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Ab Initio Study of Structure and Reactivity of $H_2CO{\cdot}H_2O^{\cdot+}$ and Related Radical Cations

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Abstract: An ab initio Hartree–Fock and Möller–Plesset study of the radical cations obtained by ionization of the formaldehyde–water hydrogen bonded dimer is reported. Two radical–cation complexes with different bonding patterns were identified at the SCF level (**2a** and **2b**), one of which (**2a**) closely resembles the formaldehyde radical cation (FRC) solvated by a water molecule. Geometry optimization at the MP2 level, however, demonstrates that **2a** is not stable as a FRC–water complex. It undergoes proton transfer instead, to end up as a $H_3O^+{\cdot}HCO^{\cdot}$ complex, with the hydronium ion bound to the C atom of the radical. The reaction paths for this complex were investigated and compared with those of FRC. It was found that the most stable complex on these reaction paths is obtained after a H_3O^+ 1,2-shift in the FRC. This product, best described as a complex of $HCO^{\cdot}$ and H_3O^+, is analogous to the recently reported $HO^{\cdot}{\cdots}H_3O^+$ and $HCO^{\cdot}{\cdots}NH_4^+$ and lies in a well deep enough to be observable experimentally. Different possible outcomes of the experiments are discussed in the light of the relative stability of the complexes obtained on the reaction paths.

Introduction

One of the simplest but fundamental reactions a molecule can suffer is the loss or gain of an electron to form the corresponding ionic radical. Consequently, these species have attracted considerable interest in recent times.[1–24] Formerly, studies of ionization processes in the gas phase were focused mainly on high-energy events produced in electron-impact mass spectroscopic experiments. With the advent of lasers[25] and molecular beams[26,27] it is now possible to study these radical ions in more controlled conditions. New experimental techniques—like matrix isolation electron paramagnetic resonance[28] or multiphoton ionization,[29–33] for instance—are based on the use of those tools. These new techniques also allowed the study of ionization of clusters formed in supersonic beams. More complex reactions than simple bond breaking and dissociation can then take place. Particularly, radical cations of hydrogen-bonded dimers—as well as solvated radical ions—and their reactions are becoming more interesting both for experimentalists and theoreticians.[6,20,34–37]

Several studies were published on radical cations of oxygen-containing compounds.[1–3,13,14,24,35,43] They showed the existence of distonic cation radicals, species in which the charge and the radical sites are—in a formal sense—centered at different atoms.[37–40] These distonic radicals can even be kinetically and thermodynamically more stable than their conventional counterparts. Some reports exist implying that these differences in stability depend on the distance between the formal location of the charge and the unpaired electron.[38,41,42]

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Postma et al.[14] recently studied the loss of CO from the glycolaldehyde radical cation, $HOCH_2CHO^{\bullet+}$, to give the ylide ion $CH_2OH_2^{\bullet+}$. They found that the dissociation of the metastable glycolaldehyde radical cation occurs at the thermochemical threshold, the process occurring through a hydrogen-bridged ion of the type $[CH_2O(H)\cdots H\cdots CO]^{\bullet+}$. Some of the structures found—i.e., **2** in Scheme 2 of ref 14—are specially interesting because the charge and the unpaired electron reside in different fragments of the hydrogen-bonded complex. Similar structures are shown in a more recent paper by Schaftenaar et al.[24] where a combined experimental and ab initio study of the gas-phase chemistry of the methyl carbamate radical cation is reported. They also found hydrogen-bridged structures as well as hydrogen-bonded distonic cation radicals with the charge in a different fragment than the unpaired electron. Finally, two papers by Radom are worth noticing. In the first one, Ma et al.[44] reported a state-of-the-art study of the rearrangement and dissociative reactions of the methanol radical cation, $CH_3OH^{\bullet+}$. In the second and most recent one, Smith et al.[43] reported a comparison between the ionized methyl formate, $CH_3OCHO^{\bullet+}$, and its distonic isomer, $^{\bullet}CH_2OC^+HOH$.

