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Polycondensation of benzyl methyl ether by reaction with gaseous benzyl cations—a potpourri of mechanisms of organic ion/molecule reactions

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Abstract

Gaseous benzyl cations (A^+) react with up to three molecules of benzyl methyl ether (**1**) generating condensation product ions B^+ , m/z 181, C^+ , m/z 271, and D^+ , m/z 361, by elimination of methanol during each condensation step. Additional product ions arise from hydride abstraction from ether **1** to generate α -methoxybenzyl cations m/z 121 and from a degenerate electrophilic substitution by attack of A^+ on the ether-O atom of **1**, resulting in a methoxy group transfer and new benzyl cation A^+ . The main final product ions correspond to protonated anthracene, m/z 179. The mechanisms of these ion/molecule reactions have been studied by Fourier transform-ion cyclotron resonance spectrometry measuring the kinetics of the individual reaction steps, using specifically deuterated reactants A^+ and **1**, and by analyzing separately the reactions of isomeric ions B^+ generated from suitable precursors. These studies reveal an interesting array of different mechanisms of the ion/molecule reaction within this system. The condensation reaction proceeds by electrophilic aromatic substitution of benzyl cation A^+ on the aromatic ring of ether **1** and specific elimination of methanol from the σ complex via benzybenzyl cations B^+ . The benzylic ions B^+ undergo a second condensation reaction with ether **1** and generate ions C^+ , which react by a further condensation with ether **1** to create ions D^+ . Starting from ions B^+ the 2-methylbenzhydryl cations B_{dip}^+ are formed as an additional isomer which is totally unreactive towards ether **1**. In addition, protonated 9,10-dihydroanthracene cations B_{cycl}^+ are formed by an intramolecular aromatic substitution of ions B^+ . Separate investigations with specifically generated *ortho*-benzybenzyl cations B_o^+ and protonated 9,10-dihydroanthracene cations B_{cycl}^+ prove the rapid interconversion of these ions. Ions B_{cycl}^+ reacts with ether **1** by a multistep reaction within a single collision complex to produce eventually protonated anthracene, a molecule of toluene, and a molecule of methanol. Finally, the degenerate electrophilic substitution by a benzyl cation A^+ at the O atom of ether **1** was studied. (Int J Mass Spectrom 179/180 (1998) 207–221) © 1998 Elsevier Science B.V.

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1. Introduction

The electrophilic substitution of arenes and alkyl arenes in the gas phase by carbenium ions has been

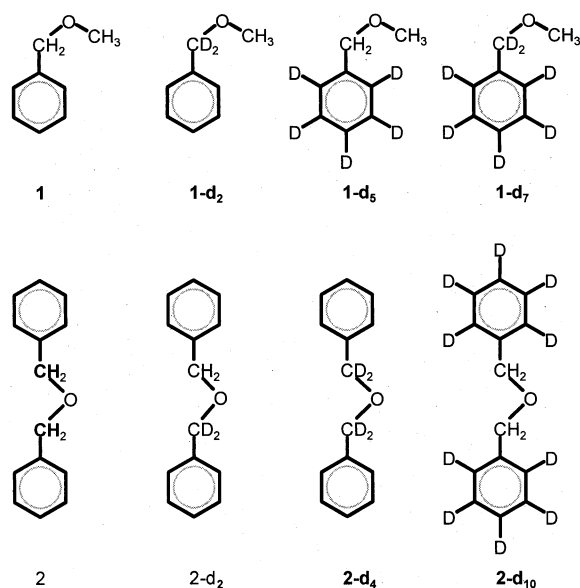
illustrated for many cases [1,2]. An interesting example is the well-known reaction of gaseous benzyl cations with toluene and other alkyl arenes [3,4], which can be used to distinguish between benzyl cations and the isomeric tropylium ions. These latter ions do not react with toluene whereas the reaction between a benzyl cation and a toluene molecule results eventually in the transfer of the benzylic CH_2 group. It was shown that this reaction starts by an

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Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

addition of the benzyl cation to toluene generating a σ complex and proceeds by elimination of a benzene molecule after proton migration within the σ complex. A σ complex corresponds to a (*ipso*-) protonated arene or arenium ion, and the elimination of benzene molecules from protonated diphenylmethanes and 1, *n*-diphenylalkanes has been demonstrated in many examples [5]. Condensation reactions, i.e. addition reactions followed by elimination of small neutral molecules by electrophilic substitution, has also been observed in other cases. Thus, the reaction of benzyl cations with benzyl chloride results not only in hydride abstraction and chloride transfer, but also in the elimination of HCl from the addition product [6]. Further, the methoxymethyl cation $\text{CH}_3\text{OCH}_2^+$ reacts with benzene or toluene by electrophilic attack followed by elimination of methanol [7] to generate “[M + 13]” cations, and this reaction has been suggested for analytical applications using dimethyl ether as the reagent gas of chemical ionization mass spectrometry of aromatic compounds [8,9].

We became interested in these type of condensation reactions of aromatic compounds in the gas phase when we observed that benzyl cations (but not tropylium ions) react not only with vinyl ether $\text{CH}_2=\text{CH}-\text{OR}$ but also with benzyl alkyl ether $\text{C}_6\text{H}_5\text{CH}_2-\text{OR}$ by addition followed by elimination of an alcohol molecule ROH. With the latter substrates a polycondensation reaction was observed which could be followed until the incorporation of up to three benzyl ether molecules. Thus, the reaction of benzyl cations with benzyl alkyl ethers also represents a gas phase polymerization initiated by a carbenium ion, another reaction type of considerable interest [10–12]. A related polycondensation reaction has been observed by Meot-Ner et al. [13] and by Cameron et al. [14] for benzyl acetate using chemical ionization. To get more detailed information about the discrete reaction steps and a better perception of the mechanism of the gas phase polycondensation reaction of benzyl cations with benzyl alkyl ethers we studied the course and the kinetics of the ion/molecule reaction of benzyl cations (A^+) with benzyl methyl ether (**1**) using deuterated derivatives and FT-ICR spectrometry with external generation of the benzyl cations.



Scheme 1.

2. Experimental

The syntheses of benzyl methyl ether **1** and its deuterated derivatives **1-d₂**, **1-d₅**, and **1-d₇** and of dibenzyl ether **2** and its deuterated derivatives **2-d₂**, **2-d₄**, **2-d₇**, and **2-d₁₀** (for structures see Scheme 1) were performed using standard procedures of organic chemistry and are described elsewhere [15]. The structures of these ethers were verified and controlled by ^1H NMR and ^{13}C NMR, and the D content (at least 97%) was determined by electron ionization (EI) mass spectrometry (benzyl methyl ether derivatives) or ^1H NMR spectrometry (dibenzyl ether derivatives).

