JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2003; **16:** 746–752

Hydride abstraction from 1,3,5-cycloheptatriene by gaseous carbenium ions, as studied by Fourier transform ion cyclotron resonance kinetics and deuterium labeling[†]

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Received 31 January 2003; revised 10 March 2003; accepted 11 March 2003

ABSTRACT: The gas-phase interaction of protonated acetone and *tert*-butyl cations with 1,3,5-cycloheptatriene was studied by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. In addition to proton transfer giving $C_7H_9^+$ ions, hydride abstraction from cycloheptatriene giving $C_7H_7^+$ ions was observed. Deuterium labeling experiments combined with the determination of the reaction kinetics excluded the formation of $C_7H_7^+$ ions by consecutive proton transfer and H_2 expulsion under these conditions. The kinetic isotope effect measured for the hydride transfer channel was found to be in the range 1.65 ± 0.1, very close to that known to operate during hydride transfer from simple alkylbenzenes to t-$C_4H_9{}^+$ ions. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: carbenium ions; 1,3,5-cycloheptatriene; Fourier transform ion cyclotron resonance mass spectrometry; gas-phase ion chemistry; hydride transfer; ion–molecule reactions; kinetics; proton transfer

INTRODUCTION

In contrast to the great interest through past decades in the gas-phase chemistry of protonated toluene, $C_6H_6CH_3^+$, and arenium ions in general, which represent key intermediates in electrophilic substitutions of arenes,[1–4] our understanding of the ring-enlarged isomers, viz. protonated cycloheptatrienes, has remained very limited.[5] However, there is a close parallel between the ring extension/ring contraction behaviour of $C_7H_7^+$, $C_7H_8^{\cdot+}$ and $C_7H_9^+$ ions and the intramolecular isomerization processes within each of these three prototypical series of carbocations has been investigated in great detail.[6–8] Within the latter, however, the gas-phase properties of the parent ring-enlarged hydrocarbon, 1,3,5-cycloheptatriene (**1**), have been elucidated only recently[9] (J. Y. Salpin, M. Mormann, J. Tortajada, M. T. Nguyen and D. Kuck submitted), along with studies on related cycloolefinic hydrocarbons.[10–12] In the course of our experimental studies on the proton affinity (*PA*) and gas-phase basicity (*GB*) of **1** in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer,[9] we observed that adduct formation and formal hydride transfer reactions compete with proton transfer. Since the expulsion of dihydrogen from protonated toluene and protonated cycloheptatriene, $[\mathbf{1}+H]^+$, giving tropylium ions, has been a process of considerable interest since 1974,[13–15] we investigated the formation of ions $C_7H_9^+$ (*m*/*z* 93) and $C_7H_7^+$ (*m*/*z* 91) during the reaction of **1** with 2-hydroxyprop-2-yl cations, $[\mathbf{2}+H]^+$, and *tert*-butyl cations, $[\mathbf{3}+H]^+$, in greater detail (Scheme 1).

RESULTS

The interaction of protonated acetone $[\mathbf{2}+H]^+$ with cycloheptatriene (**1**) generates predominantly ions $C_7H_9^+$, which have been assumed to be dihydrotropylium ions $[\mathbf{1}+H]^+$,[13–15] but, according to recent calculations, should rather be regarded as a valence tautomer, protonated norcaradiene $[\mathbf{1}'+H]^+$ (J. Y. Salpin, M. Mormann, J. Tortajada, M. T. Nguyen and D. Kuck submitted). However, the formation of $C_7H_7^+$ ions is also observed (Fig. 1). Similar reactivity is found for the interaction of *tert*-butyl cations $[\mathbf{3}+H]^+$ with **1**, along with the formation of the adduct ions, $C_{11}H_{17}^+$ (*m*/*z* 149) (Fig. 2). In the case of ions $[\mathbf{3}+H]^+$, the ratio of the product ion abundances, [*m*/*z* 93] : [*m*/*z* 91], is found to be constant, suggesting competitive reactions with respect to proton and hydride transfer. In the case of ions $[\mathbf{2}+H]^+$, however, the product ions $C_7H_7^+$ may also

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[†] Dedicated to Professor Tadeusz Marek Krygowski on the occasion of his 65th birthday.