Less information is available on radical cations derived from neutral hydrogen-bonded complexes. Some work was done on the cation radicals derived from the water dimer.[36] Essentially, a proton transfer from the water monomer losing the electron to the other monomer occurs, giving rise to the ion–dipole complex $OH_3^+\cdots OH^\bullet$. Burgers et al.[35] recently investigated the $[H_2CO\cdots H_3N]^{\bullet+}$ cation radical—within the context of a general study of the $[CH_5NO]^{\bullet+}$ potential energy surface—and found it to have a hydrogen-bridged structure of the type $[H_2CO\cdots H\cdots NH_2]^{\bullet+}$. They also found a proton-transfer complex, which can be written as $[HCO^\bullet\cdots NH_4^+]$, as the most stable structure. Postma et al. studied the radical cations derived from the vinyl alcohol–water and vinyl alcohol–methanol complexes[34a,c] as well as those obtained from the ketene–water dimer.[34b] Additional information available on cation radicals derived from hydrogen-bonded dimers can be found in the works of Burgers and Terlouw[34d] and Heinrich and Schwarz.[34e]

In this work we present a study of the radical cations derived from the formaldehyde–water dimer and their possible reaction pathways. We found several different stable structures involving conventional and distonic radical cations, arising from both the conventional hydrogen-bonded formaldehyde–water dimer and the dipole-coupled complex. The most interesting structure found—actually the global minimum on the studied potential energy surface—is of the type $HCO^\bullet\cdots H_3O^+$, being similar both to $OH_3^+\cdots OH^\bullet$ [36] and to $HCO^\bullet\cdots NH_4^+$.[35] As far as we know, no experimental information is available yet on the formaldehyde–water or water dimer radical–cation complexes.

Methods Section

Standard unrestricted Hartree–Fock and Möller—Plesset *ab initio* calculations were done using GAUSSIAN86[45] and GAUSSIAN90[46] packages. Complete geometry optimization of all the structures presented in this work was done using Schlegel's method[47] with the basis sets 4-31G[48]—for exploration of the PES—and 6-31G(d,p)[49] and 6-311+G(d,p)—for production. In all cases, spin contamination was carefully monitored and checked to be below normal thresholds. Frozen-core unrestricted Möller–Plesset[50] calculation of the correlation energy at the Hartree–Fock 6-31G(d,p) optimized geometries was done at second (MP2) and third (MP3) orders. Complete geometry optimizations at the full—i.e., no frozen cores—MP2/6-311+G(d,p) level were done using gradient techniques. Optimizations were carried out in the symmetries given in Table II and the force constant matrices were checked to have the correct number of negative eigenvalues (0 for equilibrium structures and 1 for transition states). Analytical second derivatives[51] for all the species at the 4-31G level, and for minima and first-order saddle points at the 6-31G(d,p) level, were used both for characterizing the order of the critical points on the PES and for calculating the zero-point energies (ZPE). Numerical second derivatives at the 6-311+G(d,p) were used only for characterizing the critical points. It is noted that MP2 calculations give erroneous results for the stabilization energy of the isomeric pair $H_2CO^{\bullet+}/HCOH^{\bullet+}$.[52] However, we have shown that this method can be used and gives correct results for the hydrogen-bonded cation radicals we are studying in this work[53]

Results and Discussion

Structure of the Formaldehyde–Water Radical Cations. Neutral formaldehyde–water complexes were studied theoretically with good precision in recent years. The work of Kumpf and Damewood[54] and the paper by Vos et al.[55] are particularly worth mentioning in this context. References to former work can be found in a recently published paper.[56]

Kumpf and Damewood[54] studied several possible structures for the $CH_2O\cdot H_2O$ complex. They concluded that the most stable dimer is **1a**, a strongly bent hydrogen-bonded dimer. The most exact calculations on this dimer agree in that its stabilization energy is about 4.6 kcal/mol.[54-56] A close second is the conventional hydrogen-bonded dimer, **1c**, which is 0.7 kcal/mol less stable than **1a** at the ZPE/MP2/6-31G(d,p) level.

Formaldehyde is known to be readily hydrated—a difference with higher aldehydes—according to the reaction $CH_2O + H_2O \rightarrow CH_2(OH)_2$. Kumpf and Damewood also identified a dipole-coupled complex, **1b**, that may be the precursor for this reaction. This complex is 1.4 kcal/mol less stable than **1a** at the best level of calculation, ZPE/MP4SD/6-311+G(d,p).

Geometry optimizations of the radical cations started from the optimum **1a** and **1c** geometries give rise to the same structure **2a**. However, if the optimized structure **1b** is used as the starting point, then a different cation radical structure, **2b**, is obtained. The structures and geometries of these and the other species studied in this work are shown in Figure 1. The energies of these structures at different theoretical levels are collected in Table I.

