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The Interaction of Nitrogen and Carbon Monoxide with Certain Ions and Neutral Species

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MNDO method is used to study the interaction of nitrogen and carbon monoxide molecules with a proton, hydrogen atom, hydride ion, hydrogen molecule ion and hydrogen molecule. Predicted geometries and heats of reaction of different complexes are presented. The wave functions are analyzed in terms of ground state charge distributions and overlap populations. Electronic effects accompanying complexation are also discussed.

Key words: Nitrogen fixation – Nitrogen complexes – Carbon monoxide complexes – Electronic effects.

1. Introduction

The interaction of nitrogen with various ions and neutral species is of obvious importance, since nitrogen is the most stable of all the diatomic species and is, hence, reluctant to enter into chemical combination. In fact, it does not undergo direct reduction or oxidation, but requires transition metal catalysts for most of its reactions; for example, the conversion of nitrogen molecule into ammonia, hydrazine and diimine etc., occurs by way of proteins containing molybdenum and iron [1–3], and a complex between the metal ion and nitrogen is believed to act as an important intermediate.

In view of the importance of such reactions in atmospheric molecular nitrogen fixation, we have carried out a theoretical investigation of the bonding character of nitrogen molecule towards neutral species, cations and anions [4]. For the sake of simplicity, we have restricted our attention to the hydrogen atom, the

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proton and the hydride ion, on one hand, and the diatomic species, hydrogen molecule and its cation, on the other.

We have also carried out similar calculations on the isoelectronic carbon monoxide molecule. Since it is hetero-nuclear, as opposed to the nitrogen molecule, there are expected to be differences in the bonding characters of carbon monoxide and dinitrogen towards ions and neutral species. Carbon monoxide is known to form stable complexes with transition metal ions [5], whereas dinitrogen complexes are unstable [6].

The semiempirical MNDO method [7] was used for all the calculations reported here. Complete geometry optimization was carried out for all the complexes. We have considered all possible geometries of approach of the attacking species to the diatomic molecule.

2. The Nitrogen Molecule

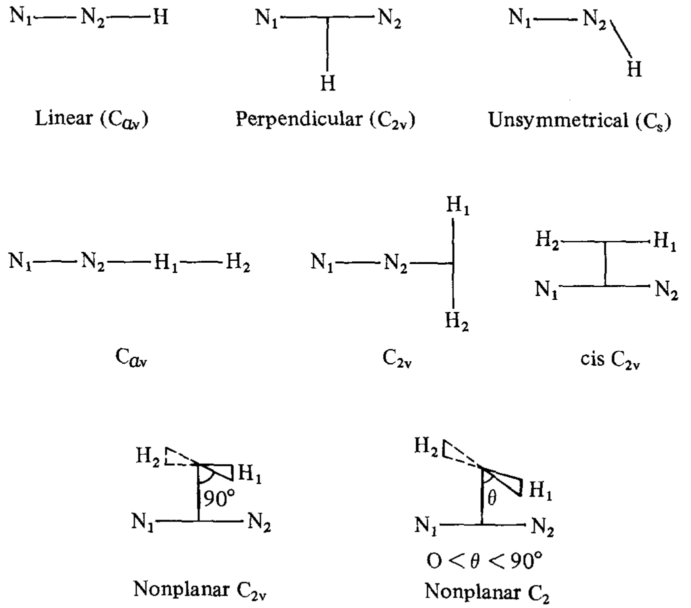
Table 1 gives the heat of reaction in each case of reaction with nitrogen molecule (see Fig. 1) as well as the change in the bond length (ΔR_{NN}) and bond order (ΔP_{NN}) accompanying complexation. It can be seen that the most stable geometry of approach for protonation is the linear one ($C_{\infty v}$), while the hydrogen atom and the hydride ion prefer an unsymmetrical approach ($\measuredangle NNH = 126.4°$ and $\measuredangle NNH^- = 114.1°$). Our calculated value for the heat of protonation (90 kcal/mol) is in agreement with the experimental [8] value of 56.5 to 113.0 kcal/mol.

