The Deprotonation of Benzyl Alcohol Radical Cations: A Mechanistic Dichotomy in the Gas Phase as in Solution

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Abstract: The gas-phase acidity of ionized benzyl alcohol and of some of its derivatives with selected reference bases has been studied by Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry. The aim was to relate the gas-phase reactivity to the behavior in aqueous solution of the radical cations of benzyl alcohols bearing methoxy substituent(s) on the phenyl ring which are known to undergo deprotonation at both the CH_2 and OH groups. The dual reactivity behavior is confirmed in the gas phase, in which the prototypical ion, $C_6H_5CH_2OH^{\bullet+}$, is deprotonated at both the CH_2 and OH groups, whereas the ring hydrogens are not involved. An increasing extent of O-deprotonation is shown as the strength of the base increases. Appropriate methyl substitution, as in the radical cations of $C_6H_5C(Me)_2OH$ and $C_6H_5CH_2OMe$, allows only O- or C-acidity. The two processes are characterized by comparable thermodynamic features with a Gas-phase Basicity (GB) value of 852 kJ mol^{-1} for the cumyloxyl radical and 850 kJ mol^{-1} for the α-methoxybenzyl radical. The possible origin of the observed mechanistic dichotomy is discussed.

Keywords: cations • gas-phase reactions • mass spectrometry • proton transfer • radicals

Introduction

It is well known that alkylaromatic radical cations are strong α-carbon acids, and accordingly they react with bases to form products coming from α-carbon deprotonation.[1] However, a peculiar property was recently discovered when dealing with 4-methoxybenzyl alcohol radical cations. Whereas, in aqueous acid solutions, these species behaved, as expected, as carbon acids, in the presence of OH^- they exhibited kinetic oxygen acidity, that is, the key step in their decay involved deprotonation at the OH group.[2] This result is of considerable interest since simple calculations based on a thermochemical cycle show that from a thermodynamic point of view, α-carbon acidity of these radical cations is much stronger than oxygen acidity.

Evidence was also provided that the deprotonation at the OH group leads to a 4-methoxybenzyloxyl radical, possibly through the intermediate of a radical zwitterion, which undergoes an intramolecular electron transfer, and that the competition between carbon and oxygen acidity depended not only on the strength of the base but also upon the stability of the radical cation. Accordingly, it was observed that making the radical cation more stable (e.g., by the introduction of additional methoxy groups on the phenyl ring) depresses oxygen acidity much more than carbon acidity. Thus, the very stable 2,4,5-trimethoxybenzyl alcohol radical cation exhibited only carbon acidity in the reaction with OH^-.[3]

In view of the fundamental information associated with features of proton-transfer reactions occurring between naked species in the gas phase, it seemed of interest to investigate whether the mechanistic dichotomy displayed by the reactivity of benzyl alcohol radical cations in aqueous solutions is an intrinsic property of these species. Proton- and electron-transfer processes are known to be major reaction pathways for gaseous organic radical cations and can be exploited to identify the structures of isomeric ions.[4] We have carried out a Fourier Transform Ion Cyclotron Resonance (FT-ICR) study of the gas-phase deprotonation of the radical cations derived from benzyl alcohol (**1**), cumyl alcohol (**2**), benzyl methyl ether (**3**), and deuterium labeled compounds

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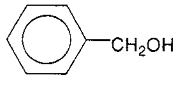

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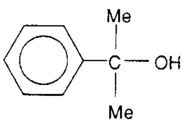

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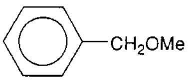

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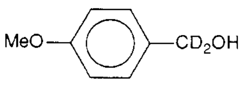

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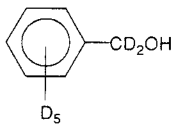

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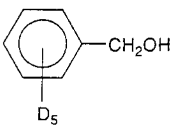

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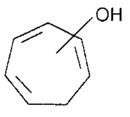

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such as 4-MeO-$C_6H_4CD_2OH$ (**4**), $C_6D_5CD_2OH$ (**5**), and $C_6D_5CH_2OH$ (**6**) by a variety of bases of different strength. For suitably labeled radical cations, carbon and oxygen acidities are easily distinguished by the transfer of either a deuteron or a proton to the reacting base. The radical cations of **2** and **3** are expected to exhibit only oxygen and carbon acidity, respectively. The results of this work are presented in this paper.