Radical-cation complexes are much more stable with respect to the formaldehyde radical cation and water than the neutral complexes are with respect to CH_2O and H_2O. In the case of the SCF optimized structures, the relative stability of the ionic complexes is opposite to that of their neutral counterparts (**1a** is more stable than **1b** while **2a** is *less* stable than **2b**—see Table I). Examining the structure of the ionic complexes shown in Figure 1, one can see that in **2a** the C1O2 bond length is similar

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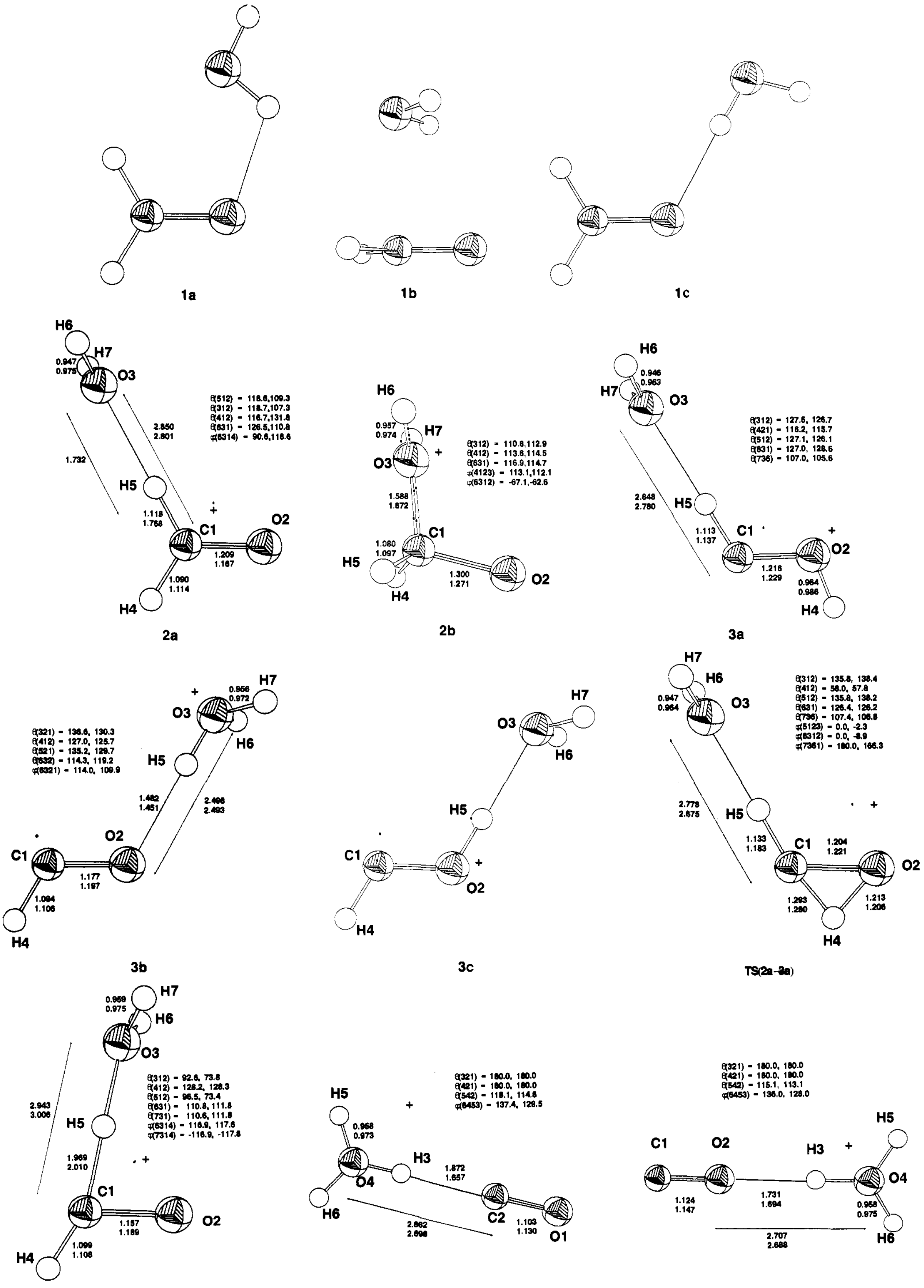