The kinetics of the ion/molecule reactions were determined using a Bruker CMS 47X FT-ICR spectrometer (Spectrospin, Fällanden, Switzerland) equipped with a 4.7 T superconducting magnet, a cylindrical Infinity cell, two magnetic valves, an external EI ion source and chemical ionization (CI) ion source, and a 24 bit Aspect 3000 computer. The C_7H_7^+ cations and their isotopomers $\text{C}_7\text{H}_{(7-x)}\text{D}_x^+$ ($x = 2, 5, 7$) were generated in the external ion source [mostly by CI(methane) at a pressure of about 10^{-4} mbar measured for the ion source housing, but occasionally also by 70 eV EI] from **1** or the appro-

priate deuterated derivative and transferred into the Fourier transform-ion cyclotron resonance (FT-ICR) cell. For some experiments the $C_7H_7^+$ cations were also produced within the FT-ICR cell by internal EI. It is known that mixtures of benzyl cations and tropylium ions may be created by EI or CI from benzylic precursors, and that the benzyl cations are the reactive component of the $C_7H_7^+$ cations [16]. An analysis by reaction with ethyl vinyl ether shows that more than 96% of the $C_7H_7^+$ cations generated from **1** under the conditions used in this work correspond to benzyl cations. The dimethyl bromonium ions $(CH_3)_2Br^+$ used for the gas phase methylation of dibenzyl ether were prepared in the external CI ion source from methyl bromide by EI at a suitable ion source pressure and transferred into the FT-ICR cell. The neutral reaction partner (**1**, **2**, or their isotopomers) was introduced into the FT-ICR cell by the inlet system of the instrument and was present in the FT-ICR cell at a constant pressure between 5×10^{-9} and 5×10^{-8} mbar. The pressure within the FT-ICR cell was measured by an ionization gauge located between the FT-ICR cell and the high vacuum pump for that region. The pressure readings of the ionization gauge were calibrated periodically by determination of the rate constants of the reaction $CH_4^+ + CH_4$ [$k = 1.5 \pm 0.3 \times 10^{-9} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$] [17]] and $NH_3^+ + NH_3$ [$k = 2.2 \pm 0.4 \times 10^{-9} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$] [18]] and were corrected for the sensitivity of the ether [19].

In order to perform kinetic experiments, the ion under study [A^+ or $(CH_3)_2Br^+$] was isolated in the FT-ICR cell by broadband ejection ($V_{p-p} = 78\text{--}88$ V, $80 \mu\text{s}$) and a series of single radiofrequency (rf) pulses (“single shots,” $V_{p-p} = 5.5\text{--}8$ V, 3 ms) to eject ions with m/z values near that of the isolated ion. This was followed by collisional cooling of the ions by introducing a pressure pulse of argon [20]. If necessary, any extra ions formed during the cooling period were ejected by a second series of single shots before the measurement of the reaction kinetics was started by acquiring mass spectra at variable reaction times. The decay of the reacting ions with reaction time followed cleanly a pseudo-first order process unless otherwise stated in the text. The experimental

pseudo-first order rate constant k_{exp} was obtained from a plot of the ion intensity versus reaction time (“kinetic plot”) by curve fitting using the ORIGIN 3.5 program [21] and was converted into the bimolecular rate constant k_{bi} by taking into account the number density of the neutral reaction partner. The reproducibility of k_{bi} was always very good, but the error of the absolute values of k_{bi} introduced by the pressure measurement is estimated as $\pm 25\%$.

3. Results and discussion

The ion mixture evolving with time in the FT-ICR cell by reaction of benzyl cations A^+ , m/z 91, with benzyl methyl ether **1** is shown in Fig. 1. At a partial pressure of **1** of 18×10^{-8} mbar the composition of the ion mixture stays almost constant after a reaction time of 10 s with ions m/z 121, m/z 179 and m/z 361 as the main reaction products (see also Table 1). For clarity the reaction products are shown in two kinetic plots, the first one presenting a series of consecutive reactions yielding product ions of m/z 181, 271, and 361, whereas the second one shows kinetic plots for a second set of product ions at m/z 121, 179, and 269. As can be deduced from the mass difference of 90 u, the product ions of the first series arise from the consecutive addition of one, two and three molecules of **1**, respectively, and one ion A^+ , with each addition followed by the elimination of a molecule of methanol. A hydride abstraction of A^+ from **1** generates the α -methoxybenzyl cation m/z 121, and the two other ions m/z 179 and 269 of the second set are derived at least formally from the product ions m/z 181 and 261 by loss of H_2 .

Thus, it appears that the benzyl cation A^+ reacts initially with the benzyl ether **1** either by hydride abstraction to yield the primary product ion m/z 121 or by electrophilic attack at the aromatic ring of **1** giving rise eventually to primary product ion m/z 181 by a condensation reaction. A rate constant $k_{\text{bi}} = 1.2 \pm 0.3 \times 10^{-9} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ of the total reaction was obtained (see Table 2). This corresponds to a reaction efficiency $100 \times k_{\text{bi}}/k_c$ of 79 [%] if the collision rate constant k_c is calculated according to the

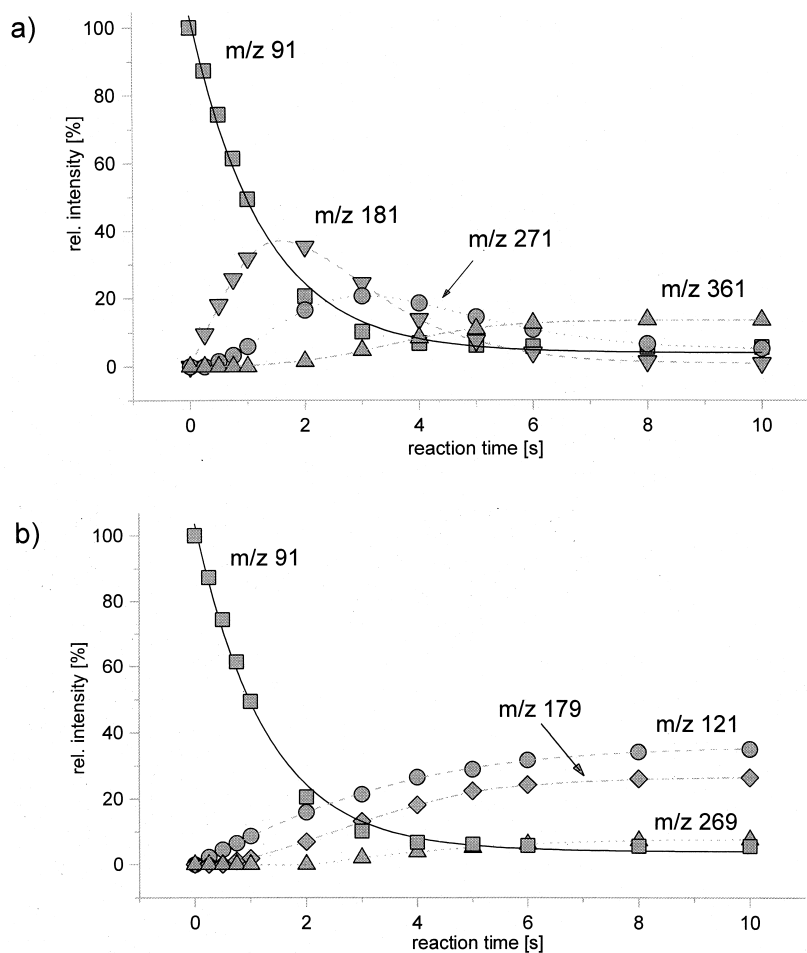


Fig. 1. Kinetic plots for the reaction of benzyl cation A^+ with benzyl methyl ether **1**: (a) condensation product ions B^+ , m/z 181, C^+ , m/z 271, and D^+ , m/z 361; (b) α -methoxybenzyl cation m/z 121 and secondary product ions m/z 179 and m/z 269.

method of Su and Chesnavich [22]. The branching ratio between condensation and hydride abstraction was obtained by extracting the bimolecular rate constants k_{cond} and k_{hydride} by curve fitting according to the kinetics of two parallel reactions to the kinetic plot at the early stages of the reaction. The branching ratio

$k_{\text{cond}}/k_{\text{hydride}} = 5:1$ shows that the condensation reaction is considerably faster than the hydride abstraction. However, the use of deuterated benzyl cations $A^+ -d_7$ in the reaction with **1** (or the reaction of A^+ with deuterated benzyl methyl ether **1-d₇**) reveals straightway a third primary reaction channel

