Solvent Effect on the Protonation of Acetylene and Ethylene – Continuum Solvent Quantum Chemical Calculations

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The protonation of acetylene and ethylene (yielding the vinyl and ethyl cation, respectively) was investigated computationally by ab initio calculations [B3LYP/6–31G(d,p)], in the gas phase and in water, as modeled by the IPCM and SCIPCM continuum methods. The structures and NBO atomic charges were thus determined for the neutral bases and their protonated forms, while the comparison of gas-phase and aqueous basicities afforded the hydration energies of the protonated bases. It was found that the aqueous protonation of acetylene is more endothermic than that of ethylene by 5 kcal/mol, owing to the lower intrinsic basicity of the former (by 7.4 kcal/mol), which is only partly compensated for by the more exothermic hydration (by 3.8 kcal/mol) of the vinyl cation.

Introduction

The acid-catalyzed addition of water or other electrophiles to a carbon−carbon double or triple bond is believed to involve carbocations that are open [carbenium (**1**) or carbynium (**2**) ion] or bridged [iranium (**3**) or irenium (**4**) ion],[1][2] as depicted in Figure 1 for protonation. Arylalkynes and -alkenes exhibit a very similar reactivity and responses to changing the acid concentration,[3] whereas substituent effects are somewhat higher for alkynes, indicating that the intrinsically lower reactivity of the triple bond is compensated for by a better charge dispersion in the hydrocarbon backbone. A comparison between the protonation of acetylene and ethylene[4,5] revealed a significant difference both in reaction rates and in the acidity dependence. In the range of acid concentration in which both substrates react with water at measurable rates, ethylene reacts 2−3 orders of magnitude faster than acetylene. However, reaction rates extrapolated to the standard state (aqueous solution) are identical within experimental error, implying that the acidity dependence of the protonation of ethylene is steeper than that of acetylene. This is indeed borne out by the activity coefficient behavior expressed by the m^* parameter[6] (1.12 and 1.50 for acetylene and ethylene, respectively[4]), which suggests that the vinyl cation has a larger solvation energy than the ethyl cation. Although the evidence reported is sound, we sought to obtain an independent verification by calculating the energetics of protonation of acetylene and ethylene, as well as the solvation energy of all the species involved in the proton-transfer process (i.e., neutral species and the carbocations derived from their protonation).

The structures and potential energy surfaces (PES) of the species resulting from the protonation of acetylene ($C_2H_3^+$) and ethylene ($C_2H_5^+$) have been extensively investigated by theoretical methods.[7] Recent high-level calculations not only indicated that the bridged structure **4** is more stable than the open one **2** by 2−4 kcal/mol, but also that **2** is either a shallow minimum or the saddle-point for the isomerization of **4**, a process in which hydrogen atoms circulate around the C_2 unit. Likewise, in the $C_2H_5^+$ PES (at correlated levels of theory) the bridged, non-classical structure **3** is more stable by 7−8 kcal/mol than the open classical $CH_3CH_2^+$ ion (**1**) which is not minimum.[8−10]

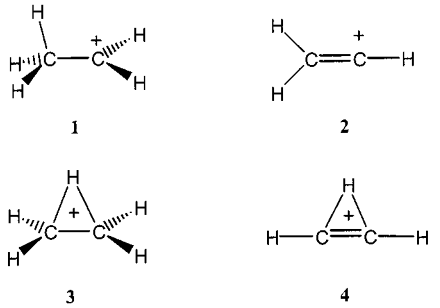

Figure 1. Open and bridged structures for protonated alkenes (**1**, **2**) and alkynes (**3**, **4**)

The above data have contributed a great deal to the understanding of the energetics of protonation in the gas phase and have afforded a deep insight into the nature of such species. As such, they are strictly comparable only with those experimentally obtained in the gas phase, whereas the complete characterization of the proton-transfer equilibrium in water requires an evaluation of the structures and hydration energies of all species involved. Schleyer[11] recently reported large medium effects on the calculated geometries of Lewis acid−base adducts, and suggested that solvent polarization may in fact induce different geometries in the species involved. Hence, for the purposes of the present investigation (in which the hydration process will be modeled) we will also consider **1** and **2** (in addition to **3** and **4**) as possible structures for the vinyl and ethyl cations despite their known instability in the gas phase.