Figure 1. Structures of the most important species studied in this paper, showing the values of the optimized geometrical parameters at the SCF/6-31G(d,p) (first entry) and MP2/6-311+G(d,p) levels. Bond lengths in Å, bond angles in degrees.

to that in CH_2O (1.209 Å vs 1.184 Å) while the hydrogen bond present in **1a** has disappeared. Both facts are consistent with an ionization from the lone-pair orbitals of the oxygen in formaldehyde. A new hydrogen bond is now formed involving the

Table I. Stability of Formaldehyde–Water Neutral and Radical-Cation Dimers

structure	4-31G[a] HF	6-31G(d,p)[a] HF	6-31G(d,p)[a] MP2[b]	6-31G(d,p)[a] MP3[b]	6-311+G(d,p) MP2
1a[c]	−7.1	−5.1	−6.3	−6.0	
1b[c]	−4.0	−3.4	−4.0	−3.8	
2a[d]	−27.9	−21.2	−25.1	−24.0	−40.7
2b[d]	−37.0	−26.1	−30.0	−29.2	−23.8

[a] Relative energies in kcal/mol. [b] At the HF/6-31G(d,p) optimum geometry. [c] With respect to isolated formaldehyde and water. [d] With respect to isolated formaldehyde radical cation and water.

hydrogen atoms of formaldehyde—due to their much increased positive formal charge. Water was transformed from a proton donor to a proton acceptor after ionization of the complex. In **2b**, on the other hand, the C1O2 bond length is considerably larger than in formaldehyde (1.300 Å vs 1.184 Å) and the previously weak C1–O3 interaction has been much reinforced (bond length of 1.588 Å in the radical cation, **2b**, vs 2.983 Å in the neutral complex, **1b**). These facts indicate ionization from the bonding π orbital in CH$_2$O. Moreover, an analysis of the spin density of both complexes shows the unpaired electron to be located on the oxygen of CH$_2$O both for **2a** (spin density of 1.29) and for **2b** (spin density of 1.13).

As can be seen from the stabilities given in Table I, the inclusion of dynamical correlation yields qualitatively different results, with **2a** more stable than **2b** at the MP2/6-311+G(d,p)//MP2/6-311+G(d,p) level. This fact arises because in the optimized geometry of **2a** at the correlated level the proton is already transferred from formaldehyde to water (see Figure 2) contrary to the case in the SCF optimized structure. The ion-dipole interaction in **2a** is stronger at the MP2 than at the SCF levels (the C1O3 distance decreases from 2.85 to 2.80 Å) because of that proton transfer.

Due to the structure of the complexes it seems reasonable to assume that the reactivity of **2a** will be closely related to that of formaldehyde radical cation, CH$_2$O$^{\bullet+}$ (FRC), while that of **2b** will parallel the chemistry of the intermediates in the water addition to formaldehyde, although the chemistry of these radical cations will be dominated by the presence of the charge. One can see, for instance, that **2b** resembles the TS for water addition to formaldehyde.[56] Moreover, **2b** can be compared with structure **e** of Burgers et al.[35] which is related to the TS for the direct addition of NH$_3$ to CH$_2$O studied by Williams.[57] Comparison of the CO and CN bond lengths in the structure of ref 35 (1.343 and 1.527 Å respectively at the SCF/6-31G(d,p) level) with the C1O2 and C1O3 bond lengths in **2b** (1.300 and 1.590 Å) shows that in both cases the structures are the products of nucleophilic addition to the FRC. In the following we will discuss only the possible reaction paths of **2a**. The study of the reactivity of **2b** will be published elsewhere.

Reactivity of FRC·W. FRC has a stable isomer, the hydroxy methylene radical cation, HCOH$^{\bullet+}$, HMRC.[55] Both structures are separated by a substantial barrier, about 46 kcal/mol, but HMRC is no more than 3.3 kcal/mol less stable than FRC (both results obtained at the ZPE/MP3/6-31G(d,p)//HF/6-31G(d) level). An oxonium ion, COH$_2^{\bullet+}$, was also found, 54 kcal/mol less stable than FRC but lying in a well deep enough—35 kcal/mol—to be experimentally observable.