Table 1

Relative abundance [%] of the product ions of the reaction of benzyl cation A^+ with benzyl methyl ether **1**

| Reaction time [s] | m/z | 91 | 121 | 179 | 181 | 269 | 271 | 361 |
|-------------------|-------|-----|------|------|-----|-----|-----|------|
| 18 | | 4.0 | 33.1 | 29.7 | 0.0 | 7.4 | 4.5 | 13.6 |
| 20 | | 3.9 | 34.0 | 29.0 | 0.0 | 7.4 | 4.3 | 13.3 |

Table 2

Rate constants k_{bi} , collision rate constants k_c , and reaction efficiency eff , for reactions of the system benzyl cation A^+ /benzyl methyl ether **1**

| Reactant ion | k_{bi}^c | $k_c^{c,d}$ | eff^e |
|---------------------------------------|------------|-------------|---------|
| A^+ , m/z 91 | 1.20 | 1.52 | 79 |
| B^+ , m/z 181 ^{a,b} | 0.78 | 1.28 | 60 |
| C^+ , m/z 271 ^{a,b} | 0.58 | 1.19 | 49 |
| D^+ , m/z 261 ^{a,b} | 0.70 | 1.15 | 61 |
| B_o^+ , m/z 181 ^b | 1.40 | 1.28 | 109 |
| B_{cycl}^+ , m/z 181 ^b | 1.20 | 1.28 | 94 |
| B_p^+ , m/z 181 ^b | 0.86 | 1.28 | 67 |

^a Ions isolated from the reaction of A^+ and **1**; correspond to mixture of isomers.

^b Kinetic data only for the reactive fraction of ions.

^c $\times 10^{-9}$ ($\text{cm}^3 \text{s}^{-1} \text{molecule}^{-1}$).

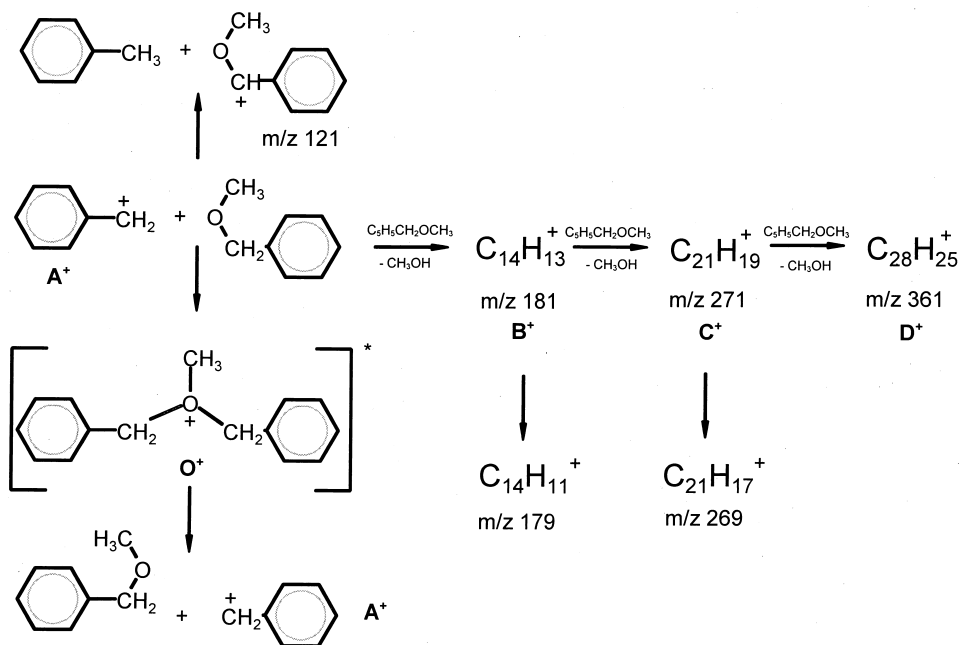
^d Calculated by the method of Su and Csanavich [22].

^e $= 100(k_c/k_{bi})$ [%].

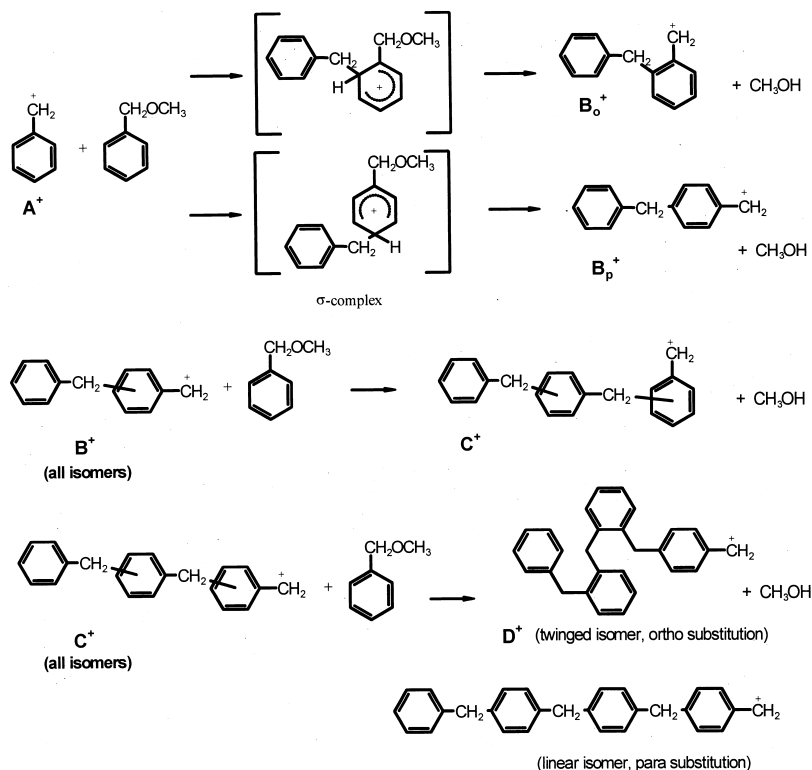
which generates undeuterated benzyl ions A^+ (or deuterated ions A^+-d_7) parallel to the other reaction products. Obviously, electrophilic addition of the benzyl cation occurs also at the electron lone pair of the ether-O atom of **1** and creates a dibenzyl methyl oxonium ion O^+ as a reactive intermediate. This electrophilic addition is not unexpected, and the

excited ion O^+ formed by the reaction dissociates back into a benzyl cation and **1**, but in between the two benzyl groups of O^+ , get mixed up. This third reaction branch is not included in the values of k_{bi} and of the reaction efficiency given above, which are therefore too small. Hence, the reaction of benzyl cations A^+ with the benzyl ether **1** is very fast and the rate almost corresponds to the collision limit. Thus, the primary and consecutive reactions proceed as depicted in Scheme 2. (In addition to the product ions shown in Scheme 2 the kinetic plots sometimes display a small amount of ions m/z 122. These ions correspond to the molecular ions of **1** and are probably generated by charge exchange with some excited ions present in the FT-ICR cell in spite of collisional cooling. This ion m/z 122 is not included in Scheme 2.)

This reaction scheme of the ion/molecule reactions of A^+ and **1** is comparable to the model developed for the reactions of benzyl acetate under the condition of chemical ionization [13,14], but the techniques of FT-ICR spectrometry allow a more explicit look into the individual reaction steps. This will be discussed in the following sections.



Scheme 2.



Scheme 3.

