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A Theoretical Study of Electrophilic Reactions

II. The Electronic Structure of Protoformyl and Protoacetylium Dications

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The electronic structures of protonated formyl and acetylium cations and their deprotonation paths leading to HCO^+, COH^+ and CH_3CO^+ have been studied by means of *ab initio* calculations. The results support Olah's theory that dipositive species can be the *de facto* reagents in electrophilic reactions.

Key words: Protoformyl, electronic structure of ~ – Protoacetylium dication, electronic structure of ~

1. Introduction

In his systematic studies on electrophilic reactions, Olah suggested [1] that the reactive species during nitration reaction in superacidic solvents could be the protonated nitronium dication. More recently, in a study of electrophilic reactions at single bonds, he found [2] that the formyl cation can interact with the superacidic solvent leading to a highly reactive dipositive species. Even if the formyl cation is known to exist in the gas phase [3], Olah was unable to observe it as a long-lived species in his superacidic solvent. He explained the HCO^+ instability by the oxygen lone pair undergoing a second protolytic interaction with the solvent. The dipositive species, which is formed by interaction of H^+ with the lone pair of the oxygen, is destabilized by charge–charge repulsion and eliminates the proton from the carbon to give protonated carbon monoxide, which then exchanges rapidly with the acid solvent

$$HCO^+ + H^+ \rightleftharpoons H^+ \ldots C{=}O \ldots H^+ \rightarrow H^+[C{=}O{-}H]^+ \rightarrow H^+ + CO \tag{1}$$

He also suggested [4] that in the reaction of alkanes with acetylium ion, always in superacidic media, the *de facto* reactive species is not the acetylium ion itself, but its protonated form.

In the first paper of this series [5] we performed an *ab initio* calculation on the protonated nitronium ion and we were not able to find a species which could be identified as the nitronium ion; however, it must be kept in mind that dications in the gas phase are generally more unfavourable than in solution.

In this paper we study the electronic structures of protoformyl and protoacetylium ions and the reaction paths leading to the formation of the corresponding monocations.

2. Calculations and Discussion

Our wave functions are *ab initio* solutions of Roothaan's equations for closed shell systems. Calculations have been performed with the standard split valence shell basis 4-31G [6], by using a modified version of the GAUSSIAN 70 program [7], which performs a simultaneous optimization of the geometrical variables it is dealing with [8].

The geometries of the HCO^+, COH^+ and $HCOH^{++}$ systems have been fully optimized, while the removal of H^+ leading to HCO^+ or to COH^+ has been verified to be linear only at a few significant points. Optimized geometries, charge distributions and relative stabilization energies for the considered systems along the dissociation paths are reported in Table 1.

The total energies for HCO^+ and COH^+ are –112.77930 a.u. and –112.74463 a.u. respectively. These results, which predict the formyl cation to be more stable than the oxygen protonated carbon monoxide, are in agreement with all previous *ab initio* calculations performed on these systems [9–11]. Our stabilization energy of 21.8 kcal/mole can be compared with the value of 18.4 kcal/mole obtained with an essentially double zeta basis set [11].

Our calculated equilibrium geometries are to be compared with the experimental data available for HCO^+: $r(CO) = 1.096$ Å and $r(CH) = 1.029$ Å [12], and with the results obtained by Bruna, Peyerimhoff and Buenker [11]:

HCO^+: $r(CO) = 1.1083$ Å, $r(CH) = 1.0847$ Å

COH^+: $r(CO) = 1.165$ Å, $r(OH) = 0.974$ Å.