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To evaluate the solvent effect on the proton-transfer equilibrium, one might perform calculations on a cluster formed by the solute and a small number of solvent molecules. However, this approach is difficult since (a) a meaningful solvation shell must comprise a substantial number of solvent molecules; (b) these systems have a large number of accessible conformations with similar energy; (c) the hydration of the neutral species is entirely due to dispersive interactions, which are notoriously difficult to model; and (d) an accurate evaluation of the energetics of hydration requires correction for the basis set superposition error, not a straightforward task in such systems. A much faster alternative for modeling solvent effects is provided by continuum methods.[12] These treat the solvent as a continuous medium, with a given dielectric permittivity ε, which contains a variously shaped cavity in which the solute is placed. Major advances were recently made in this field, and these computationally inexpensive methods have proved to be effective in several cases.[12] Such calculations were carried out to predict the solvent effect on proton transfer equilibria of, among others, ammonium ions[13] and alcohols.[14] Lately, the Isodensity Polarizable Continuum Method (IPCM) and the Self-Consistent Isodensity Polarizable Continuum Method (SCIPCM),[15] which employ a cavity whose shape is iteratively computed from the electron density, have been proposed as a general-purpose way of calculating the solvent effect on chemical equilibria and reactions. We recently reported on the very good performance of the IPCM method in predicting the relative stabilities in water of tautomeric ions from the protonation or deprotonation of polyfunctional bases[16] and acids,[17] so that this general approach seems suitable for the investigation of carbocations in water, whose hydration is known to be substantially weaker than that of oxonium or ammonium ions.[6][9] All calculations were carried out with Gaussian 94.[18]

Results and Discussion

The structure and hydration energies of the vinyl ($C_2H_3^+$) and ethyl ($C_2H_5^+$) cations were investigated by ab initio DFT methods. In view of the possible investigation of larger species (notably those stabilized by aryl groups), as a first step we evaluated the performance of several theoretical levels of varying computational cost. The $C_2H_3^+$ and $C_2H_5^+$ ions were studied both in their open (classical, **1** or **2**) and bridged (non-classical, **3** or **4**) forms, since both are conceivable structures, at least in principle (see above).

Calculations in the Gas Phase and IPCM Water

The structures of both ions were firstly optimized at the HF/3−21G level, and gas-phase energies were calculated at the HF/6−31G(d,p) level. Energies in water were computed by modeling the solvent with the IPCM method with a dielectric permittivity, ε = 78.5 (Table 1) but otherwise at the same level [HF-IPCM/6−31G(d,p)]. Atomic charges were calculated with the NBO partition scheme[19] (Figure 2).

Table 1. Gas-phase and solution energies for the vinyl and ethyl cations (HF/3−21G geometry)

Species	E (gas)[a]	E (water)[b]	E_{solv}[c]
$C_2H_3^+$	−77.092971	−77.214637	−76.3
$C_2H_5^+$	−78.320021	−78.435857	−72.7

[a] HF/6−31G(d,p)//HF/3−21G, in hartrees. − [b] HF-IPCM/6−31G(d,p)//HF/3−21G, in hartrees. − [c] E(water) − E(gas) in kcal/mol.

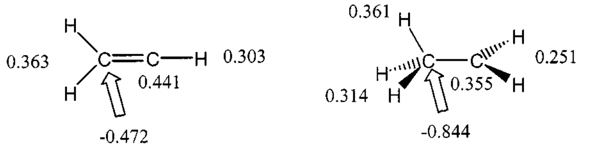

Figure 2. NBO atomic charges in the vinyl and ethyl cations (gas phase, HF/3−21G geometry)

At this level, the structures of $C_2H_3^+$ and $C_2H_5^+$ are the open $H_2C{=}CH^+$ and $CH_3CH_2^+$ ions, respectively, and the hydration energy of $H_2C{=}CH^+$ is more exothermic than that of $CH_3CH_2^+$ by 3.6 kcal/mol. The stronger hydration of the vinyl cation agrees with the larger calculated charge on the sp, carbon atom (0.44) rather than on the sp^2, carbon atom (0.35).