Table 1. Heats of reaction and changes in nitrogen-nitrogen interatomic distances and bond orders accompanying complexation

Number	System		ΔE (kcal/mol)	ΔR^a_{NN} (Å)	ΔP^b_{NN}
1	N_2H^+	$C_{\infty v}$	−90.0	~0.0	−0.170
2	N_2H	C_{2v}	−14.8	0.038	−0.262
3	N_2H	$C_{\infty v}$	1.6	0.048	−0.704
4		C_{2v}	57.0	0.103	−0.862
5		C_s	−13.3	0.051	−0.467
6	N_2H^-	$C_{\infty v}$	35.3	0.007	−1.243
7		C_{2v}	59.2	0.177	−1.438
8		C_s	−41.3	0.079	−0.614
9	$N_2H_2^+$	$C_{\infty v}$	−46.6	0.002	−0.163
10		C_{2v}	−81.5	0.094	−0.742
11		cis C_{2v}	−82.0	0.038	−0.461
12	Nonplanar	C_{2v}	53.8	0.132	−1.064
13	Nonplanar	C_2	−86.9	0.062	−0.632
14	N_2H_2	C_{2v}	52.6	0.098	−0.880
15		cis C_{2v}	25.0	0.105	−0.834
16	Nonplanar	C_{2v}	206.7	0.215	−1.734

[a] $\Delta R_{NN} = R_{NN}$ (complex) $- R_{NN}$ (Nitrogen).

[b] $\Delta P_{NN} = P_{NN}$ (complex) $- P_{NN}$ (Nitrogen).



Linear ($C_{\infty v}$) Perpendicular (C_{2v}) Unsymmetrical (C_s)

$C_{\infty v}$ C_{2v} cis C_{2v}

Nonplanar C_{2v} Nonplanar C_2

Fig. 1. Geometries considered for nitrogen complexes

The values of ΔR_{NN} and ΔP_{NN} show that, in each case, excepting protonation, there is a significant general lengthening of the N—N bond and a decrease in the bond order of the N—N bond. Since the products of the atmospheric nitrogen fixation contain unbonded, single bonded and double bonded nitrogens, the only suitable models (with bond order as a criterion) for nitrogen fixation are 3, 4, 6, 7, 9–11, 13 and 15 and, possibly, 8 and 16 (see Table 1). All these systems, except $13(N_2H_2^+C_{2v})$, are unsuitable from the point of view of energy considerations.

In Table 2 the total net charges and bond orders are collected. For both the cases of protonation, there is a shift of electron density towards the proton. We see that, in the case of the linear complex with a proton, the unbonded nitrogen becomes positively charged. There is, thus, a transfer of electron density from this nitrogen to the proton. In the case of the perpendicular complex, the proton divides about half of its positive charge equally among the two nitrogens.

In the case of hydrogen atom attack, although, initially, all the three atoms are uncharged, the nitrogens acquire a negative charge in the complex, while the hydrogen becomes positively charged. In the unsymmetrical complex with a hydride ion, the negative charge is delocalised over all the three atoms, but in the linear and perpendicular complexes, the hydride ion donates all its negative charge to the nitrogen and itself becomes positively charged.

A survey of the overlap populations indicates that, although a bond is formed between N_2 and H_1, there is not necessarily a concomitant decrease in the overlap population of the nitrogen-nitrogen bond. In the case of protonation,

Table 2. Atom charges and atom-atom bond orders for dinitrogen complexes

Number	Q_{H1}	Q_{H2}	Q_{N1}	Q_{N2}	$P_{\mathrm{H1-N2}}$	$P_{\mathrm{N1-N2}}$	$P_{\mathrm{H1-H2}}$
1	0.428	–	0.477	0.095	1.234	2.830	–
2	0.477	–	0.262	0.262	0.786	2.738	–
3	0.321	–	−0.027	−0.295	1.288	2.296	–
4	0.276	–	−0.138	−0.138	0.894	2.138	–
5	0.125	–	−0.064	−0.062	1.460	2.533	–
6	0.227	–	−0.530	−0.697	1.316	1.757	–
7	0.125	–	−0.562	−0.562	0.946	1.562	–
8	−0.225	–	−0.620	−0.155	1.277	2.386	–
9	0.379	0.090	0.447	0.084	1.179	2.837	0.255
10	0.314	0.314	0.359	0.013	1.579	2.258	0.089
11	0.326	0.326	0.174	0.174	1.471	2.539	0.039
12	0.436	0.436	0.064	0.064	1.097	1.936	0.062
13	0.336	0.336	0.164	0.164	1.509	2.369	0.113
14	0.121	0.121	−0.280	0.037	1.585	2.120	0.194
15	−0.054	0.054	−0.054	0.054	1.512	2.166	0.166
16	0.266	0.266	−0.266	−0.266	1.212	1.266	0.056

N_2 represents the nitrogen bonded to hydrogen H_1.

although the bond order of the incipient N—H bond acquires a value of about one unit, the nitrogen-nitrogen bond order remains close to 3.

