Preparation and Reactivity of Solvated Distonic Ions and Ionized Enols in the Gas Phase

V. Troude, G. van der Rest, P. Mourgues, and H. E. Audier*

*Laboratoire des Mécanismes Réactionnels, URA CNRS 1307
Ecole Polytechnique, F-91128 Palaiseau Cedex, France*

The study of solvated ions in the gas phase is of prime importance in understanding the role of the solvent in ionic chemical and biochemical reactions. Many studies deal with the physicochemistry of clusters containing a great number (*n* > 10) of solvent molecules;[1] a case in point concerns the many studies of water clusters to gain understanding of solvation and nucleation phenomena.[2] Chemical reactivity studies of organic cations or anions in microscopic systems with a small number of solvent molecules (*n* < 5) represent an increasing field of interest. For instance, the influence of solvation upon proton transfer or nucleophilic displacement reactions has been reported.[3,4] It has been shown also that solvation decreases the reactivity of enolate anions.[5] However, studies of small clusters involving organic radical cations are relatively rare.[4,6] In this vein, reactions within clusters of ionized alkenes,[4] as well as nucleophilic substitution within [halobenzene$^{•+}$, *n*NH$_3$] ions,[7] have been studied.

One of the major difficulties in this kind of study is to find, for each system, a practical and specific method to produce the desired solvated species. While it is often straightforward to generate solvated cations by using a high-pressure ion source,[8] this method is often not applicable for making solvated radical cations, the preparation of which requires removal of an electron from neutral clusters obtained in supersonic expansions of a solvent gas containing the molecule to be ionized.[4,6,7] However, that method requires that the neutral species corresponding to the radical cation is available, which is not the case when the goal is to generate solvated distonic ions or solvated ionized enols. A simple chemical method, reaction of *tert*-butyl alcohol with an ion of interest, is described herein to prepare such solvated species. Their structure and their reactivity are discussed.

The $^•CH_2CH_2O(H)CH_3^+$ β-distonic radical cation (Dis$^{•+}$) was produced by fragmentation of ionized 1,2-dimethoxyethane[9] in the external ion source of a Bruker CMS-47-X FT-ICR spectrometer. This ion reacts in the ICR cell with *tert*-butyl alcohol (eq 1) to yield $C_3H_{10}O_2^{•+}$ through isobutene loss. This ion appears to be a radical cation weakly bonded to a water molecule, [Dis$^{•+}$, H_2O], since (i) upon collision, water elimination gives back an ion that reacts by regioselective addition to CH_2O as does $^•CH_2CH_2O(H)CH_3^+$ [10] and (ii) in the presence of $H_2^{18}O$, rapid exchange of a water molecule takes place.

$$^•CH_2CH_2O(H)CH_3^+ + t\text{-}C_4H_9OH \rightarrow$$
$$[^•CH_2CH_2O(H)CH_3^+, H_2O] + \text{iso-}C_4H_8 \quad (1)$$
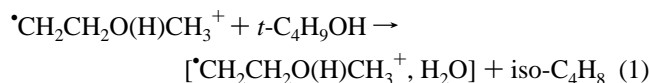
The reactions of [Dis$^{•+}$, H_2O] demonstrate that the initial ion has retained its β-distonic structure in the solvated species. For instance, I$^•$ abstraction from allyl iodide indicates the existence of a radical site in the solvated species[11] (eq 2).