Table 1. Dissociation of protoformyl dication leading to HCO^+ and COH^+. Distances are in Å and energies in kcal/mole

$r(CH)$	$r(CO)$	$r(OH)$	$q_{H(C)}$	q_C	q_O	$q_{H(O)}$	ΔE
1.079	1.096	∞	+0.516	+0.634	–0.150	+1.000	0.0
1.085	1.103	6	+0.531	+0.657	–0.188	+1.000	44.1
1.089	1.105	4	+0.542	+0.682	–0.224	+1.000	59.6
1.093	1.108	3	+0.554	+0.716	–0.268	+0.999	71.3
1.103	1.112	2	+0.583	+0.805	–0.357	+0.969	82.1
1.115	1.116	1.5	+0.614	+0.907	–0.424	+0.903	74.4
1.126[a]	1.114	1.046	+0.648	+1.019	–0.434	+0.767	56.0
1.5	1.125	1.035	+0.752	+0.982	–0.486	+0.752	75.6
2	1.135	1.016	+0.861	+0.922	–0.509	+0.726	99.6
3	1.151	0.996	+0.989	+0.855	–0.538	+0.694	99.1
4	1.156	0.989	+1.000	+0.867	–0.549	+0.682	86.0
6	1.160	0.984	+1.000	+0.889	–0.562	+0.673	68.3
∞	1.162	0.974	+1.000	+0.913	–0.572	+0.659	21.8

[a] Data corresponding to $HCOH^{++}$.

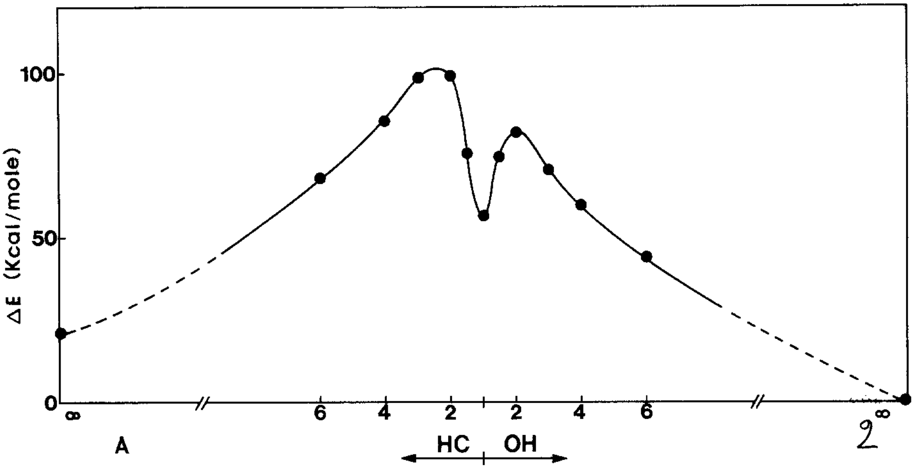

Fig. 1. Dissociation paths of $HCOH^{++}$ leading to HCO^+ and COH^+

The linearity of the cations is a well-known fact [9–12], but also the fact that the $HCOH^{++}$ system prefers a linear arrangement is not surprising, as it is the lone pair of the oxygen (or of the carbon) which interacts with the proton to give the dication.

In order to give theoretical evidence to reaction (1), the dissociation path of the protoformyl dication has been studied both for the CH bond and for the OH bond breaking. The calculation results are reported in Table 1, while Fig. 1 represents the dissociation path.

These results suggest that protonated formyl cation is a stable species which can dissociate into the corresponding stable monocations HCO^+ and COH^+ with energy barriers of about 26 and 43 kcal/mole respectively. These barrier values are very likely too high and more reasonable values could be obtained with configuration interaction calculations, but, as all species implied in the reaction are closed shell systems, it is reasonable to assume that the SCF curve is fairly reliable, at least as a qualitative suggestion. This statement is also supported by the correct behaviour of the charge distribution at large r(OH) and r(CH) values (see Table 1).

