

NON-EMPIRICAL MOLECULAR ORBITAL CALCULATIONS ON THE PROTONATION OF CARBON MONOXIDE

H. B. JANSEN and P. ROS

*Scheikundig Laboratorium, Vrije Universiteit,
Amsterdam, The Netherlands*

Received 24 February 1969

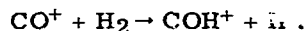
Non-empirical calculations with Gaussian functions have been performed for several configurations of protonated carbon monoxide.

The stablest configuration of protonated CO appears to be a linear $[\text{HCO}]^+$ structure. The CO distance in this structure is 0.02 Å smaller than in CO itself and the energy of the system is 152 kcal/mole below the CO-energy.

1. INTRODUCTION

Protonation of aldehydes, ketones, and carboxylic acids has been studied, both experimentally [1-4] and theoretically [5]. However, little is known about protonated species of carbon monoxide.

COH^+ may be formed in ion-molecule reactions as is, for instance, described by Henglein [6] for the reaction



The occurrence of HCO^+ in hydrocarbon flames is discussed by Calcote and Jensen [7] and by Pritchard and Harrison [8].

In this work we describe a theoretical study of the protonation of CO. We investigated the following two problems:

- 1) the geometry of protonated CO
- 2) the stability of protonated CO.

Since there are no experimental data on the geometry and stability of protonated CO, theoretical calculations are at this moment the only means to obtain information concerning these topics.

2. METHOD OF CALCULATION

The method used in this work is the single configurational LCAO Hartree Fock MO-SCF approach, which is extensively described in the literature [9]. The one-electron molecular orbitals are defined by

$$\psi_i = \sum_j c_{ij} a_j$$

where the basis functions a_j are the Gaussian functions centered on the various atoms of the system. The molecular orbital coefficients c_{ij} were determined by minimalization of the total energy of the molecule or ion. These molecular calculations were performed with a slightly modified version of the IBMOL program [10]. All calculations were performed on a CDC 3200. Because of the limitations of this computer, we were forced to limit the size of the basis set considerably. We have experimented with various sorts of Gaussian basis sets, among others a basis set that was obtained from atomic Hartree Fock calculations [11], a basis set according to Huzinaga's method [12], and a basis set consisting of Gaussian orbitals that give maximum overlap with the corresponding atomic Hartree Fock Slater functions.

Our final choice of the basis set (given in table 1) is a combination of 'Huzinaga' functions and 'overlap' functions. The 1s-orbitals are represented by 'Huzinaga' functions, since they give a lower energy than 'overlap' functions. Both types of functions give about the same energy for 2s- and 2p-orbitals, but our calculations showed the 'overlap' functions to be preferable because they give a better description of bonding effects (see also ref. [13]).

Table 1
Atomic basis functions ($G(\alpha) = N \exp(-\alpha r^2)$).

Orbital	Function
C(1s)	$0.50907 G(3.9683) + 0.47449 G(14.602) + 0.13424 G(64.787) + 0.01906 G(426.967)$
C(2s)	$G(0.1272)$
C(2s')	$G(0.3345)$
C(2p)	$G(0.2628)$
C(2p')	$G(1.0622)$
O(1s)	$0.50907 G(7.2317) + 0.47449 G(26.610) + 0.13424 G(118.067) + 0.01906 G(783.564)$
O(2s)	$G(0.2480)$
O(2s')	$G(0.6521)$
O(2p)	$G(0.5300)$
O(2p')	$G(2.1422)$
H(1s)	$G(0.2015)$
H(1s')	$G(1.3325)$

3. RESULTS OF THE CALCULATION

For the calculations on protonated CO we considered the following possibilities:

- 1) The proton is situated on the carbon side of the molecular axis of CO (linear HCO⁺)
- 2) The proton is situated on the oxygen side of the molecular axis of CO (linear COH⁺)
- 3) A number of non-linear configurations.

It turned out that the non-linear configurations were higher in energy than the linear ones. We therefore will first discuss the results for the linear systems and shall revert to the non-linear case later in this section.

