Semiempirical Study of the Interacting Potentials for $\text{H}^+ + \text{CO}$ and $\text{H}^+ + \text{NO}^+$

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Abstract Semiempirical INDO molecular orbital calculations of the minimum energy path for the formation of $\text{HCO}^+$, $\text{HOC}^+$, $\text{HNO}^{++}$ and $\text{HON}^+$ from the proton reactions $\text{H}^+ + \text{CO}$ and $\text{H}^+ + \text{NO}^+$ are presented. Energy barriers, geometry relaxations and stabilization energies are given. Comparisons with ab initio SCF (Self-Consistent Field) and CI (Configuration Interaction) calculations are performed in order to assess the reliability of the calculations.

1. INTRODUCTION

Protonation is an interesting problem of increasing research interest. It has been intensively studied in recent years. An important achievement obtained is that to reproduce existing experimental data on protonation it is of essential importance to consider geometry relaxation. In this vein it has been established that geometry relaxation due to core ionization and protonation on the same site are related. Furthermore their chemical shifts are also correlated. A possible common basis for understanding these relationships may be provided by localized perturbation theory. Therefore the changes of valence electron density upon protonation and core hole formation may be related to older problems describable in terms of atom-atom and bond-atom polarizabilities as discussed elsewhere.

Interest in protonation in diatomic systems has increased, and this is related to ion-molecule reactions occurring in the interstellar space. This has led to a number of ab initio calculations of proton reactions. An important computational aspect arising from ab initio studies of triatomic radical ions in general is that very poor prediction of the relative stability is obtained at the SCF level.
An interesting example is found for $\text{HNO}^+$ and $\text{HON}^+$. At SCF with double-
zena basis set it results that $\text{HON}^+$ is the most stable\(^{16}\). Inclusion of
polarization functions in the basis set leads to an almost inexistent
barrier\(^{16}\). The first CI calculation was performed by Marian \textit{et al}\(^{16}\)
and a barrier of 11 kcal/mole was found, with $\text{HNO}^+$ as the most stable.
The next CI result is due to McLean \textit{et al}\(^{17}\), yielding the same trend
and a barrier of 13.2 kcal/mole. A very recent CI calculation\(^{18}\) increased
this value to 16.6 kcal/mole. The necessity of including correlation corrections prompts a practical limitation since geometry op-
timization at ab initio CI level is very expensive. Furthermore, it
would become out of reach for most systems of interest. This is par-
ticularly the case for a systematic study of proton approach to a
realistic molecule.

Most semiempirical methods utilize parameters chosen directly
from experiment. Therefore there exists the belief that the model
might extend beyond the confines of the theory. Hence, despite the
difficulty in defining correlation energy in a semiempirical scheme, in
some cases it may be "built-in". At this stage, there is no concern in
separating different energy contributions but obtaining qualitative
results directly related to experiment; a modest probe for future in-
vestigations on protonation. A systematic calculation of the reactions
$\text{H}^+ + \text{CO}$ and $\text{H}^+ + \text{NO}^+$ at the two possible sites will therefore be pre-

tented within the semiempirical INDO level\(^{19}\).

2. PROTONATION OF CO AND NO\(^+$

The linear $\text{HO}^+$ and $\text{HO}^+$ systems have been studied previously
at ab initio level by Bruna \textit{et al}\(^{15}\) and Summers and Tyrrell\(^{17}\). The lat-
ter authors have also studied the double ionized linear products $\text{HNO}^{++}$
and $\text{HON}^{++}$. Comparison to their results will be presented below.

Table 1 presents the results and some details for the inter-
acting potential for the reaction $\text{H}^+ + \text{NO}^+ \rightarrow \text{HNO}^{++}$, where $\text{HNO}^{++}$ is
found to be more stable than the $\text{HON}^{++}$ product. For these cases the
potential is repulsive in the early stages and becomes attractive in a
small region lying energetically above the limit of dissociation into
$\text{NO}^+ + \text{H}^+$. Hence, these states are found to be quasibound and unstable
upon dissociation in the proton path (see Fig. 1). Our stabilization

748
Table 1. Geometry, population and energy along the minimum energy path for $H^+ + NO^+ \rightarrow HNO^{++}$

<table>
<thead>
<tr>
<th>(a) $R_{NH}$ (Å)</th>
<th>(b) $R_{NO}$ (Å)</th>
<th>(c) $P_H$</th>
<th>(d) $\Delta P_N$</th>
<th>(e) $E_T$ (a.u.)</th>
</tr>
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<tbody>
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<td>0.0</td>
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<td>-26.9197</td>
</tr>
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</table>

(a) Fixed. (b) Optimized. (c) Electronic population in the incoming $H^+$. (d) Change in nitrogen population. (e) Total (valence) energy.