3.1. The consecutive polycondensation reaction: an intermolecular aromatic substitution

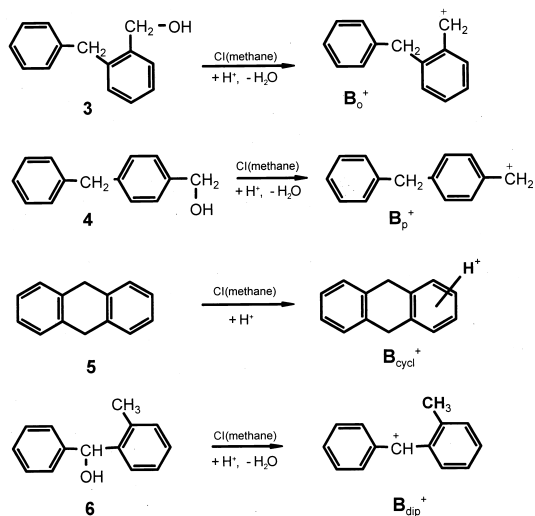
The consecutive nature of the reactions forming the ions m/z 181, m/z 271, and m/z 361 is clearly seen in the kinetic plot of Fig. 1(a). These three product ions are designated by B^+ , C^+ , and D^+ , respectively, in the following discussion. It is expected that the ions B^+ arise from an electrophilic attack of benzyl ions A^+ on the aromatic ring of **1**, which generates a σ complex as a reactive intermediate with the structure of a protonated diphenylmethane carrying a CH_3OCH_2 side chain. Proton migration within this σ complex onto the O atom of the side chain followed by elimination of methanol generates the product ion B^+ with the structure of an *ortho*- or *para*-benzylbenzyl cation (B_o^+ or B_p^+ , see Scheme 3), depending on the initial point of attack of A^+ . These substituted benzyl cations B^+ can repeat the sequence of electrophilic addition/methanol elimination by re-

action with **1** to produce ions C^+ , and because ions C^+ are again benzylic carbenium ions, the condensation reaction with ether **1** can continue to generate ions D^+ . In each of the condensation steps, the substitution by the benzylic carbenium ions occurs predominantly at the activated *ortho*- and *para*-position of the benzyl ether **1**, so that the ions C^+ and D^+ are also mixtures of regioisomers with either an elongated or a twinged structure. After formation of D^+ the condensation reaction becomes very slow or even terminates, so that no higher "benzylogues" of D^+ can be observed. Possible explanations for this effect are a decrease in the reactivity of the benzylic carbenium ions with molecular size or, more likely, an isomerization to nonbenzylic isomers (see Scheme 3).

This mechanism of the oligocondensation reaction predicts that the methanol molecule lost in each of the condensation steps is composed of the methoxy group and one of the "aromatic" hydrogen at the phenyl ring of **1**, which is mobilized by formation of the σ -com-

plex. This is confirmed by the reaction of labeled ions $A^+ - d_2$ and $A^+ - d_5$ with the correspondingly labeled ether **1**. In the former case, ions $B^+ - d_4$, m/z 185, $C^+ - d_6$, m/z 277, and $D^+ - d_8$, m/z 369, are formed specifically, but in the latter case only ions $B^+ - d_9$, $C^+ - d_{13}$, and $D^+ - d_{17}$ are observed at m/z 190, 284, and 378. These results of the reactions of labeled derivatives clearly corroborate the mechanisms shown in Scheme 3 and demonstrate that the condensation reaction of benzyl cations A^+ and benzyl ether **1** is a further example of the Friedel-Crafts alkylation in the gas phase, which has been studied carefully by Cacace and his group [1]. From these studies it is known that the σ -complex generated by the electrophilic attack of a carbenium ion isomerizes by a “ring-walk” of the proton [23], and in the present condensation reaction the proton eventually jumps on the ether-O atom to induce the elimination of methanol. It was not possible to decide by the reaction of asymmetrically labeled reactants (for example, reaction of A^+ with **1**- d_5) whether or not the “mobile” proton migrates from one phenyl ring to the other within the σ -complex. Such “proton jumping” between aromatic rings is well known from the mass spectra of protonated 1, n -diphenylalkanes and even protonated diphenylmethane [24], which are structurally comparable to the present σ complex. However, the methoxy group transfer and benzyl group exchange between ions A^+ and ether **1** is very fast, and in the case of labeled derivatives an intractable mixture of isotopomers is obtained by further reaction even at the early stages of the condensation reaction.

For additional details, the reactions of ions B^+ , C^+ , and D^+ were studied separately by isolation of the product ions at appropriate stages of the condensation reaction within the FT-ICR cell, starting the reaction with **1** again. In the case of ions B^+ the reaction was compared to those of ions $C_{14}H_{13}^+$, m/z 181, which were generated from precursors of known structures (see Scheme 4). Fig. 2 shows the kinetic plots for the reactions of product ions B^+ , C^+ , and D^+ after isolation with ether **1**. Interestingly, the plots for C^+ , and in particular for D^+ , exhibit bimodal kinetics for the decay of the reactant ions and show the presence of unreactive isomers. However, the rate



Scheme 4.

constants k_{bi} calculated from the decay of the reactive ions are still quite large and correspond to reaction efficiencies between 49% and 61% (Table 2).

As expected, the ions B^+ , m/z 181, initially yield ions C^+ , m/z 271, and α -methoxybenzyl cations, m/z 121 by reaction with **1**. Further, ions A^+ , m/z 91, are formed by addition of B^+ to the ether-O atom of **1** and dissociation of the intermediate oxonium ion. This behavior characterizes ion B^+ as a benzylbenzyl cation exhibiting a similar reactivity as the benzyl cation A^+ . Surprisingly however, besides the ion m/z 121, the main product ion at the end of the reaction is protonated anthracene, m/z 179, which is supposed to be generated by a *unimolecular* process (H_2 elimination) from excited protonated 9,10-dihydroanthracene B_{cycl}^+ , m/z 181—the cyclic isomer of ions B^+ [14]. In contrast to this assumption, the kinetic plot in Fig. 2(a) shows unambiguously that the ions m/z 179 are in fact produced by a *bimolecular* reaction between ions B^+ and **1**. This was corroborated by an experiment in which the ions B^+ were continuously ejected from the FT-ICR cell during the reaction of ions A^+ with **1**. As a consequence, the intensity of the ions m/z 179 was reduced considerably, but some ions m/z 179 were still observed. This indicates that these ions also may be formed from other precursor ions. The

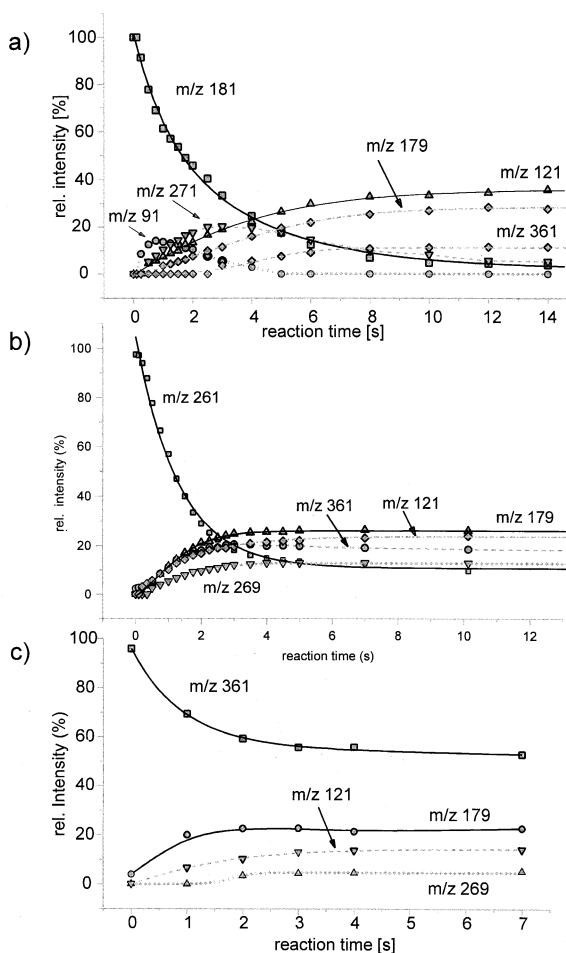


Fig. 2. Kinetic plots for the reaction of condensations product ions (isolated from the reaction mixture) with benzyl methyl ether **1**: (a) reaction of ion B^+ ; (b) reaction of ion C^+ ; (c) reaction of ion D^+ .

mechanism of the formation of ions m/z 179 by a bimolecular reaction will be discussed below.