In table 2 we have collected the internuclear distances, stretching force constants, Mulliken overlap populations and gross atomic charges for the linear systems. The total energy was computed as a function of the internuclear dis-

Table 2
Interatomic distances, stretching force constants, overlap populations and gross atomic charges.

Sys-tem	A-B	R_{AB} (Å)	k_{AB} (mdyne/Å)	p_{AB}	q_C	q_O	q_H
CO	C-O	1.15	23.8	0.38	0.03	-0.03	-
HCO ⁺	C-O	1.13	26.2	0.48	0.33	0.22	0.45
	H-C	1.11	5.8	0.32			
COH ⁺	C-O	1.18	20.0	0.38	0.54	-0.06	0.52
	O-H	1.00	7.8	0.24			

tance. Around the equilibrium distance R_e (the distance with minimal total energy), the energy can be approximated by

$$E = E_0 + \frac{1}{2}K(R - R_e)^2$$

where K is equal to the stretching force constant for this bond [14].

For the CO molecule the computed internuclear distance of 1.15 Å is a little longer than the experimental C-O distance (1.13 Å [15]). Furthermore, the computed stretching force constant (23.8 mdyne/Å) is somewhat high (experimental value is 18.5 mdyne/Å [16]).

In HCO⁺ with the proton attached to the carbon, we found the C-O distance to be 0.02 Å smaller than in CO; in COH⁺ with the proton on oxygen, the C-O distance was found to be 0.03 Å larger than in CO. This indicates a strengthening of the C-O bond in HCO⁺ and a weakening of that bond in COH⁺. The same conclusions can be drawn from the values of the stretching force constants of the C-O bond (23.8 mdyne/Å in CO, 26.2 in HCO⁺ and 20.0 in COH⁺ respectively).

The C-H distance in HCO⁺ (1.11 Å) and the O-H distance in COH⁺ (1.00 Å) seem rather normal. They are somewhat longer than the C-H and O-H distances in methanol (1.09 and 0.96 Å respectively [13]).

The total energies and the energies of protonation are shown in table 3. The difference in the computed total energy between HCO⁺ or COH⁺ and CO arises from two effects:

- a) The addition of the proton with a nuclear charge of +1 will lower the energy;
 - b) The addition of two basis functions of the hydrogen gives an extension of the basis set of CO and this too may lower the total energy.
- Only the first effect has a physical meaning and represents the energy of protonation. We therefore have to eliminate the second effect.

The effect b) can be computed by adding the two hydrogen basis functions to the CO basis without adding the proton. The extension of the CO basis obtained in this way gave, with our choice of basis set, only a slightly lower total energy, i.e., 0.002 a.u. lower when the functions

Table 3
Total energy of the systems, energy correction and energy of protonation, in atomic units.

System	Total energy	Energy correction	Protonation energy
CO	-111.858	-	-
HCO ⁺	-112.103	0.002	0.243
COH ⁺	-112.059	0.011	0.190

Table 4
Atomic orbital occupation numbers.

System	C(s)	O(s)	H(s)	C(p σ)	O(p σ)	C(p π)	O(p π)
CO	3.89	3.94	-	0.86	1.31	0.61	1.39
HCO ⁺	3.24	3.98	0.55	1.02	1.22	0.71	1.29
COH ⁺	3.90	3.60	0.48	0.71	1.30	0.42	1.58

were added at the carbon side of CO and 0.011 a.u. lower when they were added at the oxygen side. After correction for the effect b) we find for HCO⁺ $\Delta E_p = 0.243$ a.u. = 152 kcal/mole and for COH⁺ $\Delta E_p = 0.190$ a.u. = 119 kcal/mole. This means that linear HCO⁺ is more stable than linear COH⁺ by 33 kcal/mole.

The change in the charge distribution on protonation is remarkable. Gross atomic charges, calculated from the orbital populations on the atoms, are given in table 2. In table 4 atomic orbital populations are represented for each orbital separately. Table 4 shows that in HCO⁺ both the σ -electrons and the π -electrons shift towards the incoming proton, thus making the oxygen more positive. In COH⁺ this effect is even stronger. The shift of the σ -electrons towards the hydrogen and the shift of the π -electrons from carbon towards oxygen now make the carbon atom positive and the oxygen atom even more negative than before protonation.

