Theoret. Chim. Acta (Berl.) 47, 223–231 (1978)

THEORETICA CHIMICA ACTA

Ab initio Studies of the Protonation of CO, N_2 and NO^+: Calculation of the Minimum Energy Reaction Paths

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Ab initio molecular orbital calculations employing a 4-31G basis set have been used to study the minimum energy paths for the formation of HCO^+, COH^+, and $HCOH^{2+}$ from CO by protonation. The protonation of N_2 to give NNH^+ and $HNNH^{2+}$ and of NO^+ to form HNO^{2+} and NOH^{2+} have also been investigated. All species formed have linear equilibrium geometries and the minimum energy path for approach of the proton is along the line-of-centers of the heavy atoms. Energy barriers to the formation of the various species are given, where appropriate, and changes in geometry, ordering of molecular orbitals and orbital occupancy are discussed.

Key words: Reaction paths, minimum energy ~, for formation of HCO^+, COH^+, $HCOH^{2+}$ by protonation

1. Introduction

The study of ion-molecule reactions has been of considerable interest recently from the standpoint of processes observed in low-energy molecular beam experiments and because of interest in ion-molecule reactions in interstellar space. The protonation of N_2 [1] and CO [2] has been studied experimentally using low-energy molecular beam techniques and the species HCO^+ [3] and N_2H^+ [4] have been identified in a DC discharge. In addition, HCO^+ [5] and N_2H^+ [6] have been postulated as being present in interstellar clouds. There have also been a number of calculations dealing with the equilibrium structure and properties of the species HCO^+ [7–9], COH^+ [8, 10, 11] and N_2H^+ [7, 12] using a variety of basis sets. Peyerimhoff and Buenker have studied the potential surfaces of HCO^+ and COH^+ [8] and of N_2H^+ [12] using contracted Gaussian basis sets of double-zeta quality and CI. The potential surface for the dissociation of N_2H^+ [12] was calculated for a fixed N–N bond distance corresponding to the equilibrium value for

0040–5744/78/0047/0223/$01.80

ground state N_2 (1.094 Å) based on their observation that at a N–H distance of 2.0 bohr there was little change in the NN bond distance with approach of the proton. The potential surfaces for HCO^+ and COH^+ [8] were also calculated for a fixed CO distance (1.128 Å) again corresponding to the equilibrium value for CO.

The calculations reported in this paper repeat the determinations of the potential energy surfaces for HCO^+, COH^+ and N_2H^+ using a somewhat smaller basis but optimizing all geometrical parameters and compare the results obtained with those resulting from the use of a larger basis set. The results are extended to consider the potential surface resulting from the interaction of H^+ with HCO^+, COH^+ and N_2H^+ to give the doubly charged, doubly protonated species $HCOH^{2+}$ and $HNNH^{2+}$. In addition, the protonation of NO^+ to give HNO^{2+} and NOH^{2+} is also investigated. To our knowledge, there have been no calculations performed on these doubly charged species.

2. Method and Results

All calculations were carried out using the Gaussian 70 *ab initio* molecular orbital program developed by Hehre *et al.* [13] and using the Gaussian basis set, 4-31G. Tables 1–4 list the optimum geometries and energies for the minimum energy paths for the formation of HCO^+ and COH^+ from CO and the formation of $HCOH^{2+}$ from HCO^+ and COH^+. Tables 5 and 6 give the optimum geometries and energies for the minimum energy paths for the formation of HNN^+ from N_2 and $HNNH^{2+}$ from HNN^+ respectively. The optimum geometries and energies for the minimum energy paths for the formation of HNO^{2+} and NOH^{2+} are given in Tables 7 and 8 respectively. Table 9 gives the energy barriers, where appropriate, to the formation and decomposition of the species under consideration.