Results

The radical cations of **1**–**6** were obtained by electron-impact (EI) ionization at low electron energies in order to minimize any electronic and vibrational excess energy transferred to the ions during their formation process. Unreactive collisions with Ar pulsed in the ICR cell help to bring the ions into thermal equilibrium with the environment. Reference bases (B) were chosen to sample the kinetic acidity of the radical cations, namely carbonyl compounds, pyridines, and a diamine, all of which are characterized by well-established values of gas-phase basicity (GB).[5] The radical cations displayed exclusively proton (or deuteron) -transfer reactivity with bimolecular rate constants, which increased in magnitude with the strength of the base. In Table 1 the kinetic data are summarized, and the experimental rate constants (k_{exp}) and the relative efficiencies (Eff = $(k_{exp}/k_{coll}) \times 100$) obtained from the estimated values of the collisional rate constants are listed.[6] The radical cations of the deuterium labeled compounds **4** and **5** display both deuteron and proton transfer to an extent depending on the features of the base. The values listed in the last column of Table 1 that show the relative abundance of the BD^+ and BH^+ product ions are obtained from the ratio of the relative ion intensities extrapolated to initial reaction time; thus any subsequent hydrogen scrambling process can be neglected. An exemplary plot of ion intensity versus time profile that shows the competitive formation of BD^+ and BH^+ ions from the $\mathbf{5}^{\cdot+}$ reaction with pyridine is given in Figure 1. The use of specifically labeled substrates thus reveals the regiochemistry of the proton abstraction process. The exclusive H^+ transfer product from the reaction of $\mathbf{6}^{\cdot+}$ with 2,5-dimethylpyridine shows that the ring hydrogens are not involved, whereas a variable extent of D^+/H^+ transfer from $\mathbf{5}^{\cdot+}$ shows that both the α-C- and O-bound hydrogens may be attacked by the base depending on the features of the base itself. The higher basicity appears to favor the abstraction of the O-bound hydrogen.

Table 1. Kinetics of proton and/or deuteron transfer between the radical cations of benzyl alcohols and reference bases (B).