We then repeated the calculations, optimizing the structures by means of density functional theory, using Becke's hybrid three-parameter functional and Lee−Yang−Parr nonlocal correlation (B3LYP),[20] with the 6−31G(d,p) basis set (Table 2), and running frequency analyses at the same level. The neutral precursors (acetylene and ethylene) were also included. The structures thus obtained are depicted in Figure 3a, and the NBO charges are shown in Figure 3b.

Table 2. Gas-phase and solution (IPCM) energies for acetylene, ethylene, vinyl and ethyl cations

Species	E (gas)[a]	ZPE[a][b]	E (water)[c]	E_{solv}[d]
C_2H_2	−77.329566	16.8 (0)	−77.334045	−2.8
$C_2H_3^+$, closed	−77.589617	21.3 (0)	−77.710801	−76.0
$C_2H_3^+$, open	−77.591588	21.9 (0)	−77.711767	−75.4
C_2H_4	−78.593807	32.1 (0)	−78.595309	−0.9
$C_2H_5^+$,closed	−78.869023	38.1 (0)	−78.981535	−70.6
$C_2H_5^+$, open	−78.862445	37.2 (1)[e]	−78.975502	−70.9

[a] B3LYP/6−31G(d,p)//B3LYP/6−31G(d,p), in hartrees. − [b] Zero-point vibrational energies (kcal/mol, unscaled) and number of imaginary frequencies in parentheses. − [c] IPCM-B3LYP/6−31G(d,p)//B3LYP/6−31G(d,p), in hartrees. Vibrational analysis is not possible with this method. − [d] E(water) − E(gas) in kcal/mol. − [e] Imaginary frequency: −301.8 cm^{-1}.

Energies (Table 2) and charges (Figure 3c) in water were calculated at the gas-phase geometry with the IPCM method. Hydration energies were calculated without ZPEs, since the IPCM method is only available for single-point

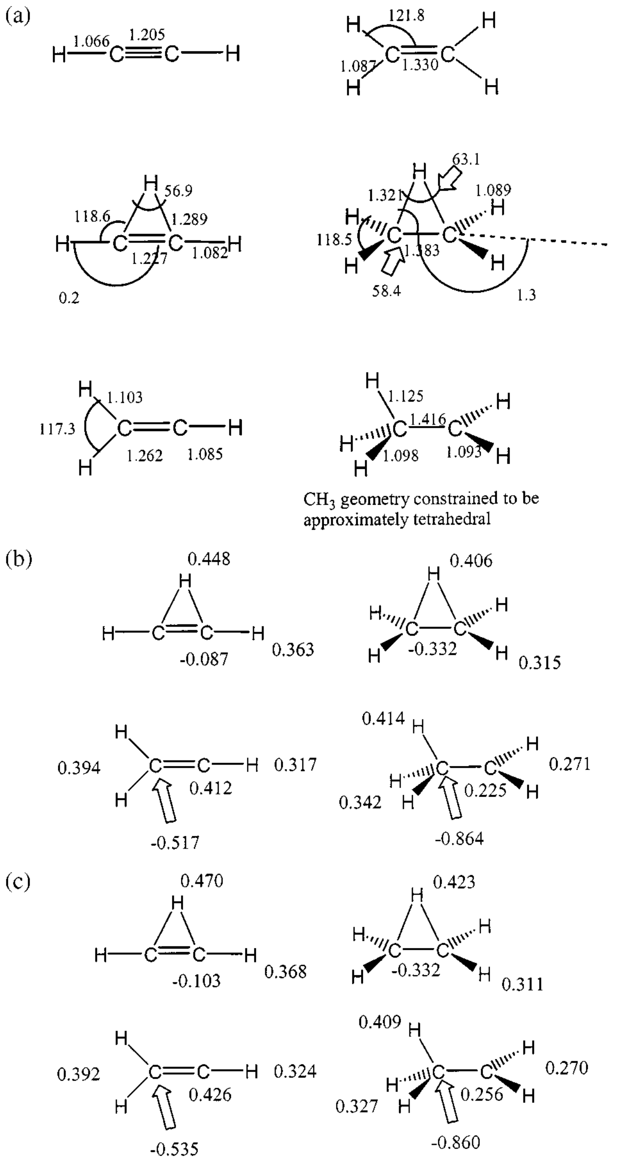

Figure 3. (a) Structures and (b) NBO atomic charges in the gas phase [B3LYP/6−31G(d,p)]; (c) NBO atomic charges in water [IPCM-B3LYP/6−31G(d,p)]

calculations and hence no vibrational analysis can be carried out.

