"Ipso" Aromatic Alkylation in the Gas Phase. Intermediacy and Structure of Gaseous Heptaalkylbenzenium Ions

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Abstract: The structure of heptaalkylbenzenium ions has been investigated in the gas phase with complementary techniques, i.e., chemical ionization mass spectrometry, alkylation of hexaalkylbenzenes by radiolytically generated cations, and collisionally induced dissociation mass spectrometry. The results allow us to assign the σ-complex (Wheland intermediate) structure to the free, gaseous heptaalkylbenzenium ions, in agreement with the established structure of their salts in solution and in the solid state. The heptaalkylbenzenium ions represent the charged intermediates of the gas-phase "ipso"-substitution reactions, whose occurrence has been demonstrated and whose mechanism is briefly discussed.

"Ipso" substitution, promoted by electrophilic attack at ring positions bearing atoms or groups other than hydrogen, is by now a well-characterized facet of aromatic reactivity. In recent years considerable progress has been made toward a better understanding of the mechanistic role of ipso attack in a variety of substitution reactions occurring in solution.[1] The remarkable stability of certain ipso-substituted arenium ions, e.g., those formed from the Friedel–Crafts alkylation of hexaalkylbenzenes, is of particular note, since it has allowed actual isolation and unusually accurate characterization by NMR[2] and X-ray diffraction[3] techniques of typical representatives of the class of intermediates postulated by the theory of aromatic substitution.

As an extension of previous studies on the reactivity of aromatic molecules toward gaseous cations,[4] we have addressed the problem of "ipso" substitution in the dilute gas state.

This report presents the results obtained from the coordinate application of complementary techniques, including chemical ionization (CI) mass spectrometry, radiolysis of appropriate gaseous systems, and collisionally induced dissociation (CID) mass spectrometry, to the problem concerning the occurrence of heptaalkylbenzenium ions as stable species in the dilute gas state, their structure, and their role as charged intermediates in the ipso substitution of gaseous arenes.

Experimental Section

Materials. The gases, having a stated purity exceeding 99.99 mol %, were obtained from Matheson Gas Products Inc., as well as from local sources. The chemicals used as substrates, or as reference standards in

GLC, were purchased from commercial sources or prepared and purified by unexceptional procedures. The components of the irradiated systems were assayed by GLC on the same columns employed for the analysis of the products. 3-Methylene-1,2,4,5,6,6-hexamethylcyclohexa-1,4-diene, henceforth indicated as **1**, was prepared by methylation of hexamethylbenzene, followed by deprotonation of the heptamethylbenzenium ion,[5] and was characterized by NMR and mass spectrometry.

Radiolytic Alkylation. The gaseous samples were prepared by conventional techniques in a greaseless vacuum line, as described in earlier reports,[4] and enclosed in sealed 250-mL Pyrex ampules. The irradiations were carried out to a total dose ranging from 4 to 8 Mrad, delivered at a rate of 1 Mrad h⁻¹, in a 220 γ cell from Nuclear Canada Ltd., fitted with a thermostatic device whose temperature could be set at any desired value in the range from 60 to 170 °C. No detectable products were formed in blank runs, carried out to exclude the occurrence of "dark" reactions between the components of the gaseous systems, under conditions identical with those prevailing in the radiolytic experiments, apart from the lack of irradiation. O_2 was used as a radical scavenger, except in those systems where formation of **1** could be anticipated. In fact, the triene is sensitive to oxidation, and the presence of O_2, even at a partial pressure as low as 5 torr, causes a dramatic decrease in its yield under the irradiation conditions. Accordingly, O_2 was replaced by propene as a radical scavenger in these alkylations.

Analysis of the Products. The products were analyzed by GLC by using Perkin-Elmer Sigma 1 and Sigma 3 or Hewlett-Packard Model 5700 instruments, equipped with FID or PID units. The identity of the products, inferred from comparison of their capacity factors with those of authentic samples, was confirmed by GLC-MS, using a Hewlett-Packard Model 5982 A quadrupole spectrometer, connected to a 5934 A data system. The following columns were employed: (i) a 3.5-m-long column, packed with SP 1200 (5%, w/w) + Bentone 34 (1.75%) on 100–120-mesh Supelcoport; (ii) a 3.5-m long column, packed with SP 2100 (20%) + Carbowax 1500 (0.1%) on 100–120-mesh Supelcoport; (iii) a 50-m-long, fused silica capillary column, coated with methyl silicone SP 2100 fluid, deactivated with Carbowax 20M.

Chemical Ionization Mass Spectrometry. The measurements were performed with the Hewlett-Packard instrument, at a source temperature of 100 °C. The reactant gas (MeF, MeCl, and CH_4) was admitted into the ion source after passing through a glass trap, enclosed within a thermostatic oven, containing the substrate(s) whose gas-phase concentration could be adjusted by changing the temperature of the oven. The pressure within the ion source was measured with a mechanical manometer of the Bourdon type, whose readings were used just for internal comparison purposes, in the lack of an independent calibration to assess their absolute accuracy.