Radical cation	Reference base	GB(B)[a]	k_{exp}[b]	Eff[c]	BD^+/BH^+
$\mathbf{1}^{\cdot+}$	cyclohexanone	811	0.31	1.6	[d]
$\mathbf{1}^{\cdot+}$	c-C_3H_7-COMe	823	1.8	9.4	[d]
$\mathbf{1}^{\cdot+}$	2,4-pentanedione	836	5.2	28	[d]
$\mathbf{1}^{\cdot+}$	2-F-pyridine	853	4.1	20	[d]
$\mathbf{1}^{\cdot+}$	2,5-hexanedione	851	4.4	40	[d]
$\mathbf{1}^{\cdot+}$	2-Cl-pyridine	869	5.9	30	[d]
$\mathbf{1}^{\cdot+}$	pyridine	898	5.0	30	[d]
$\mathbf{1}^{\cdot+}$	4-Me-pyridine	915	9.8	58	[d]
$\mathbf{1}^{\cdot+}$	2,5-Me_2-pyridine	927	9.0	55	[d]
$\mathbf{2}^{\cdot+}$	c-C_3H_7-COMe	823	n.r.	–	–
$\mathbf{2}^{\cdot+}$	2-F-pyridine	853	5.6	29	[d]
$\mathbf{2}^{\cdot+}$	2-Cl-pyridine	869	16	84	[d]
$\mathbf{2}^{\cdot+}$	pyridine	898	16	97	[d]
$\mathbf{2}^{\cdot+}$	2,5-Me_2-pyridine	927	15	89	[d]
$\mathbf{3}^{\cdot+}$	c-C_3H_7-COMe	823	0.02	0.1	[d]
$\mathbf{3}^{\cdot+}$	2-F-pyridine	853	7.1	36	[d]
$\mathbf{3}^{\cdot+}$	2-Cl-pyridine	869	13	64	[d]
$\mathbf{3}^{\cdot+}$	pyridine	898	12	76	[d]
$\mathbf{3}^{\cdot+}$	4-Me-pyridine	915	13	76	[d]
$\mathbf{3}^{\cdot+}$	2,5-Me_2-pyridine	927	14	83	[d]
$\mathbf{4}^{\cdot+}$	2,4-pentanedione	836	n.r.	–	–
$\mathbf{4}^{\cdot+}$	2-F-pyridine	853	0.1	1	100/0
$\mathbf{4}^{\cdot+}$	2-Cl-pyridine	869	2.3	12	100/0
$\mathbf{4}^{\cdot+}$	pyridine	898	4.5	28	80/20
$\mathbf{4}^{\cdot+}$	4-Me-pyridine	915	6.7	41	100/0
$\mathbf{4}^{\cdot+}$	2,5-Me_2-pyridine	927	9.0	56	100/0
$\mathbf{4}^{\cdot+}$	1,3-propanediamine	940	9.5	62	75/25
$\mathbf{5}^{\cdot+}$	c-C_3H_7-COMe	823	2.4	12	90/10
$\mathbf{5}^{\cdot+}$	2-F-pyridine	853	7.3	34	80/20
$\mathbf{5}^{\cdot+}$	pyridine	898	8.1	48	32/68
$\mathbf{5}^{\cdot+}$	4-Me-pyridine	915	11	64	30/70
$\mathbf{5}^{\cdot+}$	2,5-Me_2-pyridine	927	11	62	22/78
$\mathbf{5}^{\cdot+}$	1,3-propanediamine	940	9.4	60	16/84
$\mathbf{6}^{\cdot+}$	2,5-Me_2-pyridine	927	10	56	0/100

[a] $kJ\,mol^{-1}$. [b] $\times 10^{10}\,cm^3 s^{-1}$, n.r. stands for no reaction observed. [c] Eff = $k_{exp}/k_{coll} \times 100$. [d] BH^+ is the only product that can be formed.

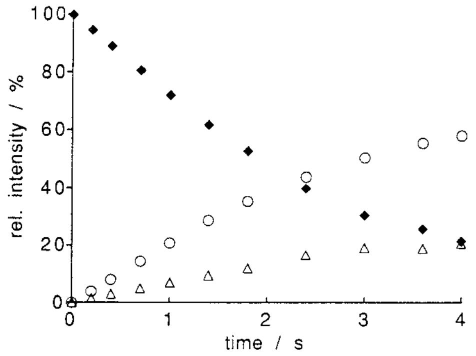

Figure 1. Relative ion intensities following the selection of $\mathbf{5}^{\cdot+}$, formed by EI ionization in the external ion source, in pyridine at 2×10^{-8} mbar in the ICR cell (◆, m/z 115; ○, m/z 80; △, m/z 81).