At this level of theory, two minima were located on the $C_2H_3^+$ PES, corresponding to the open vinyl cation $H_2C{=}C{-}H^+$ and π-protonated acetylene. The open cation is slightly more stable than the bridged one, by ca. 1 kcal/mol. Conversely, the only stable structure on the $C_2H_5^+$ PES is hydrogen-bridged (π-protonated ethylene); any unconstrained geometry optimization converged to the structure shown in Figure 3a. We also note that in the bridged ions **3** and **4** the geometry of the parent neutral species (ethylene and acetylene, respectively) is not much perturbed, as shown by the small tilt angle of the C−C−H bonds (Figure 3a) compared to the neutral species.[21]

To evaluate the relative stabilities of the open and bridged ethyl cations, the $CH_3CH_2^+$ ion was re-optimized with the methyl group constrained to an approximately tetrahedral geometry. The resulting structure was less stable than the closed one by 4.1 kcal/mol, and a vibrational analysis showed this point to have one negative frequency.

The hydration energy of the vinyl cation (whether in open or bridged form), calculated with the IPCM method, was again stronger than that of the ethyl cation, by 4−5 kcal/mol, thus essentially confirming the results obtained at the lower level. In fact, the inclusion of water by the IPCM model did not cause major changes in the charge distribution (Figures 3b−c); a larger positive charge on the sp, rather than sp^2, carbon atom was still found. In fact, in the bridged $C_2H_5^+$ ion both carbon atoms are negatively charged.

Geometry Optimizations in SCIPCM Water

The preceding calculations highlighted the differential solvation properties of vinyl and ethyl cations at the gas-phase geometry. In view of Schleyer′s results[11] concerning medium effects on the geometries of Lewis acid−base adducts, the geometries of all species were reoptimized in water as modeled by the SCIPCM method. (This different solvent modeling is necessary since the IPCM method is currently implemented[18] only for single-point energies.) Geometry optimizations were started from the previously obtained gas-phase geometry; numerical frequencies were also calculated (Table 3, Figures 4a and 4b).

The geometry of the neutral species was only negligibly affected by optimization in water; identical bond lengths were found for ethylene, whereas those for acetylene differed only by 0.002 Å at most.

The hydration energies of acetylene and ethylene were predicted to be −2.1 and −0.7 kcal/mol, respectively (as with the IPCM method). These data can be compared with the experimental values of −3.7 and −3.5 kcal/mol[22] or −3.9 and −3.5 kcal/mol.[23] Hence, our calculations correctly point out the very weak hydration of these nonpolar species, but the magnitudes are underestimated and there is a noticeable disagreement (ca. 1 kcal/mol) with experiment. With the same methods, Wiberg and co-workers reported a very good agreement with experiment (0.1−0.2 kcal/mol) for the conformational equilibrium of furfuraldehyde in various continuum solvents,[15] i.e., for *relative* rather than *absolute* solvation energies. Since to date there is no comprehensive data base concerning the performance of (SC)IPCM methods in the estimation of absolute solvation energies, we can only remark that this is a very difficult case for continuum solvent calculations, since both solutes have zero dipole moment, and solvent polarization is achieved through higher moments leading to weaker interactions. In any event, hydration enthalpies of the neutral species have only a negligible effect in the overall energy balance of the proton-transfer process (see below).

Unconstrained optimization of the open ethyl cation led again to the bridged form, which can therefore be considered the only stationary point on the PES in both gas and water phases. Conversely, the $C_2H_3^+$ PES again fea-

Table 3. Gas-phase and solution energies (SCIPCM) for acetylene, ethylene, vinyl and ethyl cations

Species	E (gas)[a]	ZPE[a]	PA[b]	E (water)[c]	ZPE[c]	PA[d]	E_{solv}[e]
C_2H_2	−77.329566	16.8 (0)	159.3[f]	−77.332928	16.8 (0)	229.0	−2.1
$C_2H_3^+$, closed	−77.589617	21.3 (0)	–	−77.705213	21.6 (0)	–	−72.2
$C_2H_3^+$, open	−77.591588	21.9 (0)	–	−77.706392	22.1 (0)	–	−71.8
C_2H_4	−78.593807	32.1 (0)	166.7[g]	−78.594821	32.0 (0)	234.0	−0.7
$C_2H_5^+$, closed	−78.869023	38.1 (0)	–	−78.977553	38.2 (0)	–	−68.0
$C_2H_5^+$, open[h]	−78.862445	37.2 (1)	–	–	–	–	–