Collisionally Induced Dissociation Spectrometry. The mass-analyzed ion kinetic energy spectra (MIKES), as well as the CID spectra, were recorded with a ZAB-2F spectrometer from VG-Micromass Ltd., fitted with a combined EI/CI ion source. The reactant gases (MeF, MeCl, CH_4, and i-C_4H_{10}) were used at pressures of ca. 0.3 torr. Typical operating conditions were as follows: accelerating voltage, 8 kV; ionizing energy, 100 eV; energy resolution, 4000 fwhm; emission current, 0.5 mA; source temperature, 150 °C. The CID spectra were obtained by admitting the collision gas (He) into the cell located in the second field-free region of the reverse-geometry instrument until the parent ion intensity

(1) (a) Norman, R. O. C.; Taylor, R. "Electrophilic Substitution in Benzenoid Compounds"; Elsevier: Amsterdam, 1965 and references therein. (b) Nightingale, D. V. *Chem. Rev.* **1947**, *40*, 117. (c) Moodie, R. B.; Schofield, K. *Acc. Chem. Res.* **1976**, *9*, 287. (d) Hartshorn, S. R. *Chem. Soc. Rev.* **1974**, *3*, 167. (e) Hahn, R. C.; Strack, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 4335, 4337. (f) Fisher, A.; Greig, C. C.; Roderer, R. *Can. J. Chem.* **1975**, *53*, 1570. (g) Barnes, C. E.; Myhre, P. C. *J. Am. Chem. Soc.* **1978**, *100*, 973, 975. (h) Feldman, K. S.; McDermott, A.; Myhre, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 505, 4768. (i) Al-Omran, F.; Fujiwara, K.; Giffney, J. C.; Ridd, J. H.; Robinson, S. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 518. (l) Bloomfield, C.; Manglik, A. K.; Moodie, R. B.; Schofield, K.; Tobin, G. D. *J. Chem. Soc., Perkin Trans. 2* **1983**, 75. (m) Eustathopoulos, H.; Court, J.; Bonnier, J.-M. *J. Chem. Soc., Perkin Trans. 2* **1983**, 803. (n) Al-Omran, F.; Ridd, J. J. *Chem. Soc., Perkin Trans. 2* **1983**, 1185. (o) Helsby, P.; Ridd, J. J. *Chem. Soc., Perkin Trans. 2* **1983**, 1191 and references therein.

(2) (a) von Doering, N.; Saunders, M.; Boyton, H. G.; Earhart, H. W.; Wodley, E. F.; Edwards, W. R.; Laber, G. *Tetrahedron* **1958**, *4*, 178. (b) Olah, G. A.; Spear, R. J.; Messina, G.; Westerman, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 4051. (c) Messina, G.; Moretti, M. D.; Lorenzoni, L.; Calcagno, B. *Chim. Ind. (Milan)*, **1979**, *61*, 709. (d) Derendyaev, B. G.; Mamatyuk, V. I.; Koptyug, V. A. *Tetrahedron Lett.* **1969**, *5*, and references therein. (e) Saunders, M. "Magnetic Resonance in Biological Systems"; Ehrenberg, A., Malmström, B. G.; Vänngerd, T., Eds.; Wiley: New York, 1967; p 90. (f) Meier, B. H.; Ernst, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 6441. (g) Borodkin, G. I.; Nagy, S. M.; Mamatyuk, V. I.; Shakirov, M. M.; Shubin, V. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1533. (h) Kuura, Kh. I.; Khaldna, Yu. L. *Reakts. Sposobn. Org. soedin.* **1966**, *3*, 162.

(3) Baenziger, N. C.; Nelson, A. D. *J. Am. Chem. Soc.* **1968**, *90*, 6602.

(4) (a) Cacace, F. *Radiat. Phys. Chem.* **1982**, *20*, 99. (b) Speranza, M. *Gazz. Chim. Ital.* **1983**, *113*, 37 and references therein.

(5) Childs, R. F.; Zeya, M.; Dain, R. P. *Can. J. Chem.* **1981**, *59*, 76. Their procedure is analogous to those reported in ref 2a and 2c.

was reduced to 75% of its original value. The spectra were recorded by scanning the electrostatic sector analyzer.

Results

Chemical Ionization Mass Spectra. Alkylation of hexamethylbenzene (HMB) and hexaethylbenzene (HEB) by Me_2F^+, Me_2Cl^+, and Et^+ has been studied by using, respectively, MeF, MeCl, and CH_4 as the reactant gas.

The methylating reagent Me_2F^+ is the most abundant (60–80%) ion in neat MeF at pressures ranging from 0.3 to 1.0 torr, accompanied only by smaller amounts of CH_2F^+. The MeF CI spectrum of HMB, recorded at ca. 0.5 torr and a [MeF]/[HMB] ratio exceeding 300, is characterized by an abundant methylated adduct, $(M + Me)^+$, of unknown structure. Typical relative abundances of the ionic species originating from HMB are as follows: $(M - H)^+$, 8%; M^+, 22%; $(M + H)^+$, 17%; $(M + Me)^+$, 48%; $(M + CH_2F)^+$, 4%. Similar relative abundances characterize the CI spectrum of HEB recorded under comparable conditions.

The methylation rates of HMB, HEB, and benzene are very close under CI conditions, as shown by the apparent reactivity ratios obtained from competition experiments performed on pairs of substrates:

$$\frac{[(HEB + Me)^+]}{[HEB]} \Big/ \frac{[(HMB + Me)^+]}{[HMB]} \Big/ \frac{[(C_6H_6 + Me)^+]}{[C_6H_6]}$$
$$= 1.0:1.2\ (\pm0.2):1.1\ (\pm0.2)$$

The ratios are unaffected by changes of pressure in the range 0.2–1.0 torr and by moderate variations of the relative concentration of the substrates.

The methylating reagent Me_2Cl^+ is the major ion in the CI spectrum of neat MeCl, reaching a relative abundance of ca. 60% at a pressure of 0.5 torr. Typical relative intensities of the ions originating from HMB and HEB (figures in parentheses) in their MeCl CI spectra are as follows: $(M - H)^+$, 5% (7%); M^+ 20% (23%); $(M + H)^+$, 8% (9%); $(M + Me)^+$, 61% (56%), $(M + CH_2Cl)^+$, 6% (5%).