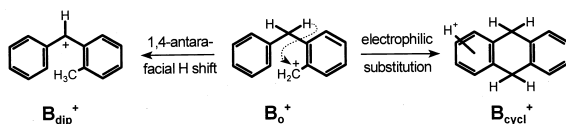
Again, as expected, the ions C^+ produce a condensation product ion D^+ , m/z 361, and the product ion m/z 121 of the hydride abstraction [Fig. 2(b)], but ions A^+ , m/z 91, are not detected any more. It is very likely that the rather asymmetrical oxonium ion formed by addition of C^+ to the ether-O atom of **1** dissociates predominantly back to ion C^+ and not to ion A^+ . Again, protonated anthracene, m/z 179, and a benzylogue of this ion with m/z 269 are the main product ions besides ions m/z 121 at the end of the reaction. This time, the formation of protonated an-

thracene m/z 179 from ions C^+ requires the formal elimination of toluene induced by the reaction with **1**. Finally, the kinetic plot of the reaction of ions D^+ with ether **1** [Fig. 2(c)] shows that roughly 50% of the ions D^+ do not react with **1**. No further condensation product ions at m/z 451 are observed even at prolonged reaction times and at increased partial pressures of **1** in the FT-ICR cell. Protonated anthracene, m/z 179, and its benzylogue, m/z 269, are the only product ions observed besides some ions m/z 121. Thus, the condensation product ions B^+ , and C^+ exhibit benzylic reactivity similar to benzyl cations A^+ , but are distinguished by an additional elimination reaction giving rise to protonated anthracene m/z 179 and its benzylogue m/z 269, and in the case of the product ion D^+ these elimination reactions represent the only abundant reaction channels.

3.2. Reactions and isomerization of ions B^+ , $C_{14}H_{13}^+$: a reversible intramolecular aromatic substitution

The typical reactions and the structures of the condensation product ions B^+ were investigated more closely by generating different ions $C_{14}H_{13}^+$ from the precursors shown in Scheme 4. The loss of H_2O from protonated *ortho*-benzylbenzyl alcohol **3** and from *para*-benzylbenzyl alcohol **4** induced by CI(methane) gives rise to $C_{14}H_{13}^+$ ions corresponding at least initially to B_o^+ and B_p^+ , respectively, while the cyclic $C_{14}H_{13}^+$ isomer B_{cycl}^+ can be generated by protonation of 9,10-dihydroanthracene **5** during CI(methane). Finally, $C_{14}H_{13}^+$ ions with the structure of a 2-methylbenzhydryl cation B_{dip}^+ were produced by elimination of H_2O from 2-methylbenzhydrol **6** using CI(methane).

Experiments to distinguish these isomeric ions $C_{14}H_{13}^+$ by collision induced dissociations (CID) failed, because the mass spectra obtained by CID of all ions B_o^+ , B_p^+ , B_{cycl}^+ , and of the condensation product ions B^+ were not significantly different. Besides some elimination of H_2 , the formation of ions m/z 166 and 165 is the main CID process in all spectra. Other possibilities to differentiate between isomeric ions are structurally significant ion/molecule



reactions. The ions B_o^+ , B_p^+ , and probably also B_{dip}^+ should exhibit the reactivity of benzyl cations, while B_{cycl}^+ behaves primarily as a proton donor towards bases. The benzyl cation A^+ reacts efficiently with ethyl vinyl ether by addition and elimination of ethanol to produce an ion m/z 117 [25]. An analogous reaction is expected for B^+ isomers of a benzylic structure. Arenium ions like B_{cycl}^+ transfer a proton to a base, which in the case of ethyl vinyl ether gives rise to the protonated ether at m/z 73 and to an ion m/z 101 as the secondary reaction product. In the case of the B^+ isomers, the ion B_p^+ reacted with ethyl vinyl ether to yield ion m/z 117 and its benzylogue m/z 207 as the main product ions, as expected. The benzhydryl cation B_{dip}^+ , however, turned out to be unreactive. Further, B_{cycl}^+ exhibited the expected proton transfer to ethyl vinyl ether yielding the ion m/z 73 and its secondary product m/z 101. Surprisingly, however, the ions B_o^+ also suffered only proton transfer and contained a small fraction of unreactive isomers. Thus, it appears that the *ortho*-benzylbenzyl cation B_o^+ isomerizes efficiently by intramolecular electrophilic aromatic substitution into the protonated dihydroanthracene B_{cycl}^+ , and probably also by an antarafacial 1,4-H shift into the unreactive 2-methylbenzhydryl cation B_{dip}^+ (Scheme 5).

As an additional test the ions B_p^+ , B_o^+ , and B_{cycl}^+ were treated with several bases with proton affinities (PA) ranging from *para*-xylene (PA 794.8 kJ mol⁻¹ [26]) to *n*-butyl amine (PA 921.4 kJ mol⁻¹ [26]) in the FT-ICR cell to determine in particular the amount of the protonated species B_{cycl}^+ in the C₁₄H₁₃⁺ ions derived from **3** and **4** by the “gas-phase titration” technique [27]. These experiments confirmed that the ions B^+ derived from protonated **3** by loss of H₂O and from protonated **5** indeed represent an identical mixture of isomers. No deprotonation is observed for all ions B^+ by using *para*-xylene as a base, which shows that the PA of any conjugated base C₁₄H₁₂ of the ions

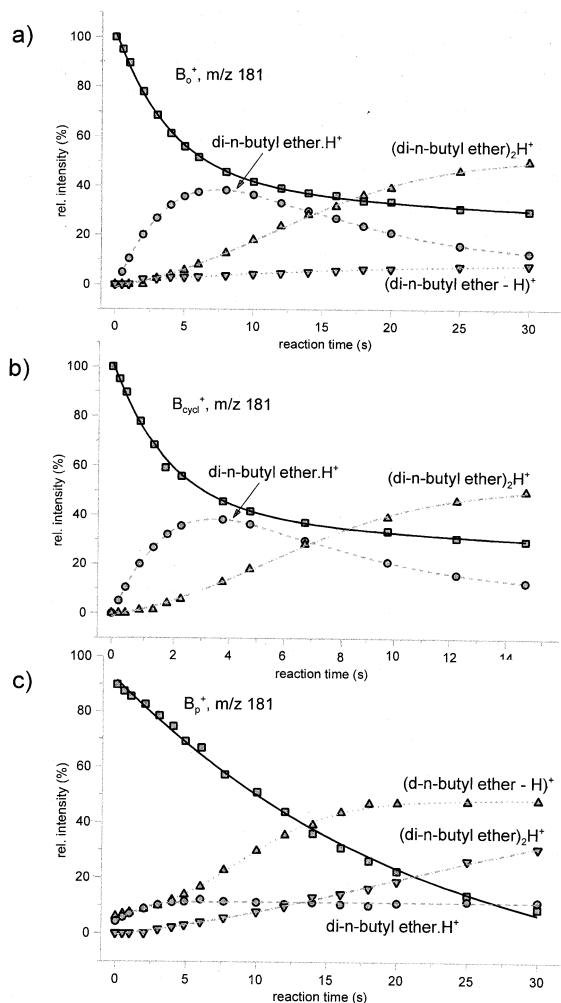
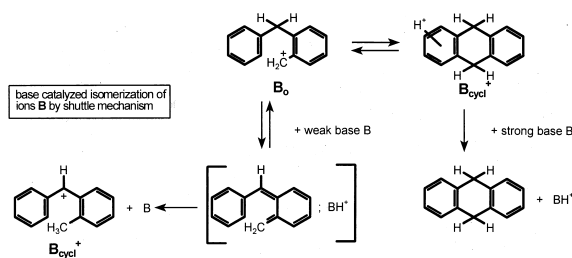