For reaction with diatomic species, the overall trends are similar to those observed for the monoatomic counterparts, differences being only in the N_2—H_1 bond orders, which are greater in magnitude in these cases. The H—H bond orders are very small in magnitude, indicating that complex formation is accompanied with a breaking of the H—H bonds. In each case bonds between nitrogen and hydrogen are established and the hydrogen-hydrogen bonds break. This is accompanied with a decrease in the bond order of the nitrogen-nitrogen bond which becomes a single or double bond (except for two cases of reaction with H_2^+).

Among the monoatomic species, the nitrogen molecule prefers attack by a proton (linear configuration) but the complex, so formed, contains triply bonded nitrogens. The next most facile reaction is with the hydride ion (unsymmetrical configuration, C_s). With diatomic systems, again the most facile reactions are with H_2^+ (nonplanar C_2, cis C_{2v} and C_{2v}). Hence the neutral nitrogen molecule prefers attack by charged species, particularly cations. The reactions with anions, however, bring about greater decrease in the N—N bond order, by the transfer of charge from the anion to the antibonding π_{NN} orbital. Therefore, the most likely models for molecular nitrogen fixation seem to be the systems N_2+H^- (C_s) and $N_2+H_2^+$ (C_{2v} and nonplanar C_2).

3. The Carbon Monoxide Molecule

Since carbon monoxide is unsymmetrical, the reacting species can approach either the carbon or the oxygen atom. Hence, there are additional geometries to be considered. These are depicted in Fig. 2.

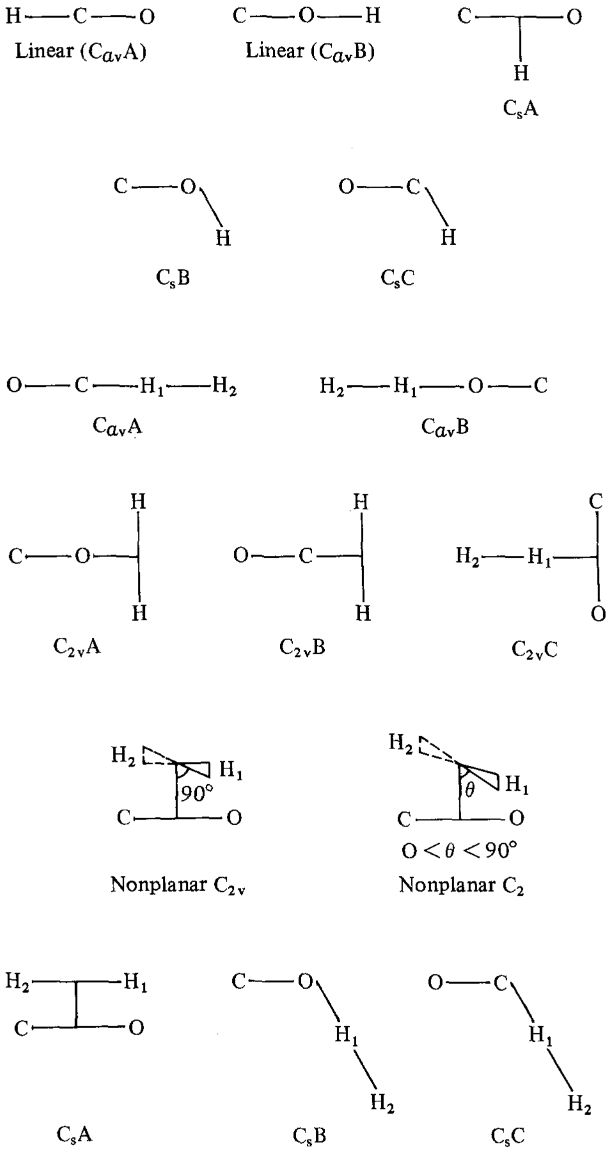


Fig. 2. Geometries considered for carbon monoxide complexes

In Table 3 is given the heat of reaction in each case, as well as the change in bond length and bond order of the carbon-oxygen bond accompanying complexation.