Since methylation of benzene by Me_2Cl^+ is quite slow, toluene has been used as a reference substrate in the competition experiments. The reactivity of toluene toward Me_2Cl^+ is appreciably lower than those of HMB and HEB, in agreement with earlier CI results,[6,7] as shown by the following apparent ratios

$$\frac{[(HEB + Me)^+]}{[HEB]} \Big/ \frac{[(HMB + Me)^+]}{[HMB]} \Big/ \frac{[(C_7H_8 + Me)^+]}{[C_7H_8]}$$
$$= 1.0:1.1\ (\pm0.2):ca.\ 0.1$$

The CH_4 CI spectra differ significantly from those obtained with methyl halides, since the two major ions of the CH_4 plasma react exclusively (CH_5^+) or predominantly (Et^+) as Brønsted acids. Ethylation of arenes is therefore a relatively minor process, whose extent depends, inter alia, on the basicity of the substrate.[8] Typical relative abundances of the ions from HMB and HEB (the latter given in parentheses), measured at 100 °C at a pressure of ca. 0.5 torr, are as follows: $(M - H)^+$, 23% (17%); M^+, 16% (23%); $(M + H)^+$, 55% (52%); $(M + Et)^+$, 5% (7%), $(M + C_3H_5)^+$, 1% (1%).

Two different sets of competition experiments, performed simultaneously on the three substrates, as well as on different pairs of substrates, have provided reasonably consistent results, leading to the following apparent reactivity ratios:

$$\frac{[(HEB + Et)^+]}{[HEB]} \Big/ \frac{[(HMB + Et)^+]}{[HMB]} \Big/ \frac{[(C_6H_6 + Et)^+]}{[C_6H_6]} =$$
$$1.4\ (\pm0.2):1.0:3.1\ (\pm0.3)$$

The efficiency of the ethylation process declines in passing from benzene to hexaalkylbenzenes, owing to the enhanced competition by other reaction channels, e.g., hydride-ion abstraction, proton

transfer, etc. The results fit into an established trend, characterized by a decrease of the relative abundance of the ethylated adduct from 12.4% in the CH_4 CI spectrum of benzene to 6.9% in that of pentamethylbenzene.[8]

Collisionally Induced Dissociation Spectra. Structural characterization of the gaseous $C_{13}H_{21}^+$ adduct (m/z 177) from the methylation of HMB has been sought through CID, which has gained wide recognition as a tool for elucidating the structure of gaseous ions.[9] Since the CID spectrum of a single species does not convey, per se, positive structural information, the general approach involves comparison between the ion of interest and a model ion of established or reasonably assumed structure.

Indistinguishable CID spectra are taken as strong evidence that the unknown species and the model ion have the same structure or at least collapse into the same structure before collisional assay.

Successful application of CID spectrometry depends on the availability of the ions required as structural models. Fortunately, a suitable reference cation, whose skeleton corresponds to that of the gaseous $C_6Me_7^+$ σ complex, can be conveniently obtained from the mild protonation of the methylenecyclohexadiene **1**.
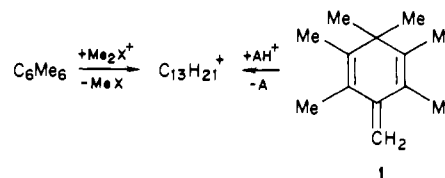
Accordingly, the CID spectra of the $C_{13}H_{21}^+$ adduct from the methylation of HMB were compared with those of the model ion from the protonation of **1**. Inspection of the spectra (Figure 1) reveals no detectable differences, except minor intensity variations affecting the ions at m/z 121, 135, 149, and 162. Separate measurements have shown that these are the only fragments formed either in the first (B/E spectra) or in the second (MIKES spectra) field-free region of the mass spectrometer by the *unimolecular* decomposition of the $C_{13}H_{21}^+$ ions from all the reactions investigated.[10] It is concluded that the minor dissimilarities in the CID spectra arise from the variable contributions of the fragments from *unimolecular* decomposition processes, reflecting differences in the internal energy rather than in the structure of the $C_{13}H_{21}^+$ ions. Indeed, it is common practice to exclude from the comparison all peaks affected by unimolecular contributions.[11]

A more quantitative method to establish whether significant differences exist in a pair of CID spectra is based on the calculation of their similarity index (SI)

$$SI = 1/N[\Sigma(100\Delta I/I_0)^2]^{1/2}$$

where $\Delta I = I - I_0$ is the difference in intensity for a given ion, I_0 being the lower intensity, and N is the number of masses used in the comparison.[11] It is apparent that the larger the difference between two spectra, the *higher* their SI. The indexes have been computed from the averages of at least 30 consecutive scans, excluding the peaks affected by unimolecular contributions. The comparison has involved pairs of CID spectra of the $C_{13}H_{21}^+$ ions obtained from different reactions, e.g., from the methylation of HMB with Me_2F^+ and Me_2Cl^+ ions and from the protonation of **1** with t-Bu^+ and $C_nH_5^+$ (n = 1 or 2) ions. The comparison has been extended to pairs of spectra of ions *from the same reaction*, recorded in separate runs. In the latter case, the differences of the spectra arise exclusively from the small casual fluctuations of the instrumental parameters, and the SI values measure the long-term reproducibility of the CID measurements.

The results, summarized in Table I, corroborate the qualitative evidence from the visual comparison of the traces, showing that

(6) Sen Sharma, D. K.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 19.

(7) (a) Stone, J. A.; Lin, M. S.; Varah, J. *Can. J. Chem.* **1981**, *59*, 2412. (b) Stone, J. A.; Splinter, W. M.; Splinter, D. E. *Can. J. Chem.* **1984**, *62*, 1373.

(8) Munson, M. S. B.; Field, F. N. *J. Am. Chem. Soc.* **1967**, *89*, 1047.

(9) For a review, see: "Collision Spectroscopy"; Cooks, R. G., Ed.; Plenum Press: New York, 1978.

(10) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. "Metastable Ions"; Elsevier: Amsterdam, 1973.