Isomer **2a** can isomerize into either **3a** or **3c**, depending on which H atom of formaldehyde undergoes a 1,2 shift—either the one hydrogen bonded to water or the other one. **3a** is the water–HMRC (HMRC·W) complex in much the same way **2a** is the water–FRC (FRC·W) complex. **3c** is a new structure which is not stable. It suffers proton transfer from the HMRC to water—as happened to the water dimer radical cation[36]—to give the structure **3b**, the actual stable species. In Figure 1 are shown the geometrical parameters of **3a** and **3b** as well as those of the transition states **TS(2a→3a)** and **TS(2a→3b)** corresponding to the reactions **2a** → **3a** and **2a** → **3b**, respectively. Total and relative energies for all the species considered in this work are collected in Tables II and III.

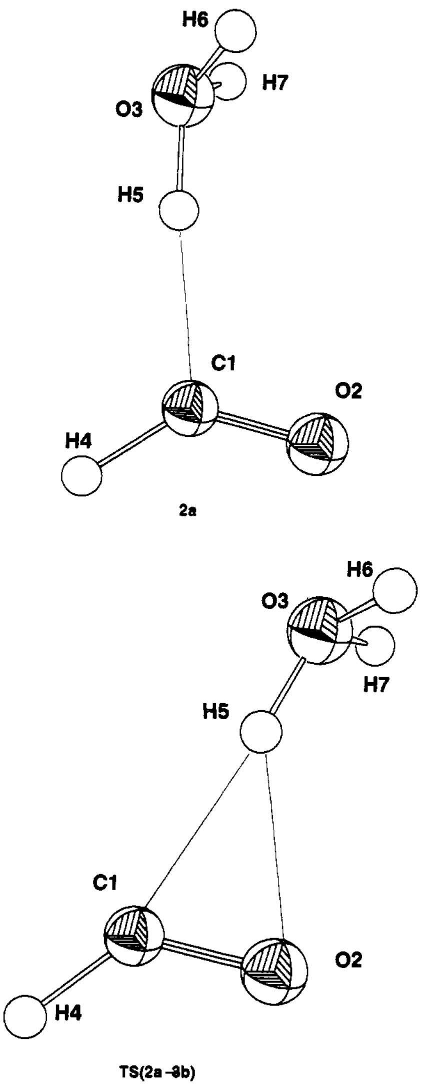

Figure 2. Structure of the **2a** and **TS(2a→3a)** species as obtained through geometry optimization using the MP2/6-311+G(d,p) method. Compare with the structures given in Figure 1.

Comparison of the transfer of the non-hydrogen-bonded H of formaldehyde in the FRC and the FRC·W complex shows that water has little effect on this 1,2-shift (**TS(2a→3a)**). Water destabilizes only slightly the HMRC with respect to FRC.

The transfer of the "hydrogen-bonded H" is very different (**TS(2a→3b)**). First, much less energy is necessary to reach the transition state. Second, the ion-dipole radical (IDR) **3b** is the most stable structure obtained, the actual global minimum on the explored PES. At the SCF level, the transition state **TS(2a→3b)** arises from the coupling of two different processes. On one side there is the 1,2-shift which is responsible for the high relative energy of the **TS(2a→3a)** transition state. However, since the basicity of the H$_2$O fragment is higher than that of HCO$^\bullet$ (protonation energy of water is approximately −179 kcal/mol at the MP3/6-31G(d,p) level vs a value of −159 kcal/mol for HCO$^\bullet$) the proton is transferred to water well before the highest point of the reaction path for the 1,2-shift is reached. A similar proton transfer was observed for the water dimer radical cation in previous works.[36] Burgers et al.[35] found a similar complex, HCO$^\bullet\cdots$HNH$_3^+$, as the most stable species in their studied [CH$_5$NO]$^{\bullet+}$ PES. Using comparable methods this

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Table II. Total Energies, in Hartrees, of the Different Species Participating in the Reactions Studied