The values of all the optimized geometrical parameters of the acetylium ion, but r(CH), ∠HCC and ∠CCO, are reported in Table 2 (first row), together with charge distribution. A C_3 symmetry at the methyl group has been assumed. The total energy is −151.81790 a.u. The equilibrium arrangement of carbon and oxygen nuclei has been found to be linear, with a $r(\mathrm{CH})$ = value of 1.087 Å and ∠HCC = 109°. All these results are to be compared with the experimental geometry of the acetylium ion [13]: $r(\mathrm{CO}) = 1.108$ Å, $r(\mathrm{CC}) = 1.385$ Å, $r(\mathrm{CH}) = 0.84–0.97$ Å (estimated) and ∠CCO = 177° ± 2°.

In Table 2 are also reported the optimized geometries, charge distributions and energy differences (with respect to CH_3CO^+) of the protoacetylium dication and of $CH_3CO^+ \ldots H^+$ system for different O…H (reaction coordinate) values. Along the reaction path the geometry of the methyl group has been kept constant at the optimized values obtained

Table 2. Linear approach of a proton to CH_3CO^+ ion. Distances are in A and energies in kcal/mole

r(OH)	r(CO)	r(CC)	$q_{H(O)}$	q_O	$q_{C(O)}$	$q_{C(CH_3)}$	$q_{H(CH_3)}$	ΔE
∞	1.110	1.450	+1.000	−0.240	+0.753	−0.545	+0.344	0.0
6	1.111	1.449	+1.000	−0.276	+0.765	−0.551	+0.354	41.3
4	1.114	1.449	+1.000	−0.315	+0.786	−0.554	+0.361	54.3
3	1.117	1.448	+1.000	−0.364	+0.815	−0.558	+0.370	63.2
2	1.124	1.441	+0.996	−0.464	+0.900	−0.567	+0.390	67.3
1.5	1.130	1.433	+0.885	−0.541	+0.997	−0.573	+0.411	52.0
1.017[a]	1.133	1.420	+0.731	−0.560	+1.100	−0.576	+0.435	24.4
0.900	1.133	1.418	+0.645	−0.510	+1.119	−0.574	+0.440	31.3

[a] Data corresponding to CH_3COH^{++}.

for the acetylium ion. This assumption is justified by the small variations obtained for CO and CC bond lengths on going from the cation to its protonated species. The linearity of the reaction path has been verified only at a few points. The plot of the energy *versus* the reaction coordinate is reported in Fig. 2. The activation energy necessary to give $CH_3CO^+ + H^+$, starting from the dipositive species, is about 43 kcal/mole.

Also in this case our results are in favour of a stable dicationic species which dissociates to the corresponding monocation only by expending a not negligible amount of energy.

It is to be kept in mind that our results refer to molecules in gas phase, while experimental data are obtained for reactions in superacidic solvents which generally provide stable ion conditions, but which on the other hand seem to participate to the reaction mechanism by means of hydrogen bond formation. Within these limits, these results fully support Olah's theory that dipositive species can be the *de facto* reagents in electrophilic reactions.

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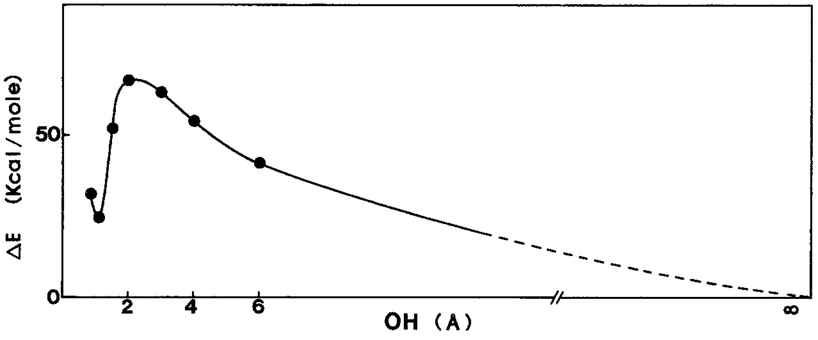

Fig. 2. Reaction path of $CH_3CO^+ + H^+$ system

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