Discussion

The Brønsted acid properties of ionized benzyl alcohols have been examined by their reaction with reference bases of known basicity and, whenever possible, comparable stuctural features. In particular, care was exercised to avoid bases of low IP (ionization potential), that is, IPs lower than the value pertaining to benzyl alcohol itself. In this way, an electron-transfer process, which was found to prevail, for example, in the reaction with tertiary amines, could be prevented. The radical cations **1**$^{\cdot+}$–**6**$^{\cdot+}$ were found to react with the selected bases by proton (deuteron) transfer as the only observed process, which may or may not be followed by the association of the protonated reference base with another base molecule to form a proton-bound dimer. However, this consecutive process does not affect in any respect the rate of the H^+/D^+ transfer process of interest. When one deals with the radical cation of an OH-substituted toluene molecule a question of primary concern is whether the benzylic skeleton is retained or whether a ring enlargement to a cycloheptatriene structure (**7**) has occurred following the ionization process.[7] The resulting isomeric radical cation(s) (**7**$^{\cdot+}$) would in the latter case be responsible for the observed H^+/D^+ transfer process. To this end, the reactivity of ionized $C_6D_5CH_2OH$ was tested with the expectation that in the event of a ring-expanded structure, such as *c*-$C_7D_5H_2OH^{\cdot+}$, fast randomization of the seven deuterium and hydrogen atoms would render them all equivalent with respect to the transfer to a strong base such as 2,5-dimethylpyridine.[8] In contrast to this hypothesis, exclusive H^+ transfer was observed. By this result it is inferred at the same time that the benzylic structure is retained, and that the ring hydrogens are not involved in the deprotonation reaction by a relatively strong base.[9] The latter finding is in line with the gas-phase basicity (GB = 852 kJ mol^{-1}) of the phenyl radical which is distinctly higher than that, for example, of the benzyl radical (GB = 801 kJ mol^{-1}).[5, 10] A notable exception to the expectedly higher kinetic acidity of the toluene radical cation with respect to the benzene radical cation has been reported recently for the termolecular proton transfer to two polar molecules; this reaction has been ascribed, however, to the association of the polar molecules with the aromatic ring within the reaction complexes.[11]

The question is then left as to which sites are involved in the deprotonation process; among these sites are the conceivable α-C- and O-hydrogens in the parent benzyl alcohol radical cation, but this leads to the problem of ascertaining the kinetic and thermodynamic features of the processes involving the two individual sites. The problem can be approached in a stepwise fashion, starting from species where only one acidic site may come into play. The radical cations of **2** and **3**, $PhC(Me)_2OH^{\cdot+}$ and $PhCH_2OMe^{\cdot+}$, can only display O- and α-C-acidity, respectively. The two ions show a comparable Brønsted acid reactivity towards bases such as *c*-C_3H_7-COMe, which is hardly reactive, and pyridine, for example, which abstracts a proton with a reaction efficiency approaching 100%. So, although the rate data are not directly comparable because in the two radical cations a different number of methyl substituents is placed on different atoms, it clearly appears that both the O- and α-C-hydrogens can be removed by a base from **2**$^{\cdot+}$ and **3**$^{\cdot+}$, respectively, and that the two processes may show similar rates.

According to the kinetic data in Table 1 the relative reaction efficiencies for the proton-transfer reactions of the radical cations of **1**–**5** increase as the strength of the base increases. The data pertaining to the radical cations of **1**–**3** are plotted in Figures 2–4 showing the Eff versus GB(B) curves fitted with a parametric function [Eq. (1)].

$$\mathrm{Eff} = \frac{a}{1 + \exp[b(-\mathrm{GB(B)} + c)]} \qquad (1)$$

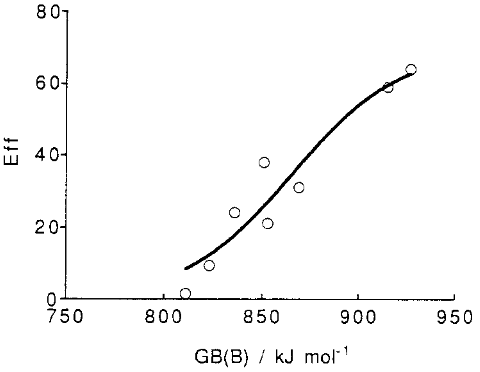

Figure 2. Plot of the efficiency (Eff) of the proton-transfer reactions from **1**$^{\cdot+}$ to reference bases B versus GB(B). The experimental values are fitted by the solid line according to Equation (1).