		4-31G			6-31G(d,p)				6-311+G(d,p)
structure	sym	HF	$\langle S^2 \rangle$	ZPE[a]	HF	$\langle S^2 \rangle$	MP2[b]	MP3[b]	MP2
H_2O	C_{2v}	−75.908 636	0.00	14.03	−76.023 615	0.00	−76.219 057	−76.225 572	−76.293 724
$CH_2O^{+\bullet}$	C_{2v}	−113.347 331	0.81	17.21	−113.525 414	0.79	−113.782 450	−113.799 746	−113.871 559
$H^\bullet$		−0.498 233	0.75	0.0	−0.498 233	0.75	−0.498 233	−0.498 233	−0.499 810
H_3O^+	C_{3v}	−76.200 603	0.00	22.70	−76.310 325	0.00	−76.505 153	−76.513 377	−76.568 950
CO	C_∞	−112.552 356	0.00	3.30	−112.737 877	0.00	−113.018 038	−113.017 324	−113.115 070
$COH^\bullet$	C_s	−113.023 793	0.76	9.17	−113.198 775	0.76	−113.465 866	−113.477 014	−113.563 802
$HCO^\bullet$	C_s	−113.070 678	0.78	8.91	−113.249 688	0.76	−113.538 520	−113.540 791	−113.636 319
2a	C_s	−189.300 489	0.80	33.38	−189.582 794	0.78	−190.041 514	−190.063 513	−190.230 098
2b	C_s	−189.314 873	0.76	36.49	−189.590 694	0.76	−190.049 244	−190.071 808	−190.203 203
TS(2a→3a)	C_1	−189.179 283	0.80	28.90	−189.484 016	0.78	−189.973 537	−189.984 815	−190.137 124
TS(2a→3b)	C_1	−189.287 999	0.76	33.25	−189.577 279	0.76	−190.068 020	−190.077 928	−190.226 498
3a	C_s	−189.280 980	0.76	33.56	−189.568 549	0.76	−190.039 269	−190.054 151	−190.200 322
3b	C_s	−189.320 402	0.77	33.44	−189.599 002	0.76	−190.082 071	−190.092 644	−190.240 223
4b	C_s	−188.779 787	0.00	27.56	−189.064 886	0.00	−189.539 158	−189.547 693	−189.696 459
4a	C_s	−188.774 014	0.00	28.19	−189.066 109	0.00	−189.549 374	−189.553 864	−189.710 546

[a] In kcal/mol. [b] At the HF/6-31G(d,p) optimized geometries.

Table III. Relative Energies, in kcal/mol, for the Isomerization of FRC and FRC·W

	4-31G	6-31G(d,p)			6-311+G(d,p)	
structure	HF	HF	MP2[a]	MP3[a]	MP2	ZPE/MP2
FRC + H_2O	0.0	0.0	0.0	0.0	0.0	0.0
2a	−27.9	−21.2	−25.1	−24.0	−40.7	−38.6
TS(2a→3b)	−20.1	−17.7	−41.7	−33.0	−38.4	−36.4
3b	−40.4	−31.4	−50.6	−42.2	−47.0	−44.8
$HCO^\bullet + H_3O^+$	−9.61	−6.89	−26.5	−18.1	−25.1	−24.7
4b + $H^\bullet$	−13.8	−8.84	−22.5	−12.9	−19.4	−23.1
TS(2a→3a)	48.1	40.8	17.6	25.4	17.7	15.4
3a	−15.7	−12.2	−23.7	−18.1	−22.0	−19.7
$COH^\bullet + H_3O^+$	19.8	25.1	19.1	21.9	20.4	21.0
4a + $H^\bullet$	−10.2	−9.61	−28.9	−16.8	−28.3	−31.4
CO + $H^\bullet + H_3O^+$	3.00	1.63	−12.5	−2.27	−11.6	−16.8

[a] At the HF/6-31G(d,p) optimum geometry.

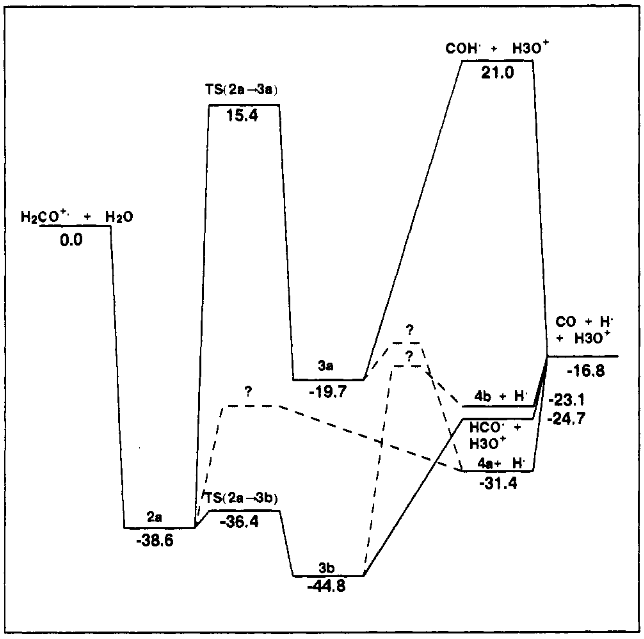

Figure 3. Scheme of the ZPE/MP2/6-311+G(d,p) energetic ordering of the different species studied in this work. Relative energies given in kcal/mol. The broken lines indicate the possible presence of transition states that have not been looked for in this work.