$$[^•CH_2CH_2O(H)CH_3^+, H_2O] + C_3H_5I \rightarrow$$
$$[ICH_2CH_2O(H)CH_3^+, H_2O] + C_3H_5^• \quad (2)$$
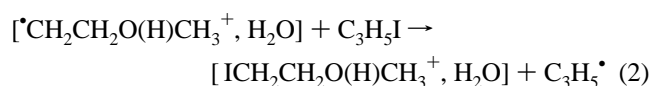
With dimethyl ether, two competing, rapid reactions occur: (i) substitution of the H_2O moiety by CH_3OCH_3, which confirms the existence of a weak bond between Dis$^{•+}$ and H_2O, and (ii) $C_2H_4^{•+}$ transfer from the [Dis$^{•+}$, H_2O] ion to CH_3OCH_3. This process is highly characteristic of ions with a β-distonic structure.[12] Consequently, the solvated species is [$^•CH_2CH_2O$-(H)CH$_3^+$, H_2O]. Using ab initio calculations[13] for the [$^•CH_2CH_2O(H)CH_3^+$, H_2O] systems, we find two minima, **a** and **b** on the potential energy surface. Structure **a**, poorly stabilized (10 kcal/mol) compared to the energy of separate partners, is an electrostatically bound complex, while the more stable form **b** is strongly stabilized by H-bonding (26 kcal/mol) (Figure 1).

The solvated species does not give all the reactions observed for the naked ion: [$^•CH_2CH_2O(H)CH_3^+$, H_2O] reacts neither with CH_3OCH_3 by H$^•$ abstraction nor with CH_2O by addition−elimination, whereas $^•CH_2CH_2O(H)CH_3^+$ does.[10] The reasons for such differences in reactivity are currently under study. Preliminary computational results show that the energy barrier

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a   **b**
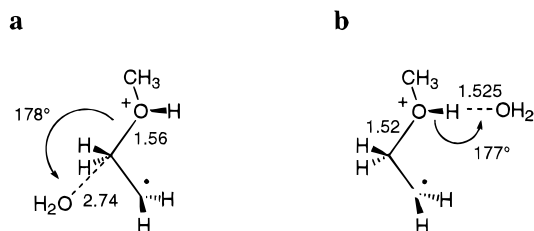
Figure 1. Calculated geometries of stationary structures **a** and **b** (ion−water and CH_2−O bond distances in Å). The C−O distances in **a** are the same (within 0.01 Å) as those calculated for the unsolvated distonic ion.

for H[•] abstraction is very sensitive to interatomic distances within the complex.[14]
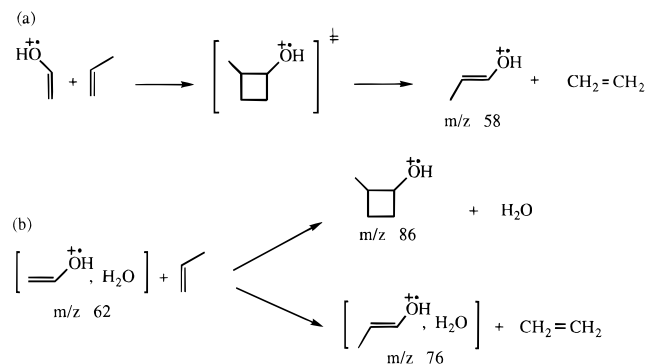
Fragmentation of ionized 1,4-butanediol yields a m/z 62 fragment ion, which has been suggested to have the structure $[CH_2CHOH^{•+}, H_2O]$.[15] In the present study, a m/z 62 ion exhibiting the same reactivity along with its higher homologues were generated by reaction of ionized enols (formed by fragmentation in the ion source of ionized cyclobutanols) with *tert*-butyl alcohol (eq 3).

$$R(R')CCHOH^{•+} + t\text{-}C_4H_9OH \longrightarrow$$
$$[R(R')CCHOH^{•+}, H_2O] + iso\text{-}C_4H_8 \quad (3)$$
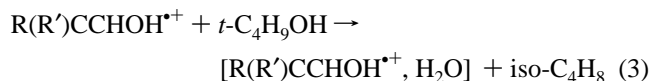
Upon collisional activation, these ions eliminate H_2O to give $R(R')CCHOH^{•+}$ (R, R' = H or CH_3) fragment ions, which exhibit reactions identical with those of the initial enol radical cations. Moreover, these solvated ions undergo a rapid ligand exchange with $H_2^{18}O$ and with other neutral molecules such as alcohols, which strongly suggests that their structure corresponds to a $CH_2CHOH^{•+}$ ion weakly bonded with a molecule of water. Finally, as will be discussed below, this solvated enol ion (as well as ionized vinyl alcohol itself) reacts with alkanes[16] and alkenes.[17] It is worth noting that recent calculations[18] show that in the $[CH_2CHOH^{•+}, H_2O]$ species the O-bonded hydrogen of the ion is weakly bonded to the oxygen of water.