3. Discussion

All of the species studied in this investigation have linear equilibrium structures as predicted by Walsh's Rules [14] and in agreement with the results of Peyerimhoff

Table 1. Geometries along the minimum energy path for the reaction $H^+ + CO \rightarrow HCO^+$

R_{H-C} (Å)	R_{C-O} (Å)	Total energy (hartrees)
∞	1.128	−112.55236
100.000	1.128	−112.55236
50.000	1.128	−112.55234
25.000	1.127	−112.55228
10.000	1.127	-112.55211_2
9.317[a]	1.127	-112.55210_9
5.000	1.124	−112.55305
3.500	1.121	−112.55918
2.500	1.114	−112.59355
1.500	1.103	−112.72146
1.078[b]	1.098	−112.77932
1.000	1.097	−112.77436

[a] Equilibrium geometry for barrier top.
[b] Equilibrium geometry for HCO^+.

and Buenker for HCO^+, COH^+ [8] and N_2H^+ [12]. Table 10 gives a comparison of the equilibrium geometries and total energies obtained by us for HCO^+, COH^+ and NNH^+ and those obtained by previous investigators. In HCO^+ our result for the equilibrium CO bond length is intermediate between that obtained in the two SCF calculations and very close to the CI value while our value for the H–C equilibrium bond length is significantly shorter than that observed in the previous calculations. For the COH^+ species the geometry obtained is in excellent agreement with the CI calculation [11] but somewhat at variance at least with the same authors' SCF calculation [11]. A comparison of the results for N_2H^+ with previous work is rather difficult because Peyerimhoff and Buenker used a fixed NN bond length equal to that for the N_2 ground state. While our NN bond length in N_2H^+ is in excellent agreement with a value obtained by Forsen and Roos [7] using *d*-type polarization functions (1.077 Å) it should be noted that the NN equilibrium bond length obtained for N_2, 1.085 Å is significantly shorter than the

Table 2. Geometries along the minimum energy path for the reaction $H^+ + CO \rightarrow COH^+$

R_{O-H} (Å)	R_{C-O} (Å)	Total energy (hartrees)
∞	1.128	−112.55236
100.000	1.128	−112.55237
50.000	1.128	−112.55239
25.000	1.128	−112.55249
10.000	1.129	−112.55326
5.000	1.131	−112.55671
3.500	1.134	−112.56265
2.500	1.140	−112.57931
1.500	1.156	−112.66647
1.000	1.160	−112.74421
0.976[a]	1.160	−112.74465

[a] Equilibrium geometry for COH^+.

Table 3. Geometries along the minimum energy path for the reaction $HCO^+ + H^+ \rightarrow HCOH^{2+}$

R_{O-H} (Å)	R_{C-O} (Å)	R_{H-C} (Å)	Total energy (hartrees)
∞	1.098	1.078	−112.77932
100.000	1.098	1.078	−112.77411
50.000	1.098	1.078	−112.76905
25.000	1.098	1.079	−112.75935
10.000	1.099	1.080	−112.73333
5.000	1.101	1.084	−112.69849
3.500	1.103	1.088	−112.67576
2.500	1.107	1.094	−112.65535
1.972[a]	1.110	1.101	−112.64859
1.500	1.113	1.112	−112.66089
1.046[b]	1.115	1.128	−112.69011
1.000	1.114	1.130	−112.68899

[a] Equilibrium geometry for barrier top.

[b] Equilibrium geometry for $HCOH^{2+}$.

experimental value of 1.0977 Å. As observed by Peyerimhoff and Buenker [8] for HCO^+ and COH^+ and by Summers and Tyrrell [15] for a large number of protonated species isoelectronic with these molecules the triatomic molecule resulting from the bonding of the proton to the heavy atom with smaller core charge is more stable than that in which the proton is bound to the heavy atom with larger core charge. It should be noted however, that Marian *et al.* [16] required the inclusion of CI to find a similar energy ordering for HNO^+ and NOH^+. The absence of an energy minimum in our calculations on NOH^{2+} prevents us from determining whether a similar problem occurs with HNO^{2+} and NOH^{2+}. The shortening of the CO bond in HCO^+ relative to CO is again typical of a pattern observed for triatomics protonated on the smaller core charge atom; no such regular pattern was observed in protonation of the larger core charge atom [15]. The results obtained for HNO^{2+} and NOH^{2+}, in so far as they can be compared, also appear to fit this pattern.