(11) (a) Lay, J. O.; Gross, M. L.; Zwinselman, J. J.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1983**, *18*, 16. (b) Harrison, A. G.; Gäumann, T.; Stahl, D. *Org. Mass Spectrom.* **1983**, *18*, 517.
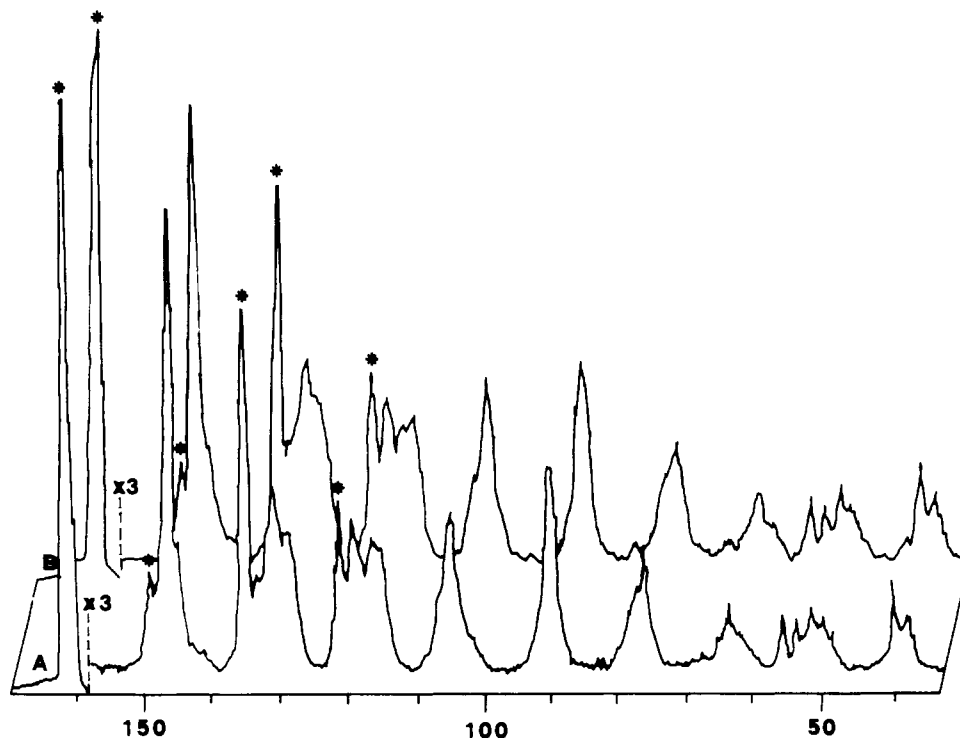
Figure 1. CID spectra of the m/z 177 ion from the methylation of HMB by Me_2Cl^+ (trace A) and from the protonation of **1** (trace B). Each trace reproduces the computer average of 30 consecutive scans. Peaks affected by unimolecular fragmentation processes are labeled with an asterisk.

Table I. Similarity Indexes (Si) of the CID Spectra of m/z 177 Ions Prepared with Different Reactions

	spectrum I			spectrum II		
substrate	reactant gas	ionic reactant	substrate	reactant gas	ionic reactant	SI^a
1	i-C_4H_{10}	t-Bu^+	HMB	MeCl	Me_2Cl^+	15.1
1	i-C_4H_{10}	t-Bu^+	HMB	MeF	Me_2F^+	22.7
HMB	MeF	Me_2F^+	HMB	MeCl	Me_2Cl^+	21.8
1	CH_4	$C_nH_5^{+b}$	HMB	MeCl	Me_2Cl^+	97.8
1	CH_4	$C_nH_5^+$	HMB	MeF	Me_2F^+	90.4
1	CH_4	$C_nH_5^+$	1	i-C_4H_{10}	t-Bu^+	88.7

^{a} The SI of pairs of spectra of the ions from the same reaction, corresponding to the lower limit of SI values allowed by the reproducibility of the measurements, ranged from 14.2 to 27. ^{b} $n = 1$ or 2; see text.

Table II. Alkylation of Hexamethylbenzene (HMB) by Gaseous Cations^a

	system composition, torr						yields of products G_{+M}^b		
substrate	C_2H_6	CH_4	MeF	O_2	other additives	C_6Me_5Et	PhEt	PhMe	1^c
HMB, 0.54	690			6.0		1.4×10^{-2}			
HMB, 0.54	690			5.0	C_6H_6, 5.4	4.6×10^{-3}	1.07		
HMB, 0.54	690			6.0	C_6H_6, 0.90	1.2×10^{-2}	0.62		
HMB, 0.54	690			10.0	Me_3N, 2.50	n.d.^{d}			
HMB, 0.54		690		6.0	C_6H_6, 1.74	1.05×10^{-2}	1.47		
HMB, 0.54			690	5.0	C_6H_6, 1.40			1.65	
HMB, 0.54			690		C_6H_6, 1, 27; C_3H_6, 3.0			2.30	
HMB, 0.54			690	7.5	Et_3N, 2.80				n.d.^{d}
HMB, 0.54			690		Et_3N, 4.07				1.1×10^{-2}
HMB, 0.54			690		Et_3N, 2.12				8×10^{-3}
HMB, 0.54			690		Et_3N, 4.42				5×10^{-3}
HMB, 0.54			690		Et_3N, 2.24; C_3H_6, 3.10				6×10^{-3}
PMB^e, 1.40	690			10.0		0.205^f			

^{a} Irradiation temperature, 100 °C. ^{b} Number of molecules formed per 100 eV of absorbed energy. Standard deviation of the yields, ca. 10%. ^{c} 3-Methylene-1,2,4,5,6,6-hexamethylcyclohexa-1,4-diene. ^{d} Below detection limit, $<5 \times 10^{-4}$. ^{e} Pentamethylbenzene. ^{f} Isomeric C_6HMe_4Et products are also formed, with a combined G_{+M} value of 2.1×10^{-2}.

indeed the m/z 177 ions from the methylation of HMB by Me_2F^+ and Me_2Cl^+ and those from the protonation of **1** by t-Bu^+ give indistinguishable CID spectra, strongly suggestive of a common structure. In fact, their SI fall well below the threshold customarily taken as indicative of significant structural differences,[11b] and, in addition, are quite comparable to, or even lower than, the SI of pairs of spectra of the same ion recorded in separate runs.