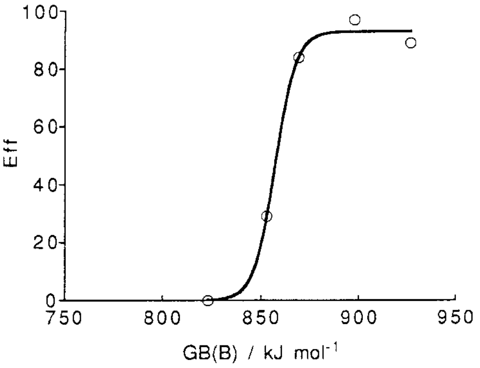

Figure 3. Plot of the efficiency (Eff) of the proton-transfer reactions from **2**$^{\cdot+}$ to reference bases B versus GB(B). The experimental values are fitted by the solid line according to Equation (1).

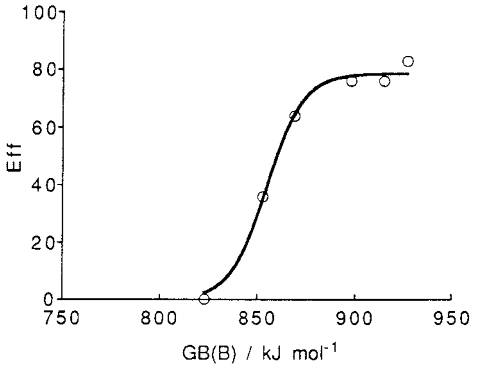

Figure 4. Plot of the efficiency (Eff) of the proton-transfer reactions from **3**$^{\cdot+}$ to reference bases B versus GB(B). The experimental values are fitted by the solid line according to Equation (1).

The observed trends match the expectation that as the GB of the base increases and the reaction becomes increasingly exoergonic the bimolecular rate constant increases until the collisional limit is reached. In the case of ion–molecule reactions lacking a kinetic barrier, a distinct reaction onset is typically found as the process becomes thermodynamically allowed. Proton-transfer reactions generally fall into this category and are adequately described by a single-well potential energy profile. Rare exceptions are due to the manifestation of steric effects such as those involving 2,6-di-*tert*-butylpyridine.[12] Rather, the proton transfer from arenium ions shows normal behavior, unaffected by steric effects even in the presence of bulky *tert*-butyl groups.[13] The radical cations from alkylbenzenes have been found to react by proton transfer to a series of gaseous reference bases in a quite similar way to the radical cations of benzylic alcohols and derivatives. The ensuing relationship between the kinetics and the thermodynamics of their proton-transfer reactions has been analyzed to derive thermochemical data.[14] Taking into account the reactivity behavior of these related systems, one may assume that the radical cations of benzylic alcohols and ethers do behave as well as normal Brønsted acids. If this condition is fulfilled, their proton-transfer reactions can be described by a correlation between reaction rate constants and standard free energy changes that has been derived and found to hold for a variety of proton-transfer reactions. Within this framework, the parametric function fitting the reaction efficiencies for the proton-transfer reactions from the selected radical cations to the reference bases [Eq. (1)] is analyzed to allow the evaluation of the GB of the conjugate base of the radical cation ($\mathrm{GB(A^{\bullet})}$) as described in Equation (2).[15]

$$c = \mathrm{GB(A^{\bullet})} + 1/b \qquad (2)$$

The relationship between the kinetics (the reaction efficiency) and the thermodynamics (the free energy change: $\mathrm{GB(A^{\bullet})} - \mathrm{GB(B)}$) of the proton-transfer reaction was derived for the simple kinetic scheme of Equation (3) and provides a quantitative analysis of the so-called bracketing method, also named the thermokinetic method.

$$\mathrm{AH^{\bullet+} + B \rightleftharpoons [AHB]^{\bullet+} \longrightarrow A^{\bullet} + BH^{+}} \qquad (3)$$

The application of this method, which relies on kinetic data to obtain thermodynamic information, is necessary as a result of the problem of acidic species, the radical cations, which lack a stable neutral conjugate base. In fact, the assessment of relative GBs by the direct determination of the proton-transfer equilibrium constant, which is normally feasible in the FT-ICR cell, requires a stationary concentration of both neutral partners exchanging the proton; this is hardly possible in the present case as one of them is a radical species.