Table 4. Geometries along the minimum energy path for the reaction $H^+ + COH^+ \rightarrow HCOH^{2+}$

R_{H-C} (Å)	R_{C-O} (Å)	R_{O-H} (Å)	Total energy (hartrees)
∞	1.160	0.976	−112.74465
100.000	1.160	0.976	−112.73942
50.000	1.160	0.976	−112.73431
25.000	1.160	0.977	−112.72442
10.000	1.159	0.979	−112.69712
5.000	1.156	0.984	−112.65848
3.500	1.151	0.989	−112.63224
2.500	1.142	1.000	−112.61375
2.394[a]	1.140	1.002	−112.61338
2.000	1.133	1.013	−112.62057
1.500	1.122	1.032	−112.65890
1.128[b]	1.115	1.046	−112.69011
1.000	1.112	1.051	−112.67943

[a] Equilibrium geometry for barrier top.

[b] Equilibrium geometry for $HCOH^{2+}$.

Table 5. Geometries along the minimum energy path for the reaction $H^+ + N_2 \rightarrow HNN^+$

R_{H-N} (Å)	R_{N-N} (Å)	Total energy (hartrees)
∞	1.085	−108.75423
100.000	1.085	−108.75423
50.000	1.085	−108.75423
25.000	1.085	−108.75425
10.000	1.085	−108.75449
5.000	1.085	−108.75636
3.500	1.084	−108.76091
2.500	1.084	−108.77922
1.500	1.081	−108.87949
1.017[a]	1.077	−108.95026

[a] Equilibrium geometry for HNN^+.

No energy barrier was observed for the protonation of CO to form COH^+ and only a negligibly small barrier (0.15 kcal/mole) for the formation of HCO^+. This is in agreement with the results of Peyerimhoff and Buenker [8] in that they observed no barrier either for the formation of HCO^+ or COH^+. The small barrier observed in the formation of HCO^+ is almost certainly spurious as it was not observed in Peyerimhoff and Buenker's [8] CI calculations which indicate that correlation effects play a somewhat more significant part at intermediate CH distances giving greater reliability to the CI results though these authors do agree that the SCF potential curves are fairly reliable. Peyerimhoff and Buenker [8] did not optimize the geometries of HCO^+ and COH^+, using a fixed bond length for the CO bond. Our results as illustrated in Tables 1 and 2 would suggest that such an approximation is inappropriate in the case of HCO^+ and COH^+ while apparently not too unreasonable in the case of N_2H^+ (Table 5). The enhanced stabilities of

Table 6. Geometries along the minimum energy path for the reaction $H^+ + HNN^+ \rightarrow HNNH^{2+}$

R_{H-N} (Å)	R_{N-N} (Å)	R_{N-H} (Å)	Total energy (hartrees)
∞	1.077	1.017	−108.95026
100.000	1.077	1.017	−108.94503
50.000	1.077	1.017	−108.93993
25.000	1.077	1.017	−108.93010
10.000	1.077	1.019	−108.90313
5.000	1.077	1.024	−108.86529
3.500	1.076	1.029	−108.83918
2.500	1.075	1.037	−108.81514
2.043[a]	1.073	1.045	−108.80877
1.500	1.068	1.063	−108.82711
1.081[b]	1.063	1.081	−108.85639

[a] Equilibrium geometry for barrier top.

[b] Equilibrium geometry for $HNNH^{2+}$.

Table 7. Geometries along the minimum energy path for the reaction $H^+ + NO^+ \rightarrow HNO^{2+}$

R_{H-N} (Å)	R_{N-O} (Å)	Total energy (hartrees)
∞	1.048	−128.66967
100.000	1.048	−128.66440
50.000	1.048	−128.65917
25.000	1.048	−128.64883
10.000	1.048	−128.61882
5.000	1.048	−128.57231
3.500	1.047	−128.53646
2.500	1.046	−128.49651
1.750	1.043	−128.46415
1.529[a]	1.042	−128.46137
1.400	1.041	−128.46220
1.218[b]	1.039	−128.46411
1.050	1.037	−128.45733

[a] Equilibrium geometry for barrier top.