Fig. 3. “Gas phase titration” of isomeric ions B^+ with di-*n*-butyl ether: (a) reaction of *ortho*-benzylbenzyl cation B_o^+ ; (b) reaction of protonated 9,19-dihydroanthracene B_{cycl}^+ ; reaction of *para*-benzylbenzyl cation B_p^+ .

B^+ is greater than 785 kJ mol⁻¹. Efficient proton transfer from the ions B^+ from **3** and **5** is observed first for acetone (PA 812.8 kJ mol⁻¹ [26]). However, the proton transfer from the ions B^+ to most bases clearly exhibits bimodal kinetics owing to the presence of an almost unreactive isomer. As an example, Fig. 3 displays the kinetic plots of a deprotonation of the isomeric B^+ by di-*n*-butyl ether (PA 846.1 kJ mol⁻¹ [26]). It is not very likely that the unreactive or only slowly deprotonated fraction of the ions B^+ in the kinetic plots corresponds to the *ortho*-benzylbenzyl iso-



Scheme 6.

mer B_o^+ . Ions B^+ , which are prepared from *para*-benzylbenzyl alcohol **4** by CI(methane) and which correspond unambiguously to ions B_p^+ , react with di-*n*-butyl ether and related bases mainly by hydride abstraction [Fig. 3(c)], as expected for benzylic carbenium ions. Moreover, the relative amount of the less reactive isomer of ions B^+ derived from **3** and **5** depends primarily on the PA of the base used for the deprotonation, and not on the structure of the precursor. The fraction of less reactive ions B^+ is particularly large if a weak base is used, and small if the titration base is strong. This behavior points to a shuttle mechanism [28], by which the base catalyzes the tautomerization by proton shifts in an ion containing two acidic positions [29]. In the present case a base catalyzed transport of a proton from the internal CH_2 group between the two phenyl rings of ion B_o^+ to the external benzylic CH_2 group converts the reactive benzylic ion B_o^+ into the unreactive benzhydryl isomer B_{dip}^+ . A formation of this unreactive ion B_{dip}^+ from protonated 9,10-dihydroanthracene B_{cycl}^+ requires initial opening to generate ion B_o^+ . Thus, formation of B_{dip}^+ also from B_o^+ clearly proves the rapid interconversion of these isomers (Scheme 6).

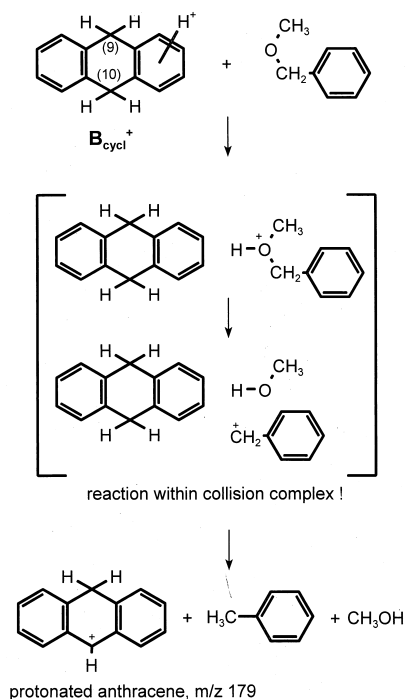
Finally, the reactions of the ions B^+ produced by CI(methane) from **3–5** with benzyl methyl ether **1** were studied to determine which isomer is responsible for the condensation reactions and which one gives the protonated anthracene m/z 179. The corresponding kinetic plots show that the ions B_o^+ and B_{cycl}^+ behave identically, as expected from the deprotonation experiments, and generate almost only protonated anthracene m/z 179 besides a few condensation product ions m/z 271 and m/z 361. However, a noticeable fraction of both ions does not react with ether **1**. Obviously, ether **1** reacts with ions B^+ also as

a proton-shuttle base, converting the ions B^+ into unreactive ions B_{dip}^+ . The rate constant measured for the deprotonation of the reactive ions B_o^+ and B_{cycl}^+ (see Table 2) corresponds to the collision rate within the limits of error (reaction efficiency $100 \pm 10\%$). In contrast, the rate constant for the reaction of *para*-benzylbenzyl cations B_p^+ with **1** is significantly smaller (efficiency $65 \pm 5\%$), and the main reaction pathways are condensation producing ions m/z 271 and m/z 361 and hydride abstraction generating ions m/z 121, as expected for benzylic ions B^+ .

3.3. Formation of protonated anthracene m/z 179: A multistep reaction within a single collision complex

It has been suggested [14] that the protonated anthracene, m/z 179, which is generated from benzyl acetate under CI-conditions, arises by elimination of H_2 from an excited protonated 9,10-dihydroanthracene B_{cycl}^+ , m/z 181 (Scheme 7). However, ions trapped within a FT-ICR cell have lost their excess energy within less than a few seconds and cannot decompose spontaneously. Indeed, the course of the reaction of B_{cycl}^+ with benzyl methyl ether **1** shows clearly that protonated anthracene m/z 179 does not arise from B_{cycl}^+ by spontaneous elimination of H_2 , but by a very fast bimolecular reaction of B_{cycl}^+ with ether **1**. At first sight it appears possible that the elimination of H_2 from B_{cycl}^+ is initiated by an electrostatic activation of these ions caused by ion/dipole interaction with a molecule of ether **1** within the collision complex. However, CID of ions B_{cycl}^+ by collision with argon produces abundant ions m/z 166 and m/z 165, which are not observed by reaction with **1**, and only a minor amount of ions m/z 179. Further, only deprotonation and not elimination of H_2 is observed by the reaction of other bases with B_{cycl}^+ . Thus, it is certain that protonated anthracene, m/z 179, arises from B_{cycl}^+ by a specific ion/molecule reaction with ether **1** and not simply by electrostatic activation with the collision complex.

A clue to the mechanism of this process is given by the reaction of deuterated derivatives. The reaction of ions B_{cycl}^+ with the fully deuterated ether **1- d_7** results cleanly in the generation of ions m/z 179, excluding



Scheme 7.

any H/D exchange between the reactants. The reaction of protonated 9,10-tetradeutero-9,10-dihydroanthracene, m/z 185, which is prepared conveniently by the reactions of benzyl cations $A-d_2$ with ether **1**- d_2 in the external CI-ion source, specifically produces an ion m/z 182 by reaction with **1** corresponding to a *formal* elimination of HD. Thus, the formation of protonated anthracene from ion B_{cycl}^+ and **1** is a specific process, by which one H atom from the 9(10) position and a second one from the aromatic rings of ion B_{cycl}^+ (or the proton) is removed. A mechanism that meets these specific requirements is depicted in Scheme 7.