On the other hand, the CID spectrum of the $C_{13}H_{21}^+$ ion from the protonation of **1** with $C_nH_5^+$ ions differs from all other spectra, pointing to a diverse structure (or mixture of structures) of the

adduct thus formed. The sharp increase of the corresponding SI, which incidentally demonstrates the required sensitivity of the CID spectra to structural differences of isomeric ions, can be traced to the large exothermicity of the proton transfer from $C_nH_5^+$ to **1** (vide infra), which most likely promotes extensive isomerization of the protonated adduct before collisional assay.

Radiolytic Alkylation of Hexaalkylbenzenes. The yields of the neutral products from the alkylation of HMB by cationic reagents generated with established radiolytic techniques are given in Table II. The reactions have been studied in the presence of an efficient

Table III. Alkylation of Hexaethylbenzene (HEB) in the Gas Phase[a]

system composition, torr				yields of products G_{+M}[b]		
MeF	O_2	HEB	other additives	C_6Et_5Me	toluene	isodurene
725	6.0	0.52		7.0×10^{-2}		
725	6.0	0.52	C_6H_6, 0.79	5.8×10^{-2}	0.85	
625	8.0	0.52	MeCl, 33; mesitylene, 0.30	4.9×10^{-2}		9.4×10^{-2}
625	8.0	0.52	Me_2O, 33; mesitylene, 0.21	0.41		0.18
690	6.0	0.22	Me_3N, 1.3	n.d.[c]		

[a] Irradiation temperature, 120 °C. [b] See footnote b of Table II. [c] Below detection limit, $<5 \times 10^{-4}$.

radical scavenger (generally O_2), in excess over HMB. The ionic character of the reactions investigated is independently witnessed by the depression of their yields caused by additives, such as gaseous trialkylamines, which effectively intercept the alkylating cations.

The occurrence of ethyldemethylation of HMB by gaseous Et^+ ions from the radiolysis of CH_4 or C_2H_6 is demonstrated by the formation of C_6Me_5Et, albeit the process is highly inefficient, as shown by comparison with the much larger yields of PhEt formed from benzene in competition experiments.

Although it is clear that no neutral alkylated arenes other than the substrate itself can be obtained from the methylation of HMB, solution-chemistry studies[2a] suggest a practicable way to trap and characterize the intermediate $C_6Me_7^+$ ion, based on its deprotonation to the structurally diagnostic methylenecyclohexadiene 1. Accordingly, the gas-phase methylation of HMB by Me_2F^+ ions has been studied in the presence of a strong gaseous base, Et_3N, although the amine could be expected to intercept a large fraction of the alkylating reagent, thus severely reducing the attainable yield of 1. Initial runs met with failure, later traced to the well documented[2a] sensitivity of 1 to oxygen, used as a radical scavenger. Following replacement of O_2 with propene, the approach has proved fruitful, allowing isolation of 1 in the expected yields, which provide direct evidence for the intermediacy of gaseous heptamethylbenzenium ions. The last entry of Table II refers to ethylation of pentamethylbenzene (PMB), included for comparison purposes. The ethylated product, C_6Me_5Et, is formed in fair yields, together with much smaller amounts of the ipso-substituted products, i.e., C_6HMe_4Et isomers, whose combined yields approach that of C_6Me_5Et from HMB.

Table III summarizes the results of the radiolytic methylation of HEB by Me_2F^+. Despite the alkylating ability of the cation, demonstrated by the high yields of toluene from benzene, the yield of C_6MeEt_5 from HEB is nearly as low as that of C_6Me_5Et from HMB. The efficiency of the methyldeethylation process does not decline in those systems containing MeCl in large excess over HEB, where methylation is effected by Me_2Cl^+, a much milder reagent than Me_2F^+. Still more noteworthy is the sharp *increase* of the C_6MeEt_5 yields from the systems containing Me_2O in large excess over HEB, where methylation is promoted by the still milder Me_3O^+ ion.

Discussion

Structure of Gaseous Heptaalkylbenzenium Ions. A useful starting point for the discussion is provided by the structural models considered in related solution-chemistry studies

2   **3**   **4**
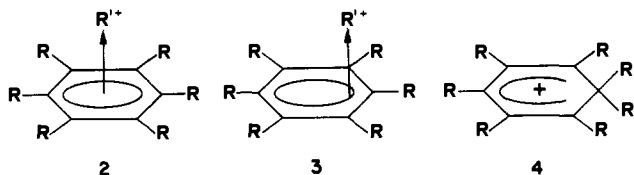
As to heptamethylbenzenium ion (R, R', = Me), analysis of the NMR spectra of its chloride in concentrated HCl ruled out the hexagonally symmetrical π complex **2**. The σ complex **4** was preferred, although the asymmetric π complex **3** could not be

excluded on the basis of the NMR evidence.[2a] Subsequent X-ray diffraction studies unambiguously assigned structure **4** to the heptamethylbenzenium cation in its crystalline tetrachloroaluminate.[3] ^{1}H and ^{13}C NMR investigations led to assignment of the σ-complex structure **4** (R, R' = Et) to heptaethylbenzenium ion in liquid SO_2, detecting, in addition, anomalous deshielding effects traced to the highly crowded character of the ion.[2b]

Restricting initially the discussion to the alkylated adducts from HMB, the structural evidence from the present study can be outlined as follows. Occurrence of ethyldemethylation suggests that a σ complex, having two alkyl groups bound to the same ring carbon, must be formed at some point along the reaction path, albeit not necessarily corresponding to a local minimum on the energy surface. In other words, the σ complex may be formed just in the transition state of the reaction, rather than representing a true ionic intermediate. However, methylation of HMB in the presence of Et_3N provides strong evidence that a gaseous Wheland intermediate is actually involved, since the structure of the product 1 reflects that of the σ complex, and its formation requires that the latter is sufficiently long-lived (at least 10^{-7} s) to undergo deprotonation by the amine.