complex is however much less stable than **3b** toward decomposition into $HCO^\bullet$ and NH_4^+ (or H_3O^+ for **3b**). Some years ago, Postma et al.[34a] studied the vinyl alcohol–water dimer radical cation. In this case however, although formally similar to the other ones, there is not a clear transfer of the proton from the alcohol to water, which seems to be a genuine effect of the more alike basicity of water and the vinyl alcohol radical (better calculations than the ones reported in that paper—MP2/6-311G(d,p) geometry optimizations—support the same qualitative arguments). A complete discussion of this point is given elsewhere.[59]

At the MP*n*/6-31G(d,p)//HF/6-31G(d,p) (n = 2, 3) levels the relative energy of TS(**2a**→**3b**) is lower than that of **2a**. This fact implies that dynamic correlation is not only quantitatively but also qualitatively important in this case. As was pointed out in the previous section, the MP2/6-311+G(d,p) results show that the proton is already transferred to the water molecule in **2a**, before the FRC undergoes the 1,2-shift. Looking at the MP2 optimized structures of TS(**2a**→**3b**) shown in Figure 2, it is clear that the overall isomerization process corresponds to an H_3O^+ 1,2-shift. The energetics of the process at the MP2/6-311+G(d,p) level is also shown in Tables II and III.

FRC and HMRC can, according to what was observed in mass-spectroscopic experiments, decompose through hydrogen loss in the following three ways

$$H_2CO^{\bullet+} \rightarrow HCO^+ + H^\bullet \qquad \text{(I)}$$

$$HCOH^{\bullet+} \rightarrow HCO^+ + H^\bullet \qquad \text{(II)}$$

$$HCOH^{\bullet+} \rightarrow COH^+ + H^\bullet \qquad \text{(III)}$$

The complexes of FRC and HMRC may behave in a similar way, but now the presence of water forces the consideration of some other structures. For reaction I we have instead

$$[H_3O^+{\cdot}HCO^\bullet]\ (\mathbf{2a}) \rightarrow [H_2OH{\cdot}CO]^+\ (\mathbf{4a}) + H^\bullet \rightarrow H_3O^+ + CO + H^\bullet \qquad \text{(i)}$$

Reaction II is transformed now to

$$[H_2O{\cdot}HCOH]^{\bullet+}\ (\mathbf{3a}) \rightarrow [H_2OH{\cdot}CO]^+\ (\mathbf{4a}) + H^\bullet \rightarrow H_3O^+ + CO + H^\bullet \qquad \text{(ii)}$$

and, finally, reaction III gives

$$[HCO{\cdot}H_3O]^{+\bullet}\ (\mathbf{3b}) \rightarrow [CO{\cdot}H_3O]^+\ (\mathbf{4b}) + H^\bullet \rightarrow H_3O^+ + CO + H^\bullet \qquad \text{(iii)}$$