[a] Data from Table 2. – [b] $E(\text{cation}_{(g)}) - E(\text{neutral}_{(g)})$ in kcal/mol with respect to the most stable ion (open for acetylene, closed for ethylene), including unscaled ZPEs. – [c] SCIPCM-B3LYP/6−31G(d,p)//SCIPCM-B3LYP/6−31G(d,p) energies in hartrees. Zero-point vibrational energies (kcal/mol) and number of imaginary frequencies in parentheses. – [d] $E(\text{cation}_{(aq)}) - E(\text{neutral}_{(aq)})$ in kcal/mol with respect to the most stable ion (open for acetylene, closed for ethylene). [e] E(water) − E(gas) in kcal/mol, including unscaled ZPEs. – [f] Experimental PA[26] = 153.3. – [g] Experimental PA[31] = 162.6. – [h] Unconstrained geometry optimization with initial open geometry led to the bridged form (see previous line).

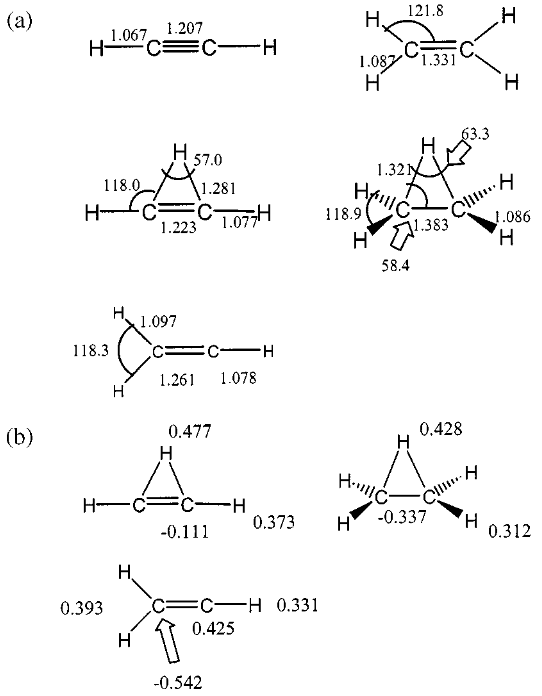

Figure 4. (a) Structures and (b) NBO atomic charges in water [SCIPCM-B3LYP/6−31G(d,p)]

tured the open and bridged ions as minima, characterized as such by vibrational analysis. At this level, the former is more stable, albeit by a smaller amount of energy (0.7 kcal/mol) than in the gas phase. SCIPCM optimization caused very small structural changes in all species.

The hydration energies of the open and bridged forms of $C_2H_3^+$ differ by just 0.04 kcal/mol, and can be considered equivalent for the purpose of this work. Even with SCIPCM geometries, the hydration of $C_2H_5^+$ is still less exothermic than that of either form of $C_2H_3^+$ by ca. 4 kcal/mol, essentially in agreement with the above results obtained with gas-phase geometries and IPCM water, and especially with experimental m^* values obtained from kinetic acidity dependences.[4]

The stronger hydration of $C_2H_3^+$ might originate from the fact that in the open vinyl cation the sp, carbon atom has a much higher positive charge than the sp^2, carbon atom in the bridged ethyl cation, as noted above. However, this trend is reversed in the bridged ion (whose stability is quite comparable to the open one) where the carbon atoms are negatively charged, so this feature does not seem adequate to explain the observed energetics. The stronger hydration of $C_2H_3^+$ rather seems to be due to the larger charge residing on its hydrogen atoms both in gas and water phase. Moreover, the solute polarization induced by the continuum is slightly larger for $C_2H_3^+$, as shown by the changes in atomic charges, which are more positive for $C_2H_3^+$ than for $C_2H_5^+$.