As stated above it is clear that both the OH group of $\mathbf{2}^{\bullet+}$ and the CH_2 group of $\mathbf{3}^{\bullet+}$ may act as acidic sites. A quantitative evaluation of this property can be derived from the plots of the efficiencies of the deprotonation of $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ versus the GB of the reference bases, as shown in Figures 3 and 4, respectively. The fitting treatment obtained by using Equations (1) and (2) yields a GB value of 852 kJ mol^{-1} for $\mathrm{PhC(Me)_2O^{\bullet}}$ and GB = 850 kJ mol^{-1} for $\mathrm{PhCH(OMe)^{\bullet}}$ (Table 2), if no isomerization or other reactive process of the formed radicals is taking place in the proton-transfer event. The two values should be considered equal as they fall within the ±5 kJ mol^{-1} error range estimated for this method;[15] this is apparently in contrast with the expectation that the O-acidity is thermodynamically less favored than the α-C-acidity. It is, however, not appropriate to compare two species, $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$, differing in terms of the number and position of methyl groups.

Table 2. GB values evaluated for the conjugate bases of the radical cations of benzyl alcohol and its derivatives.

Radical cation	GB [kJ mol^{-1}][a]
$\mathbf{1}^{\bullet+}$	861
$\mathbf{2}^{\bullet+}$	852
$\mathbf{3}^{\bullet+}$	850
$\mathbf{4}^{\bullet+}$	902
$\mathbf{5}^{\bullet+}$	856

[a] GB values obtained from the fit parameters of the plots in Figure 2–4 and similar ones drawn for $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ according to Equations (1) and (2). Error estimated for the fitting procedure ±6 kJ mol^{-1}.

As anticipated, the behavior of $\mathbf{1}^{\bullet+}$ and the labeled analogue $\mathbf{5}^{\bullet+}$ is more complex, potentially involving the competition of O-acidity and α-C-acidity. The efficiency versus GB(B) curve reported for $\mathbf{1}^{\bullet+}$ in Figure 2 displays a fitting curve showing somewhat different behavior with respect to that reported for $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$, for which the efficiency rises steeply as the proton-transfer reaction becomes thermodynamically allowed. In the case of $\mathbf{1}^{\bullet+}$, the transition from negligible reactivity to reactivity upon every collision is relatively smooth, as if reflecting the contribution of more than one process. The same kind of behavior is shown when curve fitting the data of $\mathbf{5}^{\bullet+}$. Two distinct contributions do in fact coexist because the reference base abstracts both D^+ and H^+ from $\mathbf{5}^{\bullet+}$ in a ratio that depends on its GB. Thus, whereas D^+ transfer is by far the most dominant process to cyclopropylmethylketone (GB = 823 kJ mol^{-1}), H^+ transfer is favored by a factor of five in the case of 1,3-propanediamine (GB = 940 kJ mol^{-1}). Other bases show an increasing amount of H^+ transfer as their GB increases. Thus, the unsubstituted (apart from D-labeling) benzyl alcohol radical cation, which has been studied as a naked species in the gas phase, displays the same mechanistic dichotomy observed in substituted benzyl alcohol radical cations in solution, in which the strongly basic OH^- deprotonates the OH group in contrast to the H_2O induced α-C-deprotonation. The observed change in the acidic site involved as the strength of the base increases prevents us from evaluating the GB of the conjugate base of $\mathbf{1}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$. The GB parameters obtained for $\mathbf{1}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ according to Equations (1) and (2) (Table 2) should therefore be viewed as a mean between the values pertaining to the two processes taking place.

In order to confirm the observed change in the acidic site involved as the base strength increases, the radical cation $\mathbf{4}^{\bullet+}$, the topic of detailed studies in solution, has been included in the proton-transfer reactivity survey. Overall the acidity of this radical cation, highly stabilized by the electron-donating effect of the methoxyl group, is lower than that of its unsubstituted analogue. The estimated GB of the conjugate base of $\mathbf{4}^{\bullet+}$ is in fact higher than that of $\mathbf{1}^{\bullet+}$ by approximately 38 kJ mol^{-1} (Table 2). However, two common features are found, namely the smooth change in the rate coefficients versus the standard free energy variation of the proton-transfer reaction and the competition of O-acidity with α-C-acidity when stronger bases are used. The latter finding is displayed by the comparable contribution of H^+ and D^+ transfer from $\mathbf{4}^{\bullet+}$ to bases such as 2,5-dimethylpyridine and 1,3-propanediamine.