While CI spectra provide no direct structural insight, the observation of abundant $(C_6Me_6 + R)^+$ adducts requires that the latter survive long enough to undergo detection, despite the severe CI conditions (100 °C, pressures below 1 torr), which entails a degree of stability typical of true ionic intermediates. Furthermore, considerations based on the energetics of the methyl transfer from Me_2X^+ to HMB tend to discount the possibility that the observed $(C_6Me_6 + Me)^+$ ions are mere electrostatic adducts.[12] In summary, the CI results are best accommodated by intervention of "bound" alkylated adducts, e.g., corresponding to one of the structures **2–4**.

Finally, in failing to reveal detectable differences between the spectrum of the $C_{13}H_{21}^+$ ion from the methylation of HMB and that of the model ion from the mild protonation of **1**, CID spectrometry substantiates the evidence from the radiolytic and the CI results, showing that the methylated adduct from HMB has indeed the σ-complex structure **4** or at least isomerizes into **4** within 10^{-6}–10^{-5} s. To summarize, converging and mutually supporting lines of evidence from complementary experimental techniques *allow us to safely assign the σ-complex (Wheland intermediate) structure to the free, gaseous heptamethylbenzenium ion*, in agreement with the available data on the structure of its salts in solution[2a] and in the solid state.[3]

It is tempting to generalize the above conclusion, taking $C_6Me_7^+$ as the structural model of all gaseous heptaalkylbenzenium ions. Indeed, the evidence from the methylation of HEB, investigated with radiolytic and CI techniques, is consistent with the assignment of structure **4** (R = Et, R' = Me) to the $C_6MeEt_6^+$ cation as well, although confirmatory CID experiments have been prevented by the lack of suitable model ions.

Ionic Alkylation of Gaseous Hexaalkylbenzenes. The charged reagents, namely Et^+, Me_2F^+, and Me_2Cl^+, have been obtained from the radiolysis of appropriate precursors, according to processes well established by extensive mass spectrometric and radiolytic studies.[4,6,7,13-16] The standard heats of formation of the species of interest, together with other pertinent thermochemical

(12) Me^+ transfer from dimethylhalonium ions to hexaalkylbenzenes requires overcoming the methyl cation affinity of the methyl halides (some 64 kcal mol^{-1} for MeCl). Thus, the reaction is energetically allowed only when an equivalent, or higher amount of energy is released from the association of the Me^+ cation with the arene, which appears unlikely in the formation of a mere "electrostatic" adduct, cf. ref 6.

(13) Pepe, N.; Speranza, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1430 and references therein.

(14) Aue, D. H.; Bowers, M. I. In "Gas-Phase Ion Chemistry"; Bowers, M. I., Ed.; Academic Press: New York, 1979; Vol. 2, p 32 and references therein.

(15) Beauchamp, J. L.; Holz, D.; Woodgate, S. D.; Patt, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 2798.

(16) Calculated from the methyl cation affinity of MeCl, 64.2 kcal mol^{-1}, ref 6, and the $H_f°$ values of Me^+, ref 14, and of MeCl, from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

"*Ipso*" Aromatic Alkylation

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Table IV. Pertinent Thermochemical Data[a]

neutral molecule (M)	proton affinity (PA)	methyl cation affinity (MCA)	$(M + H)^+$, $H_f°$	$(M + Me)^+$, $H_f°$
CH_4	128[b]		CH_5^+, 219[b]	
C_2H_4	163[b]		Et^+, 219[b]	
i-C_4H_8	196[b]		t-Bu^+, 165[b]	
NMe_3	231[b]		NMe_3H^+, 128[b]	
MeF		44[c]		Me_2F^+, 161[c]
MeCl		64[d]		Me_2Cl^+, 176[d]
Me_2O		95[e]		Me_3O^+, 122[e]
C_6HMe_5		109[f]		$C_6HMe_6^+$, 134[f]
C_6Me_6	206[f]		$C_6Me_6H^+$, 134[f]	

[a] In kilocalories per mole, referred to gaseous ions at 25 °C. [b] Reference 14. [c] Reference 15. [d] Reference 16. [e] Reference 6. [f] Reference 17.

data, are given in Table IV. Besides its alkylating ability, the ethyl cation can behave as a Brønsted acid as well, the relatively low proton affinity of its conjugate base allowing exothermic proton transfer to the aromatic substrates.

It is convenient to discuss first the methylation of HMB, whose charged intermediate could successfully be trapped by deprotonation to **1**. The structure of the product and direct mass spectrometric detection of the charged intermediate suggest a reaction sequence promoted by the methyl-transfer process

$$Me_2F^+ + HMB \longrightarrow MeF + \left[\text{(arenium ion)}\right]^* \quad (1)$$
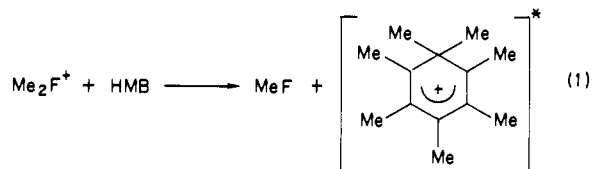
The reaction is considered to be strongly exothermic, since the methyl cation affinity (MCA) of HMB, unknown at the present time, is expected to greatly exceed that of MeF. This view is supported by the high MCA of PMB,[17] a substrate sufficiently close to HMB to allow meaningful comparison.