Energetics of Protonation of Acetylene and Ethylene

The data obtained so far allow us to calculate the enthalpy for the dissociation process $BH^+_{(aq)} \rightarrow B_{(aq)} + H^+_{(aq)}$ from the Born−Haber cycle (Figure 5) as in Equation 1:

$$\Delta H_{(aq)} = H_{(g)}(B) + H_{(g)}(H^+) - H_{(g)}(BH^+) + \Delta H_{aq}(B) + \Delta H_{aq}(H^+) - \Delta H_{aq}(BH^+) \quad (1)$$

$H_{(g)}(i)$ denotes the enthalpy in the gas phase, and $\Delta H_{aq}(i)$ the enthalpy of hydration (gas-phase to water transfer) of species i. Since calculated energies have been corrected with zero-point energies, they may be regarded as approximations of the enthalpy. Introducing $\Delta H_{aq}(H^+) = -262.2$ kcal/mol[24], we estimate that $\Delta H_{(aq)} = -33.2$ and -28.2 kcal/mol for acetylene and ethylene, respectively. Although these figures depend on $\Delta H_{aq}(H^+)$, which is an estimated value, relative values are of course not affected.

Hence, the protonation of acetylene in water is more endothermic than that of ethylene by 5 kcal/mol. This is due to the fact that in the gas phase acetylene is less basic than ethylene by 7.4 kcal/mol, which was attributed to a weaker π bond in the latter.[25] This is only partly compensated for by the more exothermic hydration (by 3.8 kcal/mol) of the vinyl cation, the remainder originating from the hydration of the neutral species.

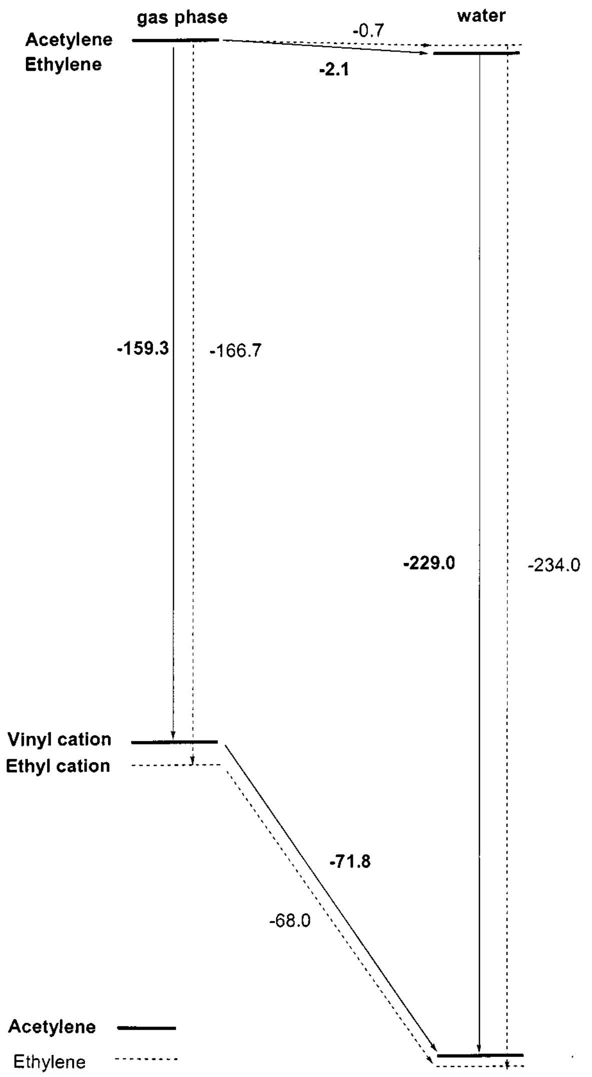

Figure 5. The Born−Haber cycle for the protonation of acetylene and ethylene; energies in kcal/mol

Conclusions

Even though an evaluation of all factors affecting the proton-transfer equilibrium of acetylene and ethylene in water may require an explicit consideration of solvent molecules, continuum solvent calculations provide a convenient means of investigating the solvent effect on such equilibria. Thus, the lower basicity of acetylene (both in the gas and water phases) is due to the intrinsically lower stability of the vinyl cation, although this cation is more strongly hydrated than the ethyl cation, in agreement with kinetic data. However, within the scope of the SCIPCM model, the solvent water does not cause any noticeable geometry change in any of the species investigated.

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