From the gas-phase titration experiments discussed in the previous section, the PA(9,10-dihydroanthracene) = $804 \pm 8 \text{ kJ mol}^{-1}$ was derived. This value is larger than PA (*ortho*-xylene) = 796 kJ mol^{-1} [26], and is practically identical to PA(diphenylmethane) = $802.3 \text{ kJ mol}^{-1}$, as would be expected. The greater PA (benzyl methyl ether **1**) = $817.1 \text{ kJ mol}^{-1}$ [26] signifies an exothermic and fast proton transfer as the dominant reaction between ions B_{cycl}^+ and ether **1**. The O-protonated benzyl ether **1** is not a stable species, as

can be seen from the lack of a significant signal of the quasimolecular ions in the CI mass spectrum of **1**, which only exhibits abundant benzyl ions A^+ . If the elimination of methanol occurs quickly within the collision complex of ion B_{cycl}^+ and **1** before the neutral molecule of 9,10-dihydroanthracene (which had been created within the complex by the initial proton transfer) has a chance to depart—the newly generated benzyl cation A^+ abstracts a hydride from the 9(10) position of this molecule and produces the protonated anthracene, m/z 179, a molecule toluene, and a molecule methanol as the final reaction products. Exactly the proton and one of the H atoms at the 9(10) positions of B_{cycl}^+ are eliminated, as required by the results of the labeling experiments. An estimation of the enthalpy of reaction for this total process from the available heats of formation of the relevant species [26] shows indeed, that the total reaction and each reaction step is exothermic. Thus, the formation of protonated anthracene, m/z 179, from protonated 9,10-dihydroanthracene B_{cycl}^+ by the unanticipated reaction with benzyl methyl ether **1** is one of the few examples of a definitively multistep reaction within a single collision complex [30]. It should be emphasized that the detection of such processes adds important details to the ongoing discussion of concerted versus stepwise reactions in physical organic chemistry. The reaction, depicted in Scheme 7, is undeniably a stepwise reaction that proceeds by clearly defined reaction steps (proton transfer, C–O bond dissociation, hydride abstraction). Nonetheless, macroscopically it is a concerted process because everything occurs within a single encounter complex.

3.4. Electrophilic attack of the benzyl cation A^+ on the O atom of benzyl ether **1**: the decomposition of the dibenzyl methyl oxonium ion

As shown in the previous section (see Scheme 2) the attack of the benzyl cation A^+ on the ether molecule **1** results in hydride abstraction to produce α -methoxybenzyl cations, m/z 121, by attack on the benzylic CH_2 group and in a degenerate substitution by attack on the ether O-atom, besides electrophilic aromatic substitution at the phenyl ring of **1**. Unex-

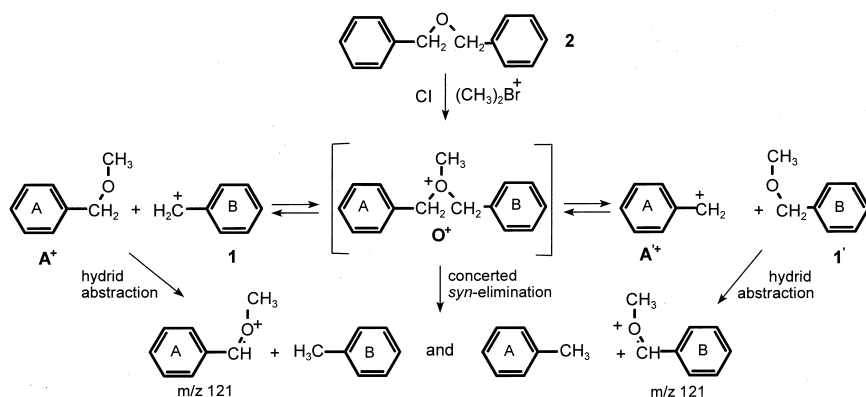
Table 3
Label distribution for the hydride abstraction product ion for reactions of labeled reactants in the reaction of benzyl cations A^+ and benzyl methyl ether **1**

| Benzyl cation | Ether | Direct product ion | Rearranged product ion |
|---------------|------------------------|--------------------|------------------------|
| A^+ | 1-d₂ | m/z 122 83% | m/z 121 17% |
| A^+-d_2 | 1 | m/z 121 17% | m/z 122 83% |
| A^+ | 1-d₇ | m/z 126 83% | m/z 121 17% |
| A^+-d_7 | 1 | m/z 121 87% | m/z 126 13% |

pectedly, however, the reaction of undeuterated A^+ with fully deuterated **1-d₇** generates not only ions m/z 127—the fully deuterated analogue of ion m/z 121 by abstraction of a D atom—but also (undeuterated) ions m/z 121 in a ratio of about 5:1. Conversely, the reaction of fully deuterated ions A^+-d_7 with undeuterated ether **1** produced ions m/z 121 and m/z 127 in a ratio of about 5:1 (Table 3). Obviously, the direct hydride abstraction from benzyl methyl ether **1** by the attacking benzyl cation A^+ is not the only pathway to the α -methoxybenzyl cations, m/z 121, but an appreciable amount of these ions must arise *after* a methoxy group transfer from **1** to ions A^+ [Scheme 8; phenyl groups of different origin are labeled by (A) and (B)] via the intermediate dibenzyl methyl oxonium ion O^+ .

Experiments to prepare the dibenzyl methyl oxonium ion O^+ either within the external CI-ion source or within the cell of the FT-ICR spectrometer failed.

Apparently this oxonium ion is unstable in the gas phase under the conditions used. Therefore, the reaction of dimethyl bromonium ions $(CH_3)_2Br^+$, which were generated in the external CI-ion source from methyl bromide, with dibenzyl ether **2** and its isotopomers in the FT-ICR cell were studied as an independent means of an investigation of the reaction of (intermediate) ions O^+ . The corresponding kinetic plot is shown in Fig. 4. Surprisingly, the expected decomposition of O^+ into the benzyl cation A^+ (which subsequently undergoes condensation reactions with ether **2**) is not the main process but the formation of the α -methoxybenzyl cation, m/z 121. Furthermore, the total reaction efficiency and the course of the reaction depend strongly on the experimental conditions. In particular, if the experiment is performed in the Infinity FT-ICR cell, in which cooling of the ions is very efficient, the ion m/z 121 is the only reaction product and is formed by a reaction efficiency of $>80\%$. In the normal FT-ICR cell the ion m/z 121 is still the main product ion, but the parallel formation of the benzyl cations A^+ and its condensation product ions increase distinctly and the efficiency of the total reaction has decreased to about 15%. This unforeseen instrumental effect of the model of a FT-ICR on the reaction cell is remarkably reproducible, and this observation indicates that the fragmentation of the dibenzyl methyl oxonium ion O^+ is extremely sensitive to any excess energy of the reactants.



Scheme 8.