The most stable protonated complex is the linear one (1) with the proton bonded to the carbon. The calculated heat of protonation (135.5 kcal/mol) is in agreement with the experimental [9] value of 131.8 kcal/mol. The hydrogen atom

Table 3. Heats of reaction and changes in carbon-oxygen interatomic distances and bond orders for carbon monoxide complexes

Number	System		ΔE(kcal/mol)	ΔR_{CO}	ΔP_{CO}
1	HCO^+	$C_{\infty v}A$	−135.5	−0.021	0.057
2	COH^+	$C_{\infty v}B$	−104.5	0.037	−0.487
3	HCO	$C_{\infty v}A$	−58.6	0.019	−0.414
4	COH	$C_{\infty v}B$	7.0	0.086	−0.965
5	COH	C_sB	−11.5	0.095	−0.720
6	OCH	C_sC	−46.3	0.027	−0.332
7	HCO^-	$C_{\infty v}A$	−17.0	0.069	−0.880
8	COH^-	$C_{\infty v}B$	51.3	0.148	−1.444
9	COH^-	C_sA	−47.3	0.082	−0.547
10	COH^-	C_sB	−5.0	0.082	−0.603
11	OCH^-	C_sC	−62.8	0.070	−0.547
12	H_2CO^+	$C_{\infty v}A$	−87.4	−0.019	0.045
13	COH_2^+	$C_{\infty v}B$	−59.7	0.037	−0.464
14	COH_2^+	$C_{2v}A$	−85.1	0.195	−1.287
15	OCH_2^+	$C_{2v}B$	−117.2	0.035	−0.262
16	H_2CO^+	$C_{2v}C$	−23.2	−0.028	−0.263
17	H_2CO^+	C_sA	−125.4	0.055	−0.570
18	COH_2	$C_{2v}A$	115.1	0.133	−1.094
19	OCH_2	$C_{2v}B$	−28.5	0.053	−0.464
20	H_2CO	Nonplanar C_{2v}	41.1	0.112	−0.600
21	H_2CO	C_sA	20.3	0.108	−0.854

Table 4. Atom charges and atom–atom bond orders for reaction of carbon monoxide with monoatomic species

Number	Q_{H_1}	Q_{H_2}	Q_C	Q_O	$P_{H\text{-}C}$	$P_{H\text{-}O}$	$P_{C\text{-}O}$	$P_{H_1\text{-}H_2}$
1	0.330	–	0.510	0.159	1.302	0.204	2.766	–
2	0.433	–	0.790	−0.233	0.339	1.198	2.222	–
3	0.243	–	−0.123	−0.120	1.341	0.203	2.295	–
4	0.333	–	0.047	−0.380	0.378	1.239	1.744	–
5	0.180	–	0.006	−0.186	0.289	1.468	1.989	–
6	0.121	–	0.055	−0.176	1.564	0.252	2.377	–
7	0.169	–	−0.771	−0.398	1.363	0.206	1.828	–
8	0.226	–	−0.701	−0.525	0.427	1.255	1.265	–
9	−0.344	–	−0.091	−0.565	1.185	0.310	2.162	–
10	−0.144	–	−0.743	−0.113	0.607	1.246	2.106	–
11	−0.289	–	−0.157	−0.554	1.335	0.348	2.161	–
12	0.259	0.155	0.458	0.128	1.136	0.171	2.754	0.439
13	0.395	0.080	0.754	−0.230	0.324	1.138	2.245	0.264
14	0.338	0.338	0.417	−0.092	0.288	1.529	1.422	0.091
15	0.266	0.266	0.312	0.156	1.454	0.193	2.447	0.024
16	0.004	0.156	0.717	0.123	0.382	0.177	2.445	0.916
17	0.351	0.251	0.462	−0.064	1.526	1.500	2.139	0.007
18	0.159	0.159	−0.397	0.079	0.630	1.507	1.615	0.185
19	−0.001	−0.001	0.292	−0.289	1.603	0.327	2.245	0.217
20	0.124	0.124	0.150	−0.398	1.570	0.149	2.109	0.253
21	0.123	−0.003	−0.019	−0.101	1.605	1.455	1.855	0.131

Table 5. Changes in σ- and π-electron distributions Δn-accompanying reaction with cations