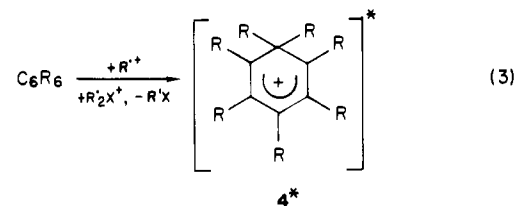Following collisional deactivation, the arenium ions can undergo deprotonation by an appropriate gaseous base

$$\left[\text{(arenium ion)}\right]^+ + B \longrightarrow \text{(product)} + BH^+ \quad (2)$$

1
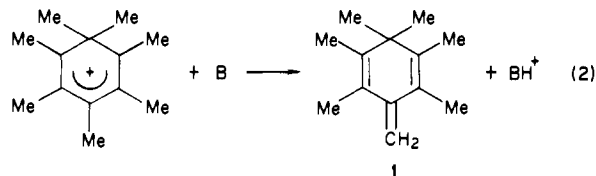
Owing to the remarkable basicity of **1**, whose PA is known[2a,h] to exceed that of HMB, proton transfer, eq 2, is energetically allowed only to strong bases, which accounts for the failure to detect formation of **1** in the absence of basic additives. Trialkylamines such as Et_3N, whose PA is very high (Table IV), easily accomplish deprotonation, although their extremely fast reaction with Me_2F^+, whose rate constants approach 10^{-9} cm^3 molecule^{-1} s^{-1},[6] consumes a large fraction of the methylating agent, substantially depressing the rate of alkylation.

In contrast with the methylation of HMB, its ethylation and the methylation of HEB lend themselves to the investigation of ipso substitution in the gas phase, since, in principle, both reactions can yield alkylated arenes other than the starting substrate.

Actually, ipso substitution has been found to occur, albeit with low yields. The nature of the products, and the detection of the corresponding charged intermediates by CI mass spectrometry suggest that the first step of the substitution gives heptaalkylbenzenium ions, excited by the appreciable exothermicity of the process

$$C_6R_6 \xrightarrow[+R'_2X^+, \ -R'X]{+R'^+} \left[\text{(cation 4*)}\right]^* \quad (3)$$

4*

comparable to that of reaction 1. Following collisional deactivation,[18] the intermediates can evolve into neutral aromatic products only by losing a R^+ moiety. Release of free carbenium ions being energetically precluded, dealkylation is likely to require intervention of a gaseous nucleophile

$$4 + Nu \rightarrow C_6R_5R' + NuR^+ \quad (4)$$
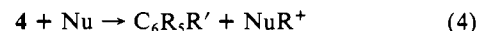
It is of interest to consider how it arises that the overall efficiency of the ipso substitution is remarkably low, at least in the absence of additives. One can consider either of two opposite views, pointing, respectively, to the alkyl transfer process (eq 3) or to the subsequent dealkylation as the slow step. Indirect indication for the first alternative comes from the appreciable activation energy of the methyl transfer from Me_2Cl^+ to the *unsubstituted* positions of benzene and toluene.[6,7] In fact, it is quite conceivable that the hindering effect of the alkyl group bound to the reaction center in hexaalkylbenzenes overbalances the activating effects of the other alkyl groups, leading to a net *increase* of the activation energy of methyl transfer from Me_2X^+. While this argument is less convincing when applied to free carbenium ions, such as Et^+, the scarce efficiency of ethylation could be rationalized on different grounds by invoking competition by other energetically allowed processes, e.g., proton transfer, hydride-ion abstraction, etc.

However, ascribing the relative inefficiency of ipso substitution exclusively or predominantly to step 3 conflicts with significant experimental features. The CI evidence from this study points to facile methylation of HMB and HEB, consistent with the known *increase* of the rate of Me^+ transfer from Me_2Cl^+ with decreasing ionization potential and hence with increasing PA of the aromatic substrate.[7b] Furthermore, it is hard to explain why the C_6MeEt_5 yield is unaffected when Me_2F^+ is replaced by Me_2Cl^+, whose lower reactivity toward arenes is well documented.[6,19] Even more significantly, the dramatic *increase* of the C_6MeEt_5 yield in the presence of Me_2O can hardly be traced to acceleration of step 3, since Me_3O^+, the alkylating reagent then involved, is much milder than Me_2F^+, consistent with the larger MCA of Me_2O as shown in Table IV.

The above difficulties are avoided by adopting the alternative view that ascribes the low overall rate of the ipso substitution to the dealkylation step. As a matter of fact, in the absence of deliberately added nucleophiles, R^+ transfer from **4** is energetically allowed, if at all, only to the C_6R_6 substrate,[20] and there are good reasons to presume that the process is then quite slow.

In general, the assumption that step 4 is rate limiting, at least in the absence of suitable additives, allows a plausible interpretation of the experimental features, including the striking enhancement of the C_6MeEt_5 yield in the presence of Me_2O, which seems to defy alternative explanations. The effect can be reasonably traced to the ability of Me_2O to accomplish fast dealkylation of the $C_6MeEt_6^+$ intermediate without depressing its formation rate.[21] Apart from the alkyl transfer 4, another reaction channel con-

(17) Calculated from the PA of HMB from: Devlin, J. L., III; Wolf, J. F.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 1990. Also calculated from the standard heats of formation of Me^+ ref 14, PMB, and HMB, ref 16.

(18) Effective collisional deactivation, typical of gaseous systems at nearly atmospheric pressure, is expected to prevent significant fragmentation of **4***. Nevertheless, occurrence of isomerization processes cannot be excluded, owing to their low activation energy, as low as 12.9 kcal mol^{-1} for 1,2 Et^+ shifts and from 15.2 to 18.8 kcal mol^{-1} for 1,2 Me^+ shifts in $C_6R_7^+$ ions, ref 2e.