The overall efficiency of H^+ and D^+ transfer from $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ to the strongest bases used appears to level off to values approaching the collisional efficiency. This fact makes the rates of the individual processes of limited significance as they reflect the competition of two processes within the same encounter complex.

D-labeled substrates are generally used to reveal the occurrence of kinetic isotope effects.[16] A primary kinetic isotope effect may be revealed in the proton-transfer event. The two bases 4-fluoropyridine and cyclopropylmethylketone both react in a prevailing deprotonation process at the α-CH_2 group of the benzyl alcohol radical cation, as shown by the large extent of D^+ transfer from $\mathbf{5}^{\bullet+}$. Both appear to react faster with $\mathbf{5}^{\bullet+}$ with respect to $\mathbf{1}^{\bullet+}$; this is an indirect kinetic isotope effect in contrast to the expected operation of a primary kinetic isotope effect. It should be noted, however, that the observed spread in the reaction efficiencies (ca. 40 %) is too close to the error, affecting the determination of absolute values of rate constants by the FT-ICR technique, to be meaningful. However, the absence of any noticeable primary kinetic isotope effect is circumstantial evidence that the proton-transfer reaction from ionized benzyl alcohol lacks a significant activation barrier and is thus appropriately described by the single-well mechanism of Equation (3).

Finally, it may be interesting to compare the bimolecular reactivity of benzyl alcohol radical cations with the proton-transfer reactivity within ionized benzyl alcohol/ammonia clusters, $[C_6H_5CD_2OH^{\bullet+}\cdot nNH_3]$. As the cluster becomes larger, n increasing from 1 to 5, deprotonation of the O-hydrogen begins to occur, at the expense of C-deprotonation, and this reaction leads to an increasing fraction of the $C_6H_5CD_2O^{\bullet}(NH_3)_k + (NH_3)_{n-k}H^+$ products with respect to $C_6H_5CDOH^{\bullet}(NH_3)_k + (NH_3)_{n-k}D^+$. Once again this result may be viewed as the prevailing attack at the O-hydrogen as the base becomes stronger. In this example the thermodynamic stability of the ammonium ion increases as the number of NH_3 molecules in the product cluster ion increases.[17]

Conclusion

The results presented above clearly show that the behavior of benzyl alcohol radical cations in the gas phase is very similar to that found in solution. Accordingly, a base-dependent C-acidity/O-acidity dichotomy is observed and reported. Thus, the relatively weak base, cyclopropylmethylketone, deprotonates $C_6D_5CD_2OH^{\bullet+}$ predominantly at the benzylic C–D bond (carbon acidity), whereas with the rather strong base, 1,3-propanediamine, O-deprotonation is the major reaction. An intermediate situation is found with the other bases. In the gas phase, the overall kinetic acidity is decreased with increasing stability of the radical cation, but oxygen acidity decreases apparently more than carbon acidity, since in 4-MeO-$C_6H_4CD_2OH^{\bullet+}$ we observe almost only carbon acidity with the usual set of reference bases. In this respect, gas-phase and solution results are somewhat different, since in solution 4-MeO-$C_6H_4CD_2OH^{\bullet+}$ also displayed distinct oxygen acidity, but this finding can depend on the actual role of the base strength in the competition between the two acidic sites, which can be different in the two environments.

Apparently, in benzylic alcohols oxygen acidity is thermodynamically less favored than carbon acidity in the gas phase, although, when the two acidities are separately examined by investigating systems, which can exhibit only one of the two properties, comparable values are found. Thus, from the gas-phase acidity of the benzyl methyl ether radical cation ($\mathbf{3}^{\bullet+}$, a carbon acid) and of the cumyl alcohol radical cation ($\mathbf{2}^{\bullet+}$, an oxygen acid), it was found that the gas-phase basicity of the α-methoxybenzyl radical is about the same as that of the cumyloxyl radical.