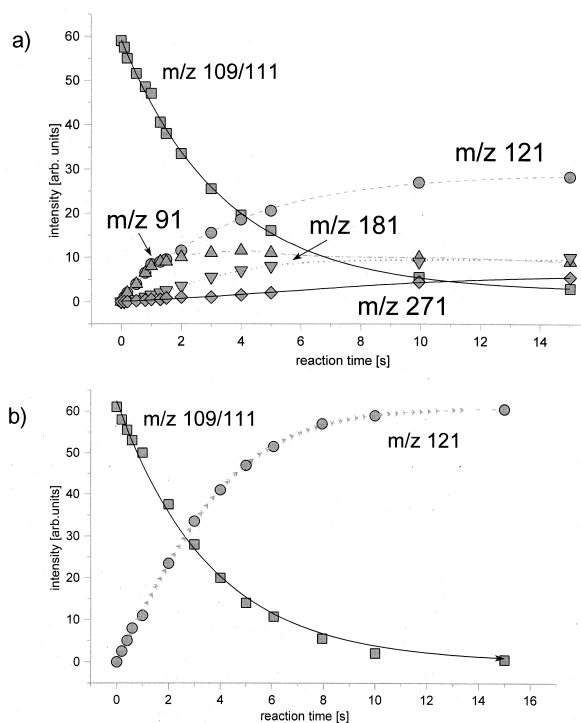


Fig. 4. Kinetic plot for the reaction of the dimethylbromonium ion $(\text{CH}_3)_2\text{Br}^+$ with dibenzyl ether **2**: (a) reaction within the normal FT-ICR cell; (b) reaction within the Infinity FT-ICR cell.

There are two possible explanations for this effect. First, the reaction proceeds by exothermic methyl cation transfer from the bromonium ion $(\text{CH}_3)_2\text{Br}^+$ onto the dibenzyl ether **2** and spontaneous dissociation of the intermediate oxonium ion O^+ into an ion/neutral complex of the benzyl cation A^+ and a molecule of the methyl benzyl ether **1**. This complex can either dissociate into a free cation A^+ , which subsequently undergoes further reaction with ether **2**, or fragment *after* hydride abstraction from the ether **1** by the benzyl cation A^+ , producing the ions m/z 121. The branching ratio of these competing reactions should depend critically on the excess energy of the ion/neutral complex, with a larger amount of excess energy favoring the direct dissociation. Because an asymmetrically deuterated analogue of O^+ is formed by the addition of a deuterated benzyl cation to an undeuterated ether **1** (and vice versa), the dissociation gives rise to two different ion/neutral complexes, the

first one consisting of deuterated A^+ and undeuterated ether **1**, and the second one consisting of undeuterated A^+ and deuterated ether **1**. This explains the results from the labeling experiment shown in Table 3 and shows that about 40% of the total hydride abstraction occurs by the ion/neutral complex mechanism. A further corollary of this mechanism is that the hydride abstraction needs less activation energy than the electrophilic aromatic substitution because, otherwise, the condensation product ion m/z 181 would be the main reaction product. However, the sigmoid intensity curve of the ion m/z 181 in the kinetic plot of Fig. 4 indicates a secondary reaction, not a reaction parallel to hydride abstraction. The second possibility corresponds to a concerted 1,2-*syn* elimination of toluene from the intermediate oxonium ion O^+ . This elimination requires a *syn* alignment of the benzylic C–O bond and a C–H bond to provide the orbital overlap for the concerted process. This again depends heavily on the excess energy of the dibenzyl methyl oxonium ion O^+ , both because of the competing dissociation and because of the excitation of internal rotations that destroys the orbital alignment. Thus, this mechanism can be expected to operate predominantly in “cool” ions O^+ .

The reaction of the bromonium ion $(\text{CH}_3)_2\text{Br}^+$ with the asymmetrically deuterated dibenzyl ether **2-*d*₂** generates the expected two hydride abstraction products m/z 123 and m/z 121 in a ratio of 1:2.7. This isotope effect $k_h/k_d = 2.7 \pm 0.1$ is in agreement with both mechanisms, and because of the poor quantitative reproducibility of the rate constants for this process, a study of the other deuterated analogues did not give any further information. However, it would be of fundamental interest to analyze the obviously delicate requirements of a concerted 1,2-*syn* elimination in gaseous ions by more suitable examples. In every case, the participation of an intermediate oxonium ion O^+ in the reactions of benzyl cations A^+ with benzyl methyl ether **1** is clearly indicated not only for the degenerate electrophilic substitution at the O atom of **1** but also as an intermediate for a substantial fraction of α -methoxybenzyl cations, m/z 121.

4. Conclusion

At the beginning of this study we expected that the reactions of benzyl cation A^+ with benzyl methyl ether **1** would be, essentially, a plain example of electrophilic aromatic substitution by a carbenium ion in the gas phase, a major research topic of Cacace and his group [1]. Indeed, the Friedel-Crafts alkylation is a prominent pathway in this system of organic ion/molecule reactions, but there are many details which show the rich gas phase chemistry occurring in this system. One obvious question about the mechanism of these reactions is the termination of the oligocondensation after three steps. In principle, the alkylation of **1** by a benzyl cation A^+ and subsequent elimination of methanol should produce a new benzylic cation predisposed to the next condensation step. The reactions of the ion D^+ , m/z 361, which is formed by three condensations steps and which are depicted in Fig. 2, show clearly that this ion does not exhibit benzylic reactivity anymore but is either unreactive or reacts by proton transfer. The reason for this is obviously isomerization either by an intramolecular hydride shift from one of the internal CH_2 groups to the external benzylic CH_2 group, which creates an unreactive benzhydrylic ion, or intramolecular aromatic substitution that results in a protonated polycyclic aromatic hydrocarbon. Both isomerization reactions are clearly detected for the smaller condensation product ion B^+ , m/z 181, and the probability of these reactions is expected to increase substantially for the more flexible oligomer D^+ . Thus, *intermolecular* polycondensation ceases chiefly because of the more and more successful competition by *intramolecular* electrophilic substitution.

A second question is concerned with the competition of electrophilic attack of the benzyl cation A^+ at a C atom of the phenyl ring and at the O atom of the ether group. Intuitively one expects that attack of A^+ at the nucleophilic electron lone pair of the ether-O atom is preferred, but this attachment gives rise to an excited oxonium ion O^+ that should return to and interchange the benzyl groups of reactants. Indeed, this exchange is observed if either the benzyl cation

A^+ or the benzyl group of the ether **1** is labeled. The experiments with deuterated reactants revealed further, however, that the direct dissociation of an intermediate dibenzyl methyl oxonium O^+ into a benzyl cation A^+ and ether **1** is not the only decomposition pathway of this oxonium ion. A second pathway eventually results in α -methoxybenzyl ion, m/z 121, which corresponds to the product of hydride abstraction from ether **1**. A generation of the oxonium ion O^+ by independent methods confirms this observation and shows, rather unexpectedly, that this pathway is in fact the main reaction route under certain conditions. The most likely explanation for this observation is decomposition of O^+ into an ion/neutral complex consisting of ion A^+ and ether **1** and a hydride abstraction within this complex. This leads to another facet of the ion/molecule reaction in the present system besides competition between different electrophilic substitution—the participation of multistep processes occurring in a single encounter complex of reactants. The most enchanting example is the formation of protonated anthracene, m/z 179, by reaction of benzyl methyl ether **1** with the protonated 9,10-dihydroanthracene, m/z 181, as shown in Scheme 7. Here, proton transfer, elimination of methanol, and hydride abstraction have to occur in a single complex to explain the experimental results. Such multistep reactions in a single collision complex have not yet attracted special attention, but they may be of general importance for ion/molecule reactions involving large and highly polarizable reactants that give the collision complex a rather long lifetime. In this connection it should be remembered that multiple reactive encounters of reactants within a solvent cage are well documented for ionic reactions in solution. Thus, at the end of our study it turns out that the actual mechanism of apparently well established ion/molecule reactions in the gas phase may be also quite complicated. This is chemistry as it is, and very likely many of the effects observed for these organic ion/molecule in the gas phase carry over to solution chemistry and hopefully are useful for a better understanding of reactivity in this area.

Acknowledgements

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