The energetics of these three processes, considering ZPE/MP2/6-311+G(d,p) results, has been arranged schematically in Figure 3. We did not consider reaction processes leading to high-energy products (as the hypervalent $H_3O^\bullet$, for instance). For low-energy content the only probable pathway from the cation radical **2a** is via the TS(**2a**→**3b**) to the $HCO{\cdot}H_3O^+$ IDR **3b**. Although we did not calculate the transition state for the direct abstraction of a hydrogen atom from the complex **2a** (reaction i)—due to the inability of the UMP2 method to cope with that problem—we believe that this reaction is unlikely to occur. The corresponding transition state must lie above the level of $H_3O^{+}{\cdot}CO$ (**4a**) + $H^{\bullet}$ (−31.4 kcal/mol in Figure 3), which, in turn, lies above the TS(**2a**→**3b**) transition state (−36.4 kcal/mol in Figure 3). Bouma et al.[58] calculate the decomposition level $H^{\bullet}$ + HCO^{+} to be 23 kcal/mol higher than FRC, while from our calculations the $CO{\cdot}H_3O^{+}$ (**4b**) + $H^{\bullet}$ level lies about 21 kcal/mol higher than **3b**. This may indicate that H_3O^{+} stabilizes only slightly the C–H bond cleavage (although this cannot be stated for sure since we did not study the transition states, a fact indicated by the question marks in Figure 3). The same indication is obtained looking at the ca. 7 kcal/mol difference between **2a** and the $H_3O^{+}{\cdot}CO$ (**4a**) + $H^{\bullet}$ decomposition products. Bouma predicted computationally—and found experimentally—that only HCO^{+} ions, as opposed to HOC^{+}, were going to be found. The proposition was based on the fact that the energy necessary for reaction II was much less than that necessary for reaction III. In the calculations described in this paper we observe the same behavior for the formaldehyde–water complex, i.e. **4a** is more stable than **4b** and, therefore, its formation is thermodinamically favored. However, **4a** arises either from **3a**, which is disfavored energetically, or from **2a** by direct H atom abstraction, and it is not likely that it is present among the products except in special conditions. Which final product actually will be found will depend on the energy content and distribution in the reactant **2a**. If enough energy is available, say by electron impact, probably all the reaction channels are open and the final products observed would be $H^{\bullet}$, CO, and H_3O^{+} (a peak at m/z 19 in the mass spectrometer). With less energy available, the reaction path through TS(**2a**→**3a**) will become unlikely. In addition to the preceding decomposition products, careful experimentation would probably produce the **4a** or **4b** cations (peaks at m/z 47). The presence of one or another will be determined by the height of the barriers for the processes **2a** → **4a** + H and **3b** → **4b** + H whose transition states have not been studied in this work. Even lower energy content in the initial reactant will allow only the formation of **3b** (m/z 48), specially if energy dissipation is fast enough. In experiments done using laser beams instead of electron impact for obtaining ionization, the energy content probably will be low. However, since these experiments are usually done in supersonic molecular beams (low temperatures) energy dissipation is not fast. Therefore, in this situation, the outcome of the reaction will depend on the total energy content and the way it is distributed among vibrational modes in **2a**. Excitation of stretching modes of the CH bond will favor H loss and the obtention of the $H_3O^{+}{\cdots}CO$ product. Excitation of bending vibrations of the HCO group will instead favor the 1,2-shift (which process actually has a lower barrier) and give the product $HCO^{\bullet}{\cdots}H_3O^{+}$. If energy dissipation does not occur, the energy diagram shows that H loss is possible in this product and $CO{\cdots}H_3O^{+}$ or HCO + H_3O^{+} will be the final species obtained.

Conclusions

An ab initio Hartree–Fock and Möller–Plesset study of the cation radicals obtained by ionization of the formaldehyde–water hydrogen-bonded dimer has been done using the 4-31G, 6-31G(d,p), and 6-311+G(d,p) basis sets.

Two radical-cation complexes with different bonding patterns were identified at the SCF level. One of them, **2a**, resembles the FRC solvated by a water molecule. It is obtained because the ionization occurs from the lone pairs of the O in formaldehyde. Consequently, the initial H bond is broken and a new one formed between water as a proton acceptor and an H from $CH_2O^{\bullet+}$. Optimization at the MP2/6-311+G(d,p) level, however, shows that this complex is not stable as such but that the equilibrium structure has the proton transferred to the water fragment. The second complex found, **2b**, was obtained starting at the structure of a dipole-coupled water–formaldehyde neutral complex. Its structure shows partial rupture of the double bond in formaldehyde and partial addition of the water molecule to $CH_2O^{\bullet+}$.

The reaction paths for **2a** only were investigated and compared with those of FRC. It was found that the most stable complex in the potential energy surface is obtained after an H_3O^{+} 1,2-shift in the FRC. This product, best described as a complex of $HCO^{\bullet}$ and H_3O^{+}, is analogous to the recently reported $HO^{\bullet}{\cdots}H_3O^{+}$ and $HCO^{\bullet}{\cdots}NH_4^{+}$ and lies in a well deep enough to be observable experimentally. It is observed that if the energy content of the initial reactant is low enough and energy dissipation is slow, the favored product of this reaction will be $CO{\cdots}H_3O^{+}$. However, if conditions favorable for a direct H atom loss from **2a** predominate, the product $H_3O^{+}{\cdots}CO$ would be observed instead.

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