Contract/grant sponsor: Fonds der Chemischen Industrie.
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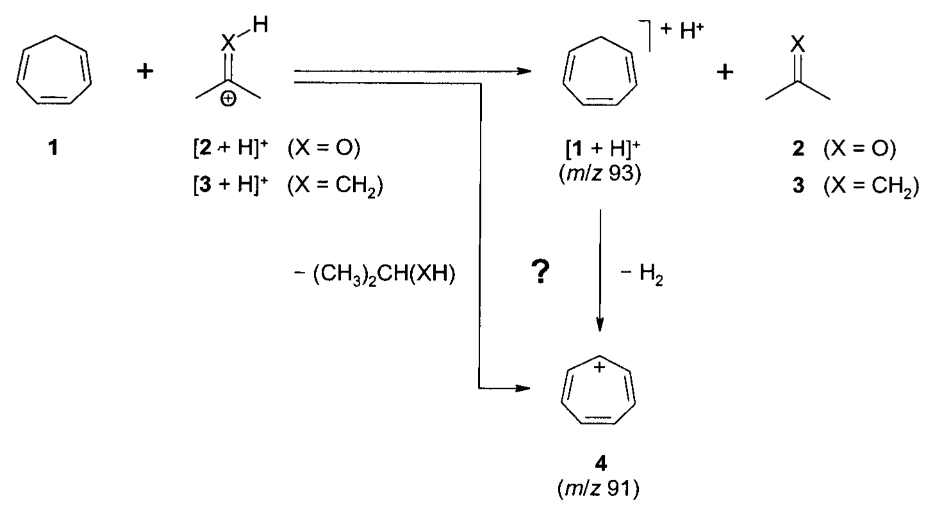


Scheme 1

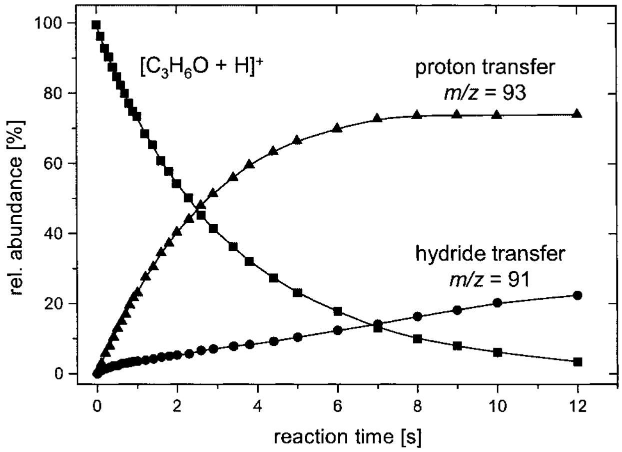


Figure 1. Time dependence of the ion–molecule reactions of protonated acetone ($[\mathbf{2}+H]^+$) and cycloheptatriene (**1**) at ca 10^{-8} mbar

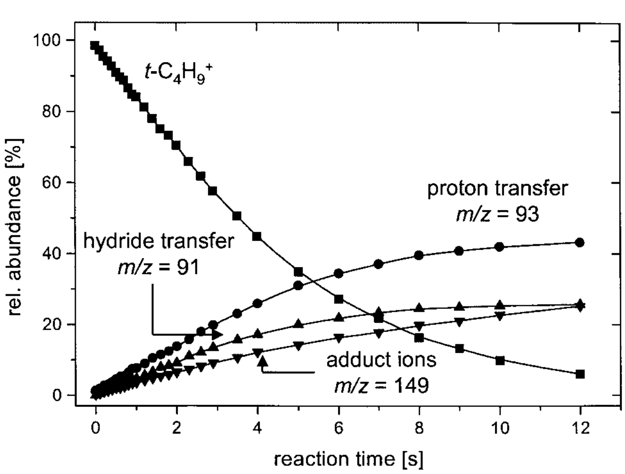
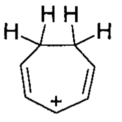
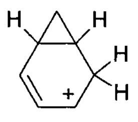


Figure 2. Time dependence of the ion–molecule reactions of *tert*-butyl cations ($[\mathbf{3}+H]^+$) and cycloheptatriene (**1**) at ca 10^{-8} mbar

be formed by a consecutive process, because their relative abundances do not reach a constant value at long reaction times.[16]



[1 + H]+



[1' + H]+

The proton transfer of ions $[\mathbf{2}+H]^+$ to **1** takes place under apparent encounter control. The reaction efficiencies (*eff*) determined as the ratio of the measured rate constant, $k(H^+)$, and the theoretical collision rate, k_{coll},[17] are given in Table 1. The rate constant determined for this process under FT-ICR conditions is $k(H^+) = 1.1 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$. By contrast, the interaction of ions $[\mathbf{3}+H]^+$ and **1** is much less efficient. In fact, the rate constant determined for the proton transfer channel, $k(H^+) = 1.8 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$, is in good accordance with the value reported by Sen Sharma and Kebarle ($1.1 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$ on the basis of high-pressure CI experiments at 423 K).[18] Obviously, proton transfer is hampered by a significant barrier in this case.