A possible explanation of the dichotomy illustrated above is the following. Theoretical calculations have shown that in benzyl alcohol radical cations the hydrogen of the OH group is the center with the largest positive charge density, whereas the α-carbon is the center where the SOMO (singly occupied molecular orbital) has the largest coefficient.[18] On this basis, we can rationalize our observations by suggesting that the adduct formed from the radical cation and the base can evolve in two ways, which depend on the base strength. When the base is relatively weak, orbital overlap is the main factor, and C–H deprotonation then ensues due to the high value of the SOMO coefficient at the α-carbon. However, by increasing the strength of the base, the charge interaction factor becomes progressively more important, and OH deprotonation takes over. The fact that with the 4-methoxy-substituted benzyl alcohol radical cation, oxygen acidity is practically not observed is in line with this interpretation. In fact, as the positive charge is more stabilized in the aromatic ring, less positive charge density will be present in the hydrogen atom of the OH group with a consequent decrease in the kinetic oxygen acidity. It should be noted that the cited PM3 semiempirical molecular orbital calculations strictly refer to gaseous species. It is reasonable, however, that the same arguments may be applied to explain the mechanistic dichotomy that is also observed in solution.

Experimental Section

Benzyl alcohol and its derivatives including $C_6D_5CH_2OH$ and $C_6D_5CD_2OH$ were obtained from Aldrich. Only 4-MeO-$C_6H_4CD_2OH$ was prepared by a previously described procedure.[2] Ar and the compounds used as reference bases were also obtained from commercial sources and used as received.

All experiments were performed on a Bruker Spectrospin Apex TM 47e mass spectrometer equipped with an external ion source, a cylindrical "infinity" cell, and a 4.7 T superconducting magnet. The radical cations were generated in the external ion source in the EI configuration, and the neutral benzyl alcohol was introduced at 2×10^{-6}–1×10^{-5} mbar (1 mbar = 100 Pa). Typical conditions were: electron energy 10–20 eV, ionizing pulse duration of 100 ms, and emission current of 10 μA. The ion population was transferred into the ICR cell containing a known pressure of a selected base. The radical cation of interest was selected by broad band selection and quenched of excess internal and translational energy by collisions with Ar, admitted through a pulsed magnetic valve up to the peak pressure of 10^{-5} mbar. After a delay time of 1 s to remove Ar from the cell, further isolation from all other fragment or product ions was achieved by a soft selective–ejection technique by using low-energy "single shots". The reagent ion was then left to react with a neutral reference base present in the cell at the constant pressure of 1×10^{-8}–4×10^{-8} mbar, introduced by a needle valve from an inlet system at room temperature. Pressure readings were obtained from an ionization gauge close to the turbo pump of the cell and calibrated with the reference reaction $CH_4^{\bullet+} + CH_4 \rightarrow CH_5^{+} + CH_3^{\bullet}$, by using the reported value of $k = 1.1 \times 10^{-9}$ molecule^{-1} cm^3 s^{-1}.[19] Pressure readings for each neutral reagent were further corrected for the different response of the neutral reagents by using appropriate factors.[20]

Kinetic processes were followed by recording the intensities of the ion signals over increasing reaction times. The cell was at the room temperature of 25 °C, which was considered as the effective reaction temperature. Pseudo-first-order rate constants were obtained from the logarithmic decrease of the reactant ion intensity and were divided by the concentration of the neutral reagents to obtain second-order rate constants. The second-order rate constants were usually the average of three experiments run at different neutral pressures. The error in the rate constants (ca. ±30%) was mainly due to the uncertainty affecting the concentration of the neutral reagent. The product ratio from competitive reaction channels was evaluated from the ion intensities of the product ions extrapolated at initial time, in order to minimize the interference by possible subsequent reactions.

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