(19) In the systems containing MeCl or Me_2O in large excess over HEB, the alkylating reagents are Me_2Cl^+ or Me_3O^+, formed via fast Me^+ transfer from Me_2F^+, occurring at rates as high as 10^{-9} cm^3 molecule^{-1} s^{-1}.

(20) R^+ transfer to other nucleophiles present in the system or formed from its radiolysis (H_2O and MeOH) would be endothermic, since their MCA is much lower than that of HMB and HEB, ref 15.

(21) In contrast with other nucleophiles that intercept Me_2F^+ ions, giving unreactive species, e.g., ammonium ions from trialkylamines, Me_2O yields Me_3O^+, a milder alkylating reagent.

ceivably open to Me$_2$O involves elimination of ethylene

$$C_6MeEt_6^+ + Me_2O \rightarrow C_6MeEt_5 + C_2H_4 + Me_2OH^+ \quad (5)$$

While the lack of necessary data prevents exact calculations, reasonable estimates suggest that neither process should significantly depart from thermoneutrality. Dimethyl ether is known to undergo fast R$^+$ transfer from gaseous cations,[6] and its reaction with C$_6$MeEt$_6^+$ is probably favored by the limited steric requirements, the high concentration attainable in the gas, and the relatively high temperature (120 °C) of the system.

Alkylation of Pentamethylbenzene. The results are of special interest, allowing quantitative comparison between the rate of ipso substitution and that of alkyldeprotonation of the same substrate. The latter process is found to predominate by an order of magnitude, despite its unfavorable statistical factor. In line with foregoing considerations, the bias against ipso substitution can be plausibly ascribed to the different rates of the processes which convert the charged intermediates into neutral aromatic products. In fact, it can be argued that demethylation of the ipso-alkylated adducts **5**

5   **6**
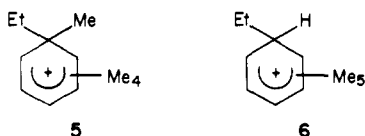
is slower than deprotonation of the intermediate **6** from the attack at the unsubstituted position of PMB. This is a reasonable proposition if one considers that proton-transfer processes are comparatively very fast in the gas phase and that the formation of proton-bound clusters can allow deprotonation of **6** even by relatively weak n-type bases. It seems likely that the observed bias in favor of alkyldeprotonation is enhanced by the partial isomerization into **6** of the unreactive intermediate **5** via facile 1,2 Et$^+$

Conclusions

The complementary results from different experimental techniques, i.e., CI mass spectrometry, CID spectrometry, and gas-phase radiolysis, provide convincing evidence for the occurrence of gaseous heptaalkylbenzenium ions having the σ-complex (Wheland intermediate) structure as stable species in the dilute gas state. The ions represent the charged intermediates of the gas-phase ipso substitution promoted by the attack of Et$^+$, Me$_2$F$^+$, and Me$_2$Cl$^+$ cations on hexaalkylbenzenes.

A New Halogen-Free Chemical Oscillator: The Reaction between Sulfide Ion and Hydrogen Peroxide in a CSTR[1]

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Abstract: Periodic oscillation and bistability occur in the potentials of Pt redox, pH, and sulfide ion selective electrodes when sulfide ion reacts with hydrogen peroxide in a continuous flow stirred tank reactor. The S^{2-}–H$_2$O$_2$ system is one of the few known and probably the simplest of the non-halogen chemical oscillators. It is the first of these systems to show bistability and the only chemical oscillator known to oscillate between acid and basic pH.

The overwhelming majority of the known homogeneous oscillatory chemical reactions are based on the chemistry of oxyhalogen anions.[2] Recently, two new discoveries have extended the realm of chemical oscillation beyond group 17[12] of the Periodic Table. Jensen[3] reported oscillation in the reaction of benzaldehyde with oxygen in the presence of Br$^-$ and Co(II). Field and Burger[4] have found oscillatory behavior in the potential of a Pt electrode and in the absorbance at 668 nm when sulfite, sulfide, methylene blue, and oxygen react in a continuous flow stirred tank reactor (CSTR). In contrast to the almost universal association of bistability with oscillation in oxyhalogen systems, neither of the above two reactions has been shown to exhibit multiple stationary states.

We report here on a halogen-free system, with apparently simpler constituents than either the Jensen or Burger–Field reactions, which gives both bistable and oscillatory behavior in a CSTR. The reaction, which involves only sulfide ion and hydrogen peroxide, has been studied previously in other contexts by several

authors,[5–7] since it offers a potentially cheap and convenient route to eliminate H$_2$S generated by industrial and municipal wastewater systems.

Several other features of the S^{2-}–H$_2$O$_2$ system should be noted. It not only exhibits both oscillations and bistability but also provides an almost classic example of the cross-shaped phase diagram,[8] which led to the first systematically designed chemical oscillators.[9] While all oxyhalogen systems and the Jensen reaction

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(1) Part 26 in the series Systematic Design of Chemical Oscillators. Part 25: Alamgir, M.; Epstein, I. R. *Int. J. Chem. Kinet.*, in press.
(2) Epstein, I. R.; Orbán, M. In "Oscillations and Traveling Waves in Chemical Systems"; Field, R. J., Burger, M., Eds.; Wiley: New York, 1985; Chapter 8.
(3) Jensen, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 2639–2641.
(4) Burger, M.; Field, R. J. *Nature (London)* **1984**, *307*, 720–721.
(5) Satterfield, C. N.; Reid, R. C.; Briggs, D. R. *J. Am. Chem. Soc.* **1954**, *76*, 3922–3923.
(6) Zietz, U. *Tech.-Wiss. Schriftenr. ATV* **1978**, *7*, 125–146.
(7) Hoffmann, M. R. *Environ. Eng. Sci.* **1977**, *11*, 61–66.
(8) Boissonade, J.; De Kepper, P. *J. Phys. Chem.* **1980**, *84*, 501–506.
(9) De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* **1981**, *103*, 6121–6127.

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