We examined the course of the hydride transfer as the origin of the $C_7H_7^+$ ions generated during the encounter of cycloheptatriene **1** and ions $[\mathbf{2}+H]^+$ and $[\mathbf{3}+H]^+$ in the FT-ICR mass spectrometer. In a first set of experiments, we reacted acetone-d_6, $[\mathbf{2a}+D]^+$, with **1**. Deuteration of **1** and consecutive hydrogen expulsion should give rise to predominant loss of the H_2 isotopomer and formation of ions $C_7H_6D^+$ (*m/z* 92). This is reasonable because the activation energy for the proton ring walk in protonated cycloheptatriene should be far below the dissociation limit, thus allowing for a complete, or almost complete, H/D equilibration in ions $[\mathbf{1}+D]^+$.[19] Recent calculations[9] yielded activation barriers lying significantly above the values determined for the proton ring walk in simple benzenium ions ($E_a = 32$–$36\,kJ\,mol^{-1}$)[20,21] but far below

Table 1. Rate constants and efficiencies of the ion–molecule reactions of protonated acetone and *tert*-butyl cations with cycloheptatriene (**1**)

Reactants	k_{coll}[a,b]	$k(H^+)$ [$eff(H^+)$]	$k(H^-)$ [$eff(H^-)$]	$k(D^-)$ [$eff(D^-)$]	$k(H^-)/k(D^-)$[c]
$\mathbf{1} + [\mathbf{2} + H]^+$	14.10	10.7 [0.76]	3.7 [0.26]	—	—
$\mathbf{1} + [\mathbf{2a} + D]^+$	13.64	9.4[d] [0.69][d]	4.2 [0.31]	—	—
$\mathbf{1a} + [\mathbf{2} + H]^+$	14.07	10.1 [0.72]	1.7 [0.12]	1.0 [0.07]	1.7
$\mathbf{1} + [\mathbf{3} + H]^+$	14.25	1.85 [0.13]	1.1 [0.08]	—	—
$\mathbf{1a} + [\mathbf{3} + H]^+$	14.22	1.28 [0.09]	0.68 [0.048]	0.42 [0.03]	1.6

[a] Calculated according to Ref. 17.

[b] In 10^{-10} cm^3 molecule^{-1} s^{-1}.

[c] Calculated from the branching ratio of H^- and D^- transfer (Ref. 29).

[d] D^+ transfer.

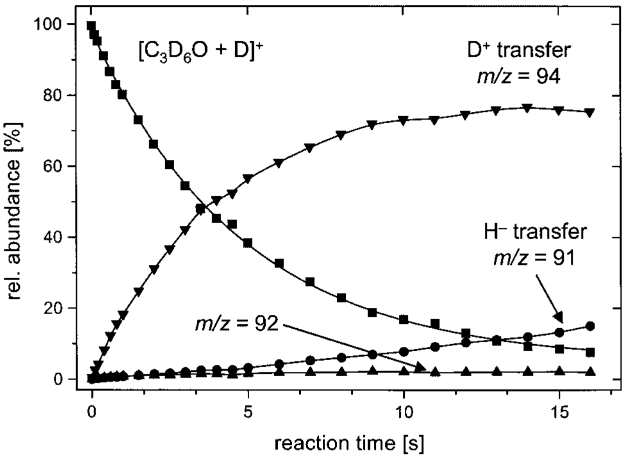
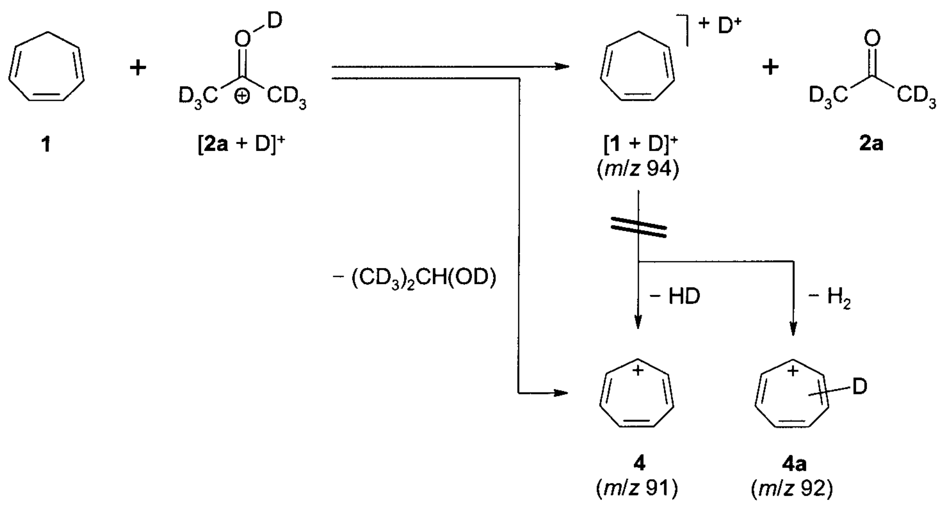