Ionized enols generally react with alkenes (e.g., propene) by regiospecific cycloaddition,[17] leading to an ionized substituted enol via a cyclic intermediate with a lifetime too short to be observed (Scheme 1a). Similarly, the $[CH_2CHOH^{•+}, H_2O]$ solvated ion reacts with propene to give the cycloaddition product (ionized 2-methylcyclobutanol) with H_2O loss, as well as to give a methyl-substituted enol[•+] solvated by H_2O (Scheme 1b). Therefore, evaporation of a water molecule decreases the internal energy of the system, allowing the cyclic intermediate $C_5H_9OH^{•+}$ (or an open distonic form) to survive long enough to be observed. Furthermore, due to changes in ionization

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Scheme 1

potentials in the system, the $[enol^{•+}, H_2O]$ ions can undergo reactions which are not observed for naked $enol^{•+}$. For instance, $CH_2CHOH^{•+}$ reacts with isobutene only by charge exchange, while $[CH_2CHOH^{•+}, H_2O]$ undergoes the cycloaddition reaction, giving both $[(CH_3)_2CCHOH^{•+}, H_2O]$ and $(CH_3)_2C_4H_5OH^{•+}$. Similar reactions occur between $[CH_3CHCHOH^{•+}, H_2O]$ and isobutene, giving $[(CH_3)_2CCHOH^{•+}, H_2O]$ and $(CH_3)_3C_4H_4$-$OH^{•+}$. The CID spectrum of this latter species gives mainly m/z 72 (ionized enol of isobutyraldehyde) and m/z 58 (ionized enol of propionaldehyde) fragment ions, consistent with an ionized trimethylcyclobutanol structure or an open distonic isomer.

In its reaction with isobutane, $CH_2CHOH^{•+}$ yields iso-$C_4H_8^{•+}$ after sequential isomerization of intermediate complexes[19] (eq 4). The reaction of the solvated enol ion stops after the first step to give only $t\text{-}C_4H_9^+$.

$$[CH_2CHOH^{•+}, C_4H_{10}] \rightleftharpoons [CH_3CHOH^{•}, t\text{-}C_4H_9^+] \rightleftharpoons$$
$$[CH_3CH_2OH, C_4H_8^{•+}] \quad (4)$$

In conclusion, a new method to generate monosolvated radical cations is described in this work. These solvated ions undergo ligand exchange with many neutral reactants (alcohols, aldehydes, ketones, etc.), yielding a variety of new solvated radical cations. The $[^{•}CH_2CH_2O(H)CH_3^+, CH_3OH]$ solvated ion formed in this way can alternatively be generated by a straightforward reaction between the $^{•}CH_2CH_2O(H)CH_3^+$ ion and *tert*-butyl methyl ether. This method of preparing solvated radical cations is widely applicable. Several solvated β-distonic ions (such as $^{•}CH_2CH_2O(H)CH_2CH_3^+$ and $^{•}CH_2CH_2OCH_2^+$) have been generated and clearly characterized by the methods described above.

Apart from ligand exchange, solvated species often give the same reactions as the corresponding naked ions, but (as outlined above) their reactivity can also be different. One aspect of the observed differences is that stabilization of the system by H_2O loss can be used to trap intermediates. Other aspects are the subject of a continuing investigation.

Supporting Information Available: Figures showing structures and energies of species **a** and **b** and of the corresponding distonic ion (3 pages). See any current masthead page for ordering and Internet access instructions.

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