System		$\Delta n(s_{H_1})$	$\Delta n(s_{H_2})$	$\Delta n(\sigma_A)$	$\Delta n(\sigma_B)$	$\Delta p(\sigma_{A-B})$	$\Delta n(\pi_A)$	$\Delta n(\pi_B)$	$\Delta p(\pi_{A-B})$	$\Delta p(H_1-H_2)$
N_2H^+	$C_{\infty v}$	0.572	–	–0.183	–0.389	–0.148	–0.294	0.294	–0.022	–
HCO^+	$C_{\infty v}A$[a]	0.670	–	–0.129	–0.451	–0.062	–0.244	0.244	0.120	–
COH^+	$C_{\infty v}B$[b]	0.567	–	–0.234	–0.332	–0.238	–0.342	0.342	–0.250	–
$N_2H_2^+$	$C_{\infty v}$	0.410	0.121	–0.167	–0.364	–0.143	–0.280	0.280	–0.020	–0.245
H_2CO^+	$C_{\infty v}A$[a]	0.345	0.241	–0.117	–0.469	–0.067	–0.224	0.224	0.111	–0.061
COH_2^+	$C_{\infty v}B$[b]	0.420	0.105	–0.214	–0.310	–0.228	–0.328	0.327	–0.236	–0.236

B is the atom attached to H_1. For the nitrogen complexes $A = N_1$, $B = N_2$.

[a] A = oxygen, B = carbon.

[b] A = carbon, B = oxygen.

prefers a linear approach for CO. As in the case with nitrogen, the hydride ion prefers an unsymmetrical approach (C_sC).

A comparison of Table 3 with Table 1 indicates that most of the complexation reactions are exothermic with carbon monoxide. Hence carbon monoxide is predicted to be more reactive than nitrogen in complexation reactions. An approach to the carbon atom is always preferred over an approach to the oxygen.

In each case, excepting linear protonation (1) and reaction with H_2^+ ion (12 and 16) there is a general weakening of the C—O bond, as evidenced by the increase in bond length. For these cases (1, 12 and 16) there is an actual shortening of the C—O bond.

The values of the charges and overlap populations in the CO complexes, shown in Table 4, indicate that the electronic effects accompanying reaction with carbon monoxide are similar to those accompanying reaction with nitrogen.

To see if there are any differences in the σ and π electronic effects for the reactions of the two molecules with cations, we have separated the electron distribution into a σ-component and a π-component and analysed these separately.

The results of a population analysis for σ and π are given in Table 5. We see that there is a very general shift in electron density towards the proton. Comparing the first two cases (nitrogen and carbon monoxide, $C_{\infty v}A$), we find that there is no essential difference in the σ systems of the two molecules, although the shift in electron density is larger for carbon monoxide. In the π system, the shift is larger for nitrogen. However, there is a remarkable difference in the change in the π overlap populations of the two molecules. In carbon monoxide the overlap population becomes larger because the π electrons, concentrated mainly on oxygen, are now distributed more symmetrically. In nitrogen, however, the π system is symmetrical to begin with and becomes asymmetrical after the electron shift, resulting in a weakening of the π bond. In HCO^+ $C_{\infty v}B$, the proton attaches itself to the oxygen atom. There is hence a further shift of electron density from the carbon to the oxygen, making the π electron distribution more unsymmetrical. This is responsible for the considerable weakening of the π bond in this case.

The changes in σ and π electron distributions (excepting $\Delta p(\pi_{AB})$ for N_2H^+ are in between those for HCO^+ ($C_{\infty v}A$) and COH^+ ($C_{\infty v}B$), indicating that these changes depend on the atomic numbers of the atoms concerned.

The reactions of carbon monoxide and nitrogen with the hydrogen molecule ion are similar to those with the proton.

4. Conclusions

The reactions of nitrogen and carbon monoxide with various atoms and ions have been compared, and it has been shown that, whereas the nitrogen molecule prefers attack by cations and, to a smaller extent, by anions, carbon monoxide can react spontaneously with neutral molecules, too. All the reactions of nitrogen, and most reactions of carbon monoxide (excepting protonation), are accompanied with a decrease in the bond order of the diatomic bond.

This difference in the protonation reactions of the two molecules has been shown to be due to the inherent differences in the symmetries of the π systems of the two molecules. In nitrogen, the protonation reaction weakens the π bond by making it unsymmetrical, whereas, in carbon monoxide, protonation results in a strengthening of the π bond. This accounts for the observed shortening of the carbon-oxygen bond following protonation.

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