Figure 3. Time dependence of the ion–molecule reactions of acetone-d_6 ($[\mathbf{2a} + D]^+$) and cycloheptatriene (**1**)

that found recently for protonated cyclobutadiene ($E_a = 182$ kJ mol^{-1}).[21] Even if the proton ring walk in ions $[\mathbf{1} + H]^+$ did compete at all with the 1,2-elimination of H_2,[13–15] the ratio of H_2 versus HD loss, and [*m/z* 91] : [*m/z* 92], should be <1, accounting for kinetic isotope effects. In any mechanistic case concerning the consecutive process, ions $C_7H_6D^+$ (*m/z* 92) should be observed in considerable relative abundance. The kinetic course of the interaction between ions $[\mathbf{2a} + D]^+$ and **1** is illustrated in Fig. 3.

In addition to the dominant peak for ions $C_7H_8D^+$ (*m/z* 94) due to D^+ transfer, a minor peak for ions $C_7H_7^+$ (*m/z* 91) is observed at longer reaction times. However, the signal at *m/z* 92 accounts exclusively for the naturally occurring isotopomer of the latter ions, $^{13}C^{12}C_6H_7^+$. This finding corroborates the occurrence of the hydride transfer reaction and excludes the H_2 and HD elimination path from deuterated cycloheptatriene, $[\mathbf{1} + D]^+$ (Scheme 2). Thus, protonated cycloheptatriene $[\mathbf{1} + H]^+$ cannot represent an intermediate in the course of the hydride abstraction from **1** by protonated acetone, $[\mathbf{2} + H]^+$.

To obtain information about the kinetic isotope effects associated with the hydride transfer reactions, [7-D]cycloheptatriene (**1a**) was subjected to the ion–molecule reaction with both ions $[\mathbf{2} + H]^+$ and $[\mathbf{3} + H]^+$. Notably, *tert*-butyl cations were found to exert kinetic isotope effects in a very narrow range, $k(H^-)/k(D^-) = 1.6 \pm 0.1$, in ion–neutral complexes with simple alkylbenzenes and various α,ω-diphenylalkanes.[22–28] The kinetics of the interaction of **1a** and protonated acetone $[\mathbf{2} + H]^+$ and *tert*-butyl cations $[\mathbf{3} + H]^+$ are reproduced in Figs 4 and 5, respectively.



Scheme 2

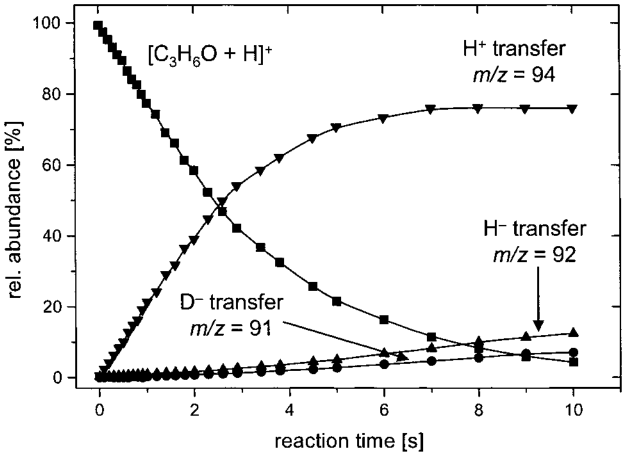


Figure 4. Time dependence of the ion–molecule reactions of protonated acetone ($\mathbf{2}+H]^+$) and [7-D]cycloheptatriene (**1a**)