[b] Equilibrium geometry for HNO^{2+}.

HCO^+ and COH^+ over CO of 142.4 kcal/mole and 120.7 kcal/mole respectively are in good agreement with those of Peyerimhoff and Buenker [8] and with experimental interpretation [17, 18] for HCO^+. Again our value of 123.0 kcal/mole for the enhanced stability of N_2H^+ over N_2 is in good agreement with the value of 126.3 kcal/mole obtained previously [12].

The equilibrium geometries for $HCOH^{2+}$ and $HNNH^{2+}$ were previously reported by us as part of a larger study of similar systems [15]. $HCOH^{2+}$ is significantly less stable than HCO^+ or COH^+ by 56 kcal/mole and 34.2 kcal/mole respectively. The barrier to the formation of $HCOH^{2+}$ from HCO^+ and COH^+ and the barrier for the reverse processes are given in Table 9. The fact that the barrier to the

Table 8. Geometries along the minimum energy path for the reaction $H^+ + NO^+ \rightarrow NOH^{2+}$

R_{H-O} (Å)	R_{N-O} (Å)	Total energy (hartrees)
∞	1.048	−128.66967
100.000	1.048	−128.66441
50.000	1.048	−128.65923
25.000	1.049	−128.64905
10.000	1.049	−128.62010
5.000	1.051	−128.57685
4.500	1.051	−128.56806
4.000	1.052	−128.55750
3.500	1.053	−128.54462
3.000	1.054	−128.52869
2.500	1.056	−128.50899
2.000	1.059	−128.48631
1.500	1.065	−128.46903
1.000	1.069	−128.45381

Table 9. Energy barriers for protonation and proton removal

Reaction	Energy barrier (kcal/mole)
$H^+ + CO \rightarrow HCO^+$	0.16
$HCO^+ \rightarrow H^+ + CO$	142.42
$H^+ + CO \rightarrow COH^+$	0
$COH^+ \rightarrow H^+ + CO$	120.66
$H^+ + HCO^+ \rightarrow HCOH^{2+}$	82.03
$HCOH^{2+} \rightarrow H^+ + HCO^+$	26.05
$H^+ + COH^+ \rightarrow HCOH^{2+}$	82.37
$HCOH^{2+} \rightarrow H^+ + COH^+$	48.15
$H^+ + N_2 \rightarrow HNN^+$	0
$HNN^+ \rightarrow H^+ + N_2$	123.01
$H^+ + HNN^+ \rightarrow HNNH^{2+}$	88.78
$HNNH^{2+} \rightarrow H^+ + HNN^+$	29.88
$H^+ + NO^+ \rightarrow HNO^{2+}$	130.71
$HNO^{2+} \rightarrow H^+ + NO^+$	1.72

Table 10. Calculated equilibrium geometrical parameters and total energies for HCO^+, COH^+ and N_2H^+ and comparison with previous calculations

H–X–Y	R_{H-X} (Å)	R_{X-Y} (Å)	Total energy (hartrees)
HCO^+	1.078	1.098	−112.7793
[a]	1.0847	1.1083	−112.9044
[b]	1.085	1.079	−113.0159
	1.090	1.101	−113.3302[e]
COH^+	0.976	1.160	−112.7447
[a]	0.974	1.165	−112.8751
[c]	0.979	1.143	−112.9307
	0.976	1.159	−113.0135[e]
NNH^+	1.017	1.077	−108.9503
[d]	1.026	1.094	−109.0748
	1.027	1.094 (ass.)	−109.2443[e]

[a] Ref. [8].
[b] Ref. [9].
[c] Ref. [11].
[d] Ref. [12].
[e] CI calculation.