Figure 1 - Energy diagram (kcal/mole). Observe that 1 hartree = 627.7 kcal/mole.
energies (barrier for dissociation) are 46.2 kcal/mole (HNO$^{++}$) and 39.2 kcal/mole (HON$^{++}$) and the equilibrium configurations are found to be 75 kcal/mole and 76 kcal/mole above this dissociation limit, respectively. The study by Summers and Tyrrell$^{17}$ on HNO$^{++}$ showed a local minimum with a barrier to dissociation of only 1.7 kcal/mole. Since this value is lower than the zero point energy along the dissociation path, it implies that the system can not be observed even at very low temperatures. Our calculation finds a larger barrier and indicates that the dissociation should proceed by tunneling with an energy release $\Delta H$ of about 75 kcal/mole. Table 1 also shows that the first effect of the proton approach is to polarize the electronic charge of the target system.

The geometrical relaxations are presented in Table 2. The results emphasize the same trend as for core holes, as noticed previously by Palma et al.$^{12}$. This same trend is also found regarding relative stabilities of the isomeric products. Protonation in the carbon side gives more stability than in the oxygen side and leads to a decrease of the bond length as compared to the original CO system. These trends could not be verified previously in HNO$^{++}$ and HON$^{++}$ because the solely ab initio calculation found no stability for HON$^{++}$.$^7$ As discussed in the introduction, this result is probably due to the absence of correlation. In agreement with the above discussed trend we find here that protonation on the nitrogen leads to a small shortening of the bond distance and is the most stable (see fig. 1).

Table 2. Geometrical Relaxation ($\bar{A}$)

<table>
<thead>
<tr>
<th></th>
<th>$R_{CO}$</th>
<th>$R_{NO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.196</td>
<td>1.118</td>
</tr>
<tr>
<td>HCO$^+$</td>
<td>1.181</td>
<td>HNO$^{++}$ 1.116</td>
</tr>
<tr>
<td>HOC$^+$</td>
<td>1.214</td>
<td>HON$^{++}$ 1.130</td>
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</table>

The relative stability of HCO$^+$ over its isomer is found as 54.7 kcal/mole as compared to 18.8 kcal/mole$^3$ and 21.7 kcal/mole$^7$. This result indicates that the preferable protonation site is cor-
rectly described but the proton affinities are overestimated. We find it to be about 260 kcal/mole as compared to about 140 kcal/mole as obtained by Forsen and Roos. The energy picture is summarized in figure 1.

In agreement with the accurate CI calculations of Bruna et al., we find no barrier for the protonation of CO to form either COH\(^+\) or HCO\(^+\). This is indicative of the qualitative reliability of the interacting potential as ab initio SCF calculation leads to a spurious barrier for the formation of HCO\(^+\).

3. SUMMARY

The proton reactions H\(^+\) + CO and H\(^+\) + NO\(^+\) producing the triatomic linear systems HCO\(^+\), HOC\(^+\), HNO\(^+++\) and HON\(^+++\) have been studied within the semiempirical INDO level. Comparison with existing data leads to good overall agreement. The results reproduce the expected trends. The interacting potential for the reactions were obtained and analyzed. The results for the HNO\(^+++\) is interesting insofar as we obtain it as an unstable system under proton dissociation but this reverse process should occur by tunneling. More accurate calculations are hereby suggested to clarify this point.

Finally, the insight gained in this pilot study will hopefully be used in a more general study of proton reactions in larger molecules.

REFERENCES


Resumo

Cálculos de orbitais moleculares no modelo semi-empírico INDO são feitos para estudar a formação de HCO+, HOC+, HNO+ e HON+ a partir do processo de protonação H+CO e H+NO ao longo da trajetória de menor energia. Barreiras de energia, relaxações geométricas e energias de estabilização são dadas. Comparações com cálculos ab initio SCF (Self-Consistent Field) e CI (Configuration Interaction) são feitas para avaliar os resultados.