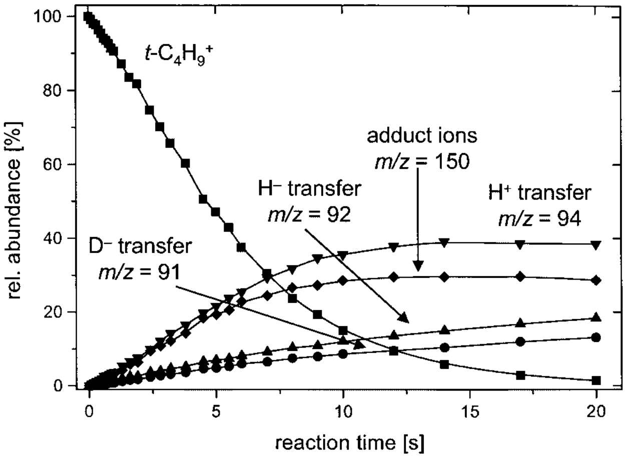


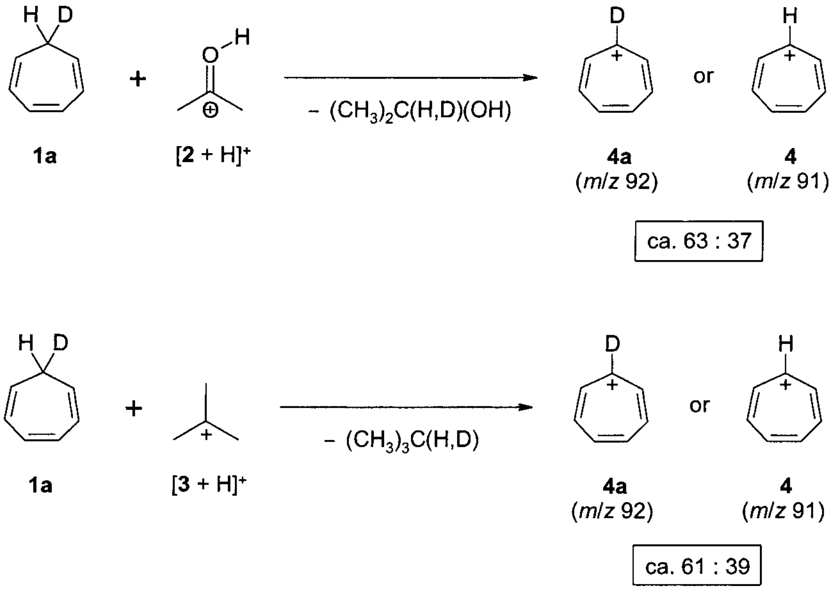
Figure 5. Time dependence of the ion–molecule reactions of *tert*-butyl cations ([**3** + H]$^+$) and [7-D]cycloheptatriene (**1a**)

In both cases, hydride and deuteride transfer reactions occur to different extents and with a significant predominance of the former (Scheme 3). The branching ratios allow us to determine the kinetic isotope effects,[29] which again were found to be in the range $k(H^-)/k(D^-) = 1.6–1.7$. This result is in good agreement with those obtained previously for alkylbenzenes and α,ω-diphenylalkanes[22–28] and can be considered a further confirmation of the mechanism of the formation of the $C_7H_7^+$ ions by competitive hydride transfer from **1**. The kinetic results of the proton and hydride transfer reactions between cycloheptatriene and ions [**2** + H]$^+$ and [**3** + H]$^+$ are given in Table 1.

DISCUSSION

A priori, the formation of $C_7H_7^+$ ions may be traced to mainly two reaction channels, viz. (i) proton transfer from the reagent ions [**2** + H]$^+$ and [**3** + H]$^+$ to **1** and subsequent loss of H_2 from the excited $C_7H_9^+$ intermediates and (ii) hydride abstraction from **1** by the same reagent ions, now reacting as Lewis acids, through a channel that directly competes with the proton transfer (Scheme 1). In both cases, the $C_7H_7^+$ product ions can be assumed to be tropylium ions (**4**).

