,5D] ^{ar}	0.2	6.5	32.5	43.3	16.2	1.3

Oligophenyl alkanes (2 to 4)

Fragmentation of MH⁺ ions. Similar to 1, ω -diphenylalkanes (refs. 1, 2), elimination of C₆H₆ is the by far dominating fragmentation of protonated oligo-

(ω -phenylalkyl) methanes 2H^+ , 3H^+ , and 4H^+ . This holds for the normal CI (source) spectra as well as for those of metastable MH^+ ions.

However, the majority of these MH^+ ions eliminate two molecules of C_6H_6 . While the signals for $[\text{MH} - \text{C}_6\text{H}_6]^+$ ions are small (2H^+) or nearly absent (4H^+) in the CI (source) spectra, those for $[\text{MH} - 2\text{C}_6\text{H}_6]^+$ ions represent the base peaks of the CI induced fragmentation. In the case of 3H^+ , similar abundances are observed for $[\text{MH} - \text{C}_6\text{H}_6]^+$ and $[\text{MH} - 2\text{C}_6\text{H}_6]^+$ ions. Surprisingly, metastable 2H^+ , 3H^+ , and 4H^+ ions eliminate two molecules of C_6H_6 within the same field-free region, showing quite characteristic $[\text{MH} - 2\text{C}_6\text{H}_6]^+ / [\text{MH} - \text{C}_6\text{H}_6]^+$ abundance ratios: 2H^+ 3.2 ± 0.7 , 3H^+ 0.10 ± 0.04 , and 4H^+ >60 . Thus, the proximity of neutral benzene nuclei to the protonated one appears to govern the relative rate of double C_6H_6 loss.

Proton exchange in MH^+ ions. 2, 3, and 4 have been penta-deuterated in one of the benzene nuclei and subjected to CI. All of the six possible isotopomers are found to be eliminated during both single and double loss of benzene. The relative abundances for 2a and 3a are given in Tables 2 and 3.

TABLE 2

MIKE spectra of labelled 2H^+ and 3H^+ ions (single benzene loss).

MH^+ / posn of label	Loss [%] of					
	C_6H_6	$\text{C}_6\text{H}_5\text{D}$	$\text{C}_6\text{H}_4\text{D}_2$	$\text{C}_6\text{H}_3\text{D}_3$	$\text{C}_6\text{H}_2\text{D}_4$	C_6HD_5
<u>2aH</u> ⁺ 1',2',3',4',5'-d ₅	8.0	29.9	39.5	18.7	3.3	0.4
<u>3aH</u> ⁺ 1',2',3',4',5'-d ₅	6.7	30.5	39.9	20.5	2.5	<0.2
Stat. A: [11H,5D] ^{ar a}	5.8	28.9	41.2	20.6	3.4	0.1
Stat. B: [6H,5D] ^{ar b}	33.5	4.3	21.7	28.9	10.8	0.9

^aCalc. for complete equilibration of the 16 'aromatic' H^+ and D^+ .

^bCalc. for compl. equilibrn of 11 'arom.' H^+ and $\text{D}^+(\text{H}^+)$, including only one of the unprotonated rings.

TABLE 3

MIKE spectra of labelled 2H^+ and 3H^+ ions (double benzene loss).

MH^+ ^a	Loss [%] of					
	' $\text{C}_{12}\text{H}_{12}$ '	' $\text{C}_{12}\text{H}_{11}\text{D}$ '	' $\text{C}_{12}\text{H}_{10}\text{D}_2$ '	' $\text{C}_{12}\text{H}_9\text{D}_3$ '	' $\text{C}_{12}\text{H}_8\text{D}_4$ '	' $\text{C}_{12}\text{H}_7\text{D}_5$ '
<u>2aH</u> ⁺	<0.1	1.4	10.8	34.5	39.2	13.3
<u>3aH</u> ⁺	<0.1	0.8	9.6	33.1	41.1	15.4
Stat. A ^a	-	0.3	6.0	30.2	45.3	18.1

^aSee Table 2.

In all cases the experimental data are in accord with the statistical values calculated for complete equilibration of all of the 16 protons at the three aromatic rings. A 'bilateral' proton exchange between two rings only prior to expulsion of

benzene does not occur. As found for protonated 1, ω -diphenylalkanes (refs 1, 2; $1dH^+$ in Table 1), the aliphatic moieties are not involved in the proton exchange. For example, MH^+ ions of $(C_6H_5CH_2)_2CDCHDC_6H_5$ (**2b**) eliminate >96 % of C_6H_6 and >98 % of ' $C_{12}H_{12}$ ' (calc. for $[16 H]^{ar}$ (A): 100 %, for participation of one D: 64.7 % and 29.4 %, resp.). - Proton exchange is found likewise for unstable $2H^+$, $3H^+$, and $4H^+$ ions; e.g., the CI (source) spectrum of phenyl- d_5 labelled tetrabenzyl methane (**4a**) affords a distinct pattern for the loss of ' $C_{12}(H,D)_{12}$ ':

TABLE 4
Partial^a CI source spectrum of 1',2',3',4',5'- d_5 -tetrabenzyl methane (**4a**)

	Loss [%] of					
	' $C_{12}H_{12}$ '	' $C_{12}H_{11}D$ '	' $C_{12}H_{10}D_2$ '	' $C_{12}H_9D_3$ '	' $C_{12}H_8D_4$ '	' $C_{12}H_7D_5$ '
Exp. ^b	1.0	10.0	25.9	35.5	20.8	6.7
Stat. A ^c	0.6	7.4	27.2	38.9	21.9	3.9

^a $[MH - 2C_6H_6]^+$ represent ≥ 97 % of the C_{17} ions in the CI spectrum of **4**.

^bCorr. for natural $^{13}C_2$ contribution.

^cCalc. for complete equilibration of the 21 'aromatic' H^+ and D^+ .

The data show that the whole of 21 protons at the four aromatic rings are completely equilibrated within the lifetime of $4H^+$ ions in the ion source. No 'bilateral' ring-to-ring proton exchange occurs prior to fragmentation.

CONCLUSION

The results presented in this work show that both intra- and inter-ring proton exchange are very fast processes in protonated di- and oligophenyl alkanes. Since all of the (equivalent) benzene nuclei participate in proton equilibration, intramolecular association complexes formed during ring-to-ring proton migration do not expulse C_6H_6 by immediate protonolysis, but rather re-dissociate to form a great number of further association complexes, thus equilibrating up to 21 protons within $\sim 10 \mu s$. Moreover, the striking observation that two molecules of C_6H_6 are lost from MH^+ ions besides, or even instead of a single one suggests that protonolysis generates bi- and ter-molecular associates, i.e., $[MH - C_6H_6]^+ \cdot C_6H_6$ and $[MH - 2C_6H_6]^+ \cdot 2C_6H_6$, respectively. Thus, the C_6H_6 molecule(s) formed upon protonolysis may be considered to serve as a (possibly proton-transferring) solvent for the incipient ion prior to final fragmentation.

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