formation of $HCOH^{2+}$ from either HCO^+ or COH^+ is essentially identical (82.0 kcal/mole for HCO^+ as compared with 82.4 kcal/mole for COH^+) suggests that the barrier in both cases is primarily due to electrostatic repulsion of the proton by the positively charged molecule. The much lower barrier 26.1 kcal/mole for the removal of a proton to give HCO^+ as compared to a barrier of 48.2 kcal/mole for formation of COH^+ from $HCOH^{2+}$ indicates that the O–H bond is significantly weaker, by almost a factor of two, than the C–H bond in $HCOH^{2+}$. It is also of interest that the difference between these barriers of 22.1 kcal/mole is almost identical to the difference in stabilization energies of HCO^+ and COH^+ (21.8 kcal/mole). The barrier to the formation of $HNNH^{2+}$ from N_2H^+ of 88.8 kcal/mole is similar in magnitude to that for the formation of $HCOH^{2+}$ and again is probably attributable to electrostatic repulsion. The removal of a proton to form N_2H^+ has a barrier of 29.9 kcal/mole similar to that for the rupture of the O–H bond in $HCOH^{2+}$. The formation of HNO^{2+} requires overcoming a significantly larger barrier (130.7 kcal/mole) and the species formed is very unstable as indicated by the very small barrier of 1.7 kcal/mole for the reverse process. The electron transfer to the proton, 0.144, in the formation of HNO^{2+} is about half that observed in the case of the formation of $HCOH^{2+}$ and $HNNH^{2+}$. Only in the case of the protonation of NO^+ to give NOH^{2+} was no minimum energy equilibrium geometry observed but there is a noticeable flattening of the curve between about a 1–3 Å OH distance suggesting that a more complete basis set might lead to an energy minimum. In every case the minimum energy path for the protonation reactions lies along the line-of-centers of the heavy atoms. All the molecular systems have a pair of degenerate π molecular orbitals which are occupied, and in the equilibrium structures of the reactants and products the lowest virtual orbitals are a pair of degenerate π^* orbitals. The reactions considered here involve the combination of a 1*s* orbital of the approaching proton with an occupied non-bonding orbital of the heavy atom in question. Where the non-bonding orbital involved was higher (more positive) in energy than the π orbitals this results in a reversal of their ordering. Where the non-bonding orbital involved is lower in energy than the π orbitals the ordering of the orbitals is unchanged for reactant and product.

The orbital occupancy distribution during protonation shows striking similarities in a number of instances. In the case of protonation of CO to give HCO^+ the principal change is a decrease in the C2*s* orbital from 1.779 in CO to 1.172 in HCO^+ with a corresponding increase in the H1*s* to 0.484 in HCO^+. There is also a noticeable but smaller shift of π electrons from oxygen to the carbon. This behavior is repeated in the formation of COH^+ from CO and of $HCOH^{2+}$ from HCO^+ indicating a movement of π electrons from the carbon to the oxygen. The proton in COH^+ appears to gain its electron density primarily at the expense of the O2*s*, $O2p_\sigma$ and $C2p_\sigma$ orbitals. This is repeated in the formation of $HCOH^{2+}$ from HCO^+ with, in addition, the H1*s* orbital of the hydrogen attached to the carbon contributing as well. In both cases the oxygen gains electron density as a result of protonation at the oxygen. On the other hand protonation of the carbon leads to an overall decrease in its electron density. Again in the protonation of N_2 to give HNN^+ there is a shift of π electron density to the nitrogen which bonds to the hydrogen and a decrease in the occupancy of the 2*s* orbital of that nitrogen from 1.875 in N_2 to 1.476 in HNN^+ this being the principal source of electron density for the proton. As a proton approaches HNN^+ to give $HNNH^{2+}$ π electron density moves back towards the nitrogen being attacked and that nitrogen's 2*s* orbital is the principal source of electron density for the approaching proton. The electron orbital occupancy changes observed in the protonation of NO^+ to give HNO^{2+} and NOH^{2+} are similar to those observed for the formation of HCO^+ and COH^+ respectively. In summary, on protonation there is a movement of π electron density towards the atom being protonated and the 2*s* orbital of that atom is usually a major source of electron density for the approaching proton though other orbitals may also contribute.

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Received June 27, 1977/September 16, 1977