The elimination of dihydrogen from metastable ions [**1** + H]$^+$ has been studied repeatedly and represents the major unimolecular fragmentation channel of $C_7H_9^+$ ions.[13–15,30] This process is exothermic but involves a particularly high activation barrier, as reflected by the large amount of kinetic energy released ($T_{kin} = 106\,kJ\,mol^{-1}$). The relevant part of the energy profile is reproduced in Fig. 6.



Scheme 3

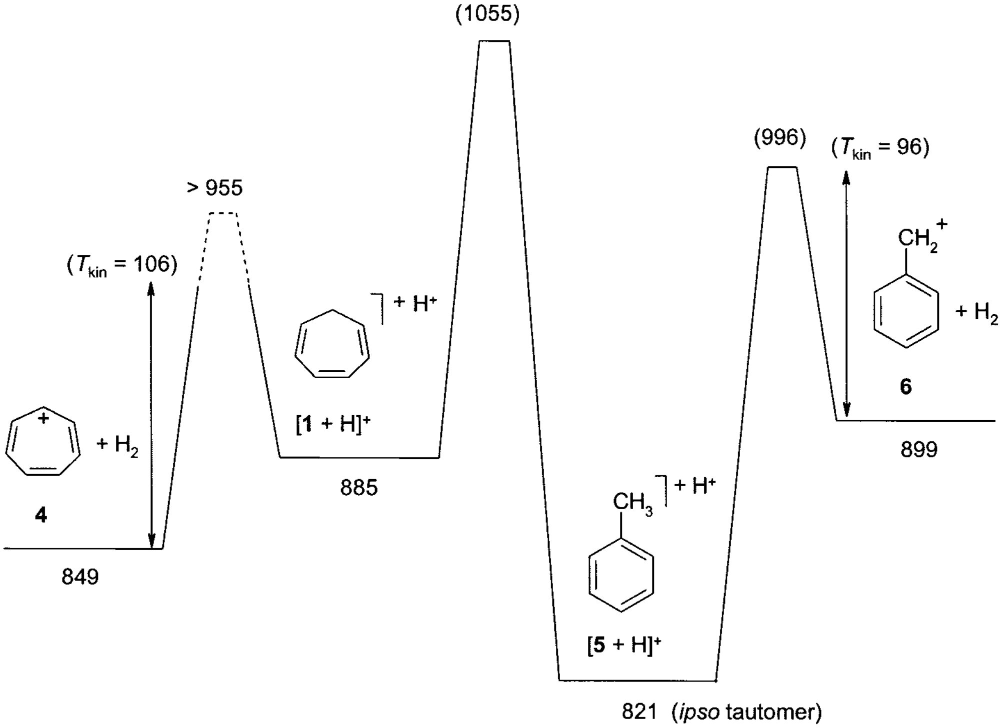


Figure 6. Energy profile (in kJ mol^{-1}) for the unimolecular isomerization and loss of H_2 from $C_7H_9^+$ isomers, protonated cycloheptatriene, $[\mathbf{1} + H]^+$, and protonated toluene, $[\mathbf{5} + H]^+$ (see text)

The activation barrier of the isomerization of ions $[\mathbf{1}+H]^+$ to toluenium ions $[\mathbf{5}+H]^+$ has recently been determined by *ab initio* calculations (J. Y. Salpin, M. Mormann, J. Tortajada, M. T. Nguyen and D. Kuck submitted) and the elimination of dihydrogen from the latter has also been studied in detail by experiment and computation (E. Motell, M. S. Robinson, R. Gareyev, V. M. Bierbaum and C. H. DePuy, personal communication, March 2000). The barrier to H_2 loss from the *ipso* tautomer of ions $[\mathbf{5}+H]^+$ was calculated to be 175 kJ mol^{-1}, consistent with that determined experimentally for the H_2 loss from protonated toluene (96 kJ mol^{-1}).[15] As the barrier for the H_2 loss from ions $[\mathbf{5}+H]^+$ is lower than that of their ring expansion to ions $[\mathbf{1}+H]^+$, the experimentally observed kinetic energy release specifically reflects the fragmentation of ions $[\mathbf{5}+H]^+$, rather than that of a mixture of isomeric $C_7H_9^+$ ions.

As another consequence, it follows from this large T_{kin} value that the barrier to the formation of tropylium ions **4** from ions $[\mathbf{1}+H]^+$ by direct elimination of H_2, i.e. without preceding ring contraction, has to be $\geq$70 kJ mol^{-1}. Hence the losses of H_2 from both $C_7H_9^+$ isomers, $[\mathbf{1}+H]^+$ and $[\mathbf{5}+H]^+$, giving ions **4** and benzyl cations **6**, respectively, are associated with high activation energies. In the course of the present FT-ICR experiments, such high excitation energies were not available. For example, the exothermicity of the proton transfer reactions induced by thermalized proton donor cations, such as ions $[\mathbf{2}+H]^+$, in particular,[31] is only $\Delta H_r = -19$ kJ mol^{-1}. Collisional activation of ions $[\mathbf{1}+H]^+$ through a Lindemann-type mechanism[32,33] can be excluded because of the low gas pressure within the ICR cell. Similarly, blackbody irradiation[34] cannot be the origin of the unimolecular fragmentation of the $C_7H_9^+$ ions since the energy distribution under the given conditions (300 K), having its maximum at 1035 cm^{-1} (12.5 kJ mol^{-1}), is not sufficient.[35] These arguments allow us to exclude the consecutive fragmentation of primarily formed dihydrotropylium $[\mathbf{1}+H]^+$ ions as the origin of the generation of the $C_7H_7^+$ ions during the reaction of protonated acetone, $[\mathbf{2}+H]^+$, with cycloheptatriene.

The alternative path for the formation of tropylium ions **4** from cycloheptatriene **1** via hydride transfer to *tert*-butyl cations has been described by Sen Sharma and Kebarle.[18] In their work, ions $[\mathbf{3}+H]^+$ were found to generate exclusively tropylium ions **4**, in spite of the fact that the proton transfer process is considerably exothermic. Notably, hydride transfer reactions from benzylic methylene groups of various alkylbenzenes to *tert*-butyl cations is energetically more favourable than the contradirectional proton transfer,[21,22] and hydride transfers involving alkyl cations and alkanes are not accompanied by proton transfer at all.[36–42] In fact, the thermochemistry of the hydride transfer from **1** to carbocations is even more favourable than the proton transfer process leading to dihydrotropylium ions $[\mathbf{1}+H]^+$.[43–45] In spite of their considerable exothermicity, the hydride abstraction of ions $[\mathbf{2}+\mathrm{H}]^+$ and $[\mathbf{3}+\mathrm{H}]^+$ from **1** occurs to a lower extent than the contradirectional proton transfer. The low efficiency of hydride transfer processes has been studied in great detail[36–40,46] and the negative temperature dependence of the reaction rate cannot be traced to the double-well potential model,[47–51] which is known to account for, *inter alia*, proton transfer reactions. Recent theoretical studies have shown that the hydride transfer between alkanes and carbenium ions in the gas phase is not subject to an internal energy barrier but to an ion–molecule complex as a local minimum.[52] The low efficiency of the process was attributed to a locked-rotor model.[46]

CONCLUSION

In the gas phase, protonated 1,3,5-cycloheptatriene ($[\mathbf{1}+\mathrm{H}]$) is known to undergo ring contraction to toluenium ions under chemical ionization conditions. Proton transfer from protonated acetone and the *tert*-butyl cation to cycloheptatriene under nearly thermalized conditions, giving ions $C_7H_9^+$ (*m/z* 93), was found to be accompanied by the formation of $C_7H_7^+$ ions (*m/z* 91). In agreement with considerations of the energy requirements, loss of H_2 from ions $C_7H_9^+$ can be excluded on the basis of deuterium labeling experiments. The formation of $C_7H_7^+$ ions is completely due to hydride abstraction from the C-7 position of cycloheptatriene, in accordance with the previous finding that hydride abstraction from this cycloalkene produces pure tropylium ions.[18] The kinetics of the proton transfer to and hydride transfer from cycloheptatriene have been determined and the kinetic isotope effect associated with the hydride transfer process was found to be in the same range, $k(\mathrm{H}^-)/k(\mathrm{D}^-) = 1.6$–$1.7$, as those determined for the hydride transfer from alkylbenzenes to *tert*-butyl cation.[22–28]

EXPERIMENTAL

Materials. 1,3,5-Cycloheptatriene (**1**) (Aldrich, Deisenhofen, Germany) was distilled before use over a 20 cm Vigreux column. Purity was checked by GC–MS analyses (>99%). Acetone (Aldrich, stated purity >99.9%) and acetone-d_6 (Deutero, Kastellaun, Germany, stated purity >99.5%, D content >99%) were used as purchased. The reagent gases were also used as purchased, viz. methane (Linde, Wiesbaden, Germany, stated purity >99.5%), methane-d_4 (Deutero, >99%, D content 99%) and isobutane (Linde, stated purity ≥99.5%).

[7-D]-1,3,5-cycloheptatriene (**1a**) was prepared by reduction of 7-ethoxy-1,3,5-cycloheptatriene with lithium aluminium deuteride in diethyl ether.[53,54] The identity and purity were checked by ^{1}H and ^{13}C NMR spectrometry (Bruker DRX 500 at 500 and 126 MHz, respectively) and by electron ionization mass spectrometry (Fisons Autospec double-focusing sector-field instrument), using a heated septum inlet, acceleration voltage 8 kV, electron energy 70 eV, emission current 200 μA and source temperature 160 ± 10 °C. The deuterium contents of **1a** was found to be 98% (by ^{1}H NMR spectroscopy).

Mass spectrometric measurements. Ion–molecule reactions were performed by use of a Bruker Spectrospin CMS 47X FT-ICR mass spectrometer equipped with a 4.7 T superconducting magnet, an external ion souce[55] and an Infinity cell.[56] The protonated pseudo-molecular ions were generated in the external ion source by chemical ionization (CI) using either methane or isobutane as the reagent gas. Typical source conditions were filament current 3.5–4.0 A, electron energy 30 eV and ionizing pulse duration 100 ms. The ions generated in the external ion source were transferred into the ICR cell and isolated by standard ejection procedures to eliminate all ions except those of interest by a broadband r.f. pulse and a series of r.f. pulses ('single shots') with the cyclotron frequencies close to that of the selected ion, in order to suppress unintended ion excitation. Subsequently, the ions were kinetically cooled by application of several argon pulses[57] using a magnetic valve. After a delay time of 1.5 s, during which the cooling gas argon was essentially pumped off the cell, single shots were again applied to remove ions formed by collision-induced fragmentation during the cooling interval. The residual ions were allowed to react with the neutral 1,3,5-cycloheptatriene isotopomers **1** and **1a** present in the cell at a constant background pressure of $(1.0$–$5.0) \times 10^{-8}$ mbar during a variable reaction time interval (t) (cf. Figs 1–5). The pressure readings of the ionization gauge close to the turbopump of the FT-ICR cell were calibrated by rate measurements of the reaction $\mathrm{NH_3^{\cdot +}} + \mathrm{NH_3} \rightarrow \mathrm{NH_4^+} + \mathrm{NH_2^{\cdot}}$[58] The sensitivity of the ionization gauge towards 1,3,5-cycloheptriene was determined from its polarizability.[59–62]

The intensities of the signals for the reagent ions were determined after Gauss multiplication of the time domain signal followed by Fourier transformation in the frequency domain. The bimolecular rate constants for the observed proton transfer reactions were derived from the first-order exponential decay [Eqn (1)] of the plot of the experimental intensities versus the reaction time t, where k_{obs} is the observed pseudo-first-order rate constant and [N] the number density of the neutral molecules within the FT-ICR cell:

$$\frac{[[\mathrm{M}+\mathrm{H}]^+]_t}{[[\mathrm{M}+\mathrm{H}]^+]_{t=0}} = \exp(-k_{\mathrm{obs}}t) = \exp(-k_{\mathrm{exp}}[\mathrm{N}]t) \qquad (1)$$

The theoretical collision constants, k_{coll}, were calculated according to the trajectory model developed by Su and Chesnavich[17] using the dipole moment of 1,3,5-cycloheptatriene, $\mu(\mathbf{1}) = 0.25$ D,[63,64] and a calculated polarizibility of $\alpha(\mathbf{1}) = 12.29\ \text{Å}^3$.[59–61] The isotope effects of hydride transfer processes were derived from the branching ratio of the hydride and deuteride abstraction processes.[29,65]

Acknowledgements

We thank Professor Charles H. DePuy (Boulder, CO, USA) for communicating his unpublished results on the fragmentation of $C_7H_9^+$ and $C_8H_{11}^+$ ions to us. We are also grateful to Dr Jean-Yves Salpin (Évry, France) for valuable discussions. D.K. is indebted to the Fonds der Chemischen Industrie (Frankfurt / Main) for financial support and M.M. gratefully acknowledges financial support from the Graduiertenförderung des Landes Nordrhein-Westfalen.

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