Calculations on non-linear systems show the following:

- 1) The energy of the non-linear situations with the proton on the carbon or oxygen side of the CO molecule is given in fig. 1 as a function of the angle of the CH or OH bond with the CO axis. This figure shows that in HCO⁺ the linear configuration is lowest in energy and that non-linear forms are rather high. In COH⁺

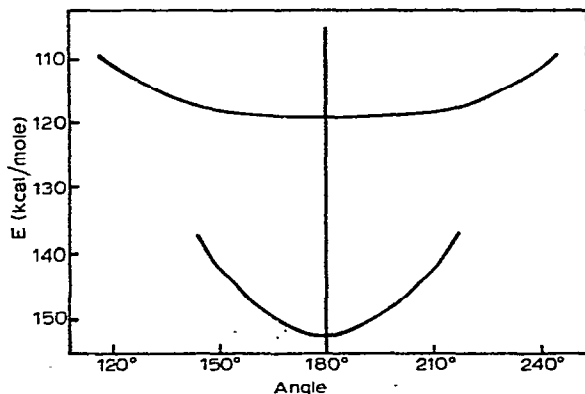


Fig. 1.

the energy difference between linear and non-linear forms is much smaller, but the linear configuration still remains lowest.

- 2) When the proton approaches along a line perpendicular to the CO π -bond, an energy-minimum is found at a distance of 1.0 Å from the center of the π -bond. In that case the protonation energy is approximately 70 kcal/mole. However, this is not a real energy-minimum since the energy of the system decreases when the proton moves along a line parallel to the CO axis.

4. DISCUSSION

The results described in the previous section indicate that HCO⁺ is the stablest protonated species of CO. Especially the interaction of the proton with the π -electrons of CO seems to be responsible for the stability of HCO⁺. Calculations on CO show that the π -bond in this molecule is polarized, i.e., the π -orbital occupation number on oxygen (1.39) is higher than on carbon (0.61) (see table 4).

In HCO⁺ the π -electrons shift towards the carbon, making the π -orbital occupation number on oxygen lower (1.29) and on carbon higher (0.71). This results in a stronger bond between carbon and oxygen, which is also confirmed by a smaller C-O distance and a higher value of the stretching force constant.

In COH⁺ the π -electrons shift in the other direction, resulting in π -orbital occupation numbers of 1.58 for oxygen and 0.42 for carbon. Therefore, the CO bond in COH⁺ is weaker, the C-O distance larger and the value of the stretching force constant smaller.

Although the computed C-O distance in carbon monoxide is longer than the experimental value and the computed stretching force constant differs from the experimental stretching force constant, we expect that the computed changes in distances and stretching force constants on protonation of CO give reliable information on the nature of the protonated system.

The total energy of CO obtained in this calculation is not very good (-111.858 a.u. to be compared with Ransil [17]: -112.344 a.u.). We feel, however, that bonding properties can be properly described using the basis of table 1 [13].

Using well known thermochemical data for CO and H⁺ and the heat of formation for HCO⁺ given by Pritchard and Harrison [8], the energy of protonation of CO is calculated to be approximately 133 kcal/mole. The energy of protonation

obtained from this non-empirical calculation (152 kcal/mol) agrees reasonably well with the thermochemical value. Furthermore, the energy is much lower than the energy of protonation of aldehydes (≈ 190 -200 kcal/mole) [5]. This may explain why until now the protonation of CO by strong acids has not been observed [2].

ACKNOWLEDGEMENT

The use of the CDC computer of the Zeeman Laboratory of the University of Amsterdam and the assistance of the staff of this computer are gratefully acknowledged.

REFERENCES

- [1] C. Maclean, J. H. Van der Waals and E. L. Mackor, *Mol. Phys.* 1 (1958) 247.
[2] H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor and C. Maclean, *Rec. Trav. Chim.* 86 (1967) 687.
[3] D. M. Brouwer, *Rec. Trav. Chim.* 86 (1967) 879.
[4] G. A. Olah, D. H. O'Brien and M. Calin, *J. Am. Chem. Soc.* 89 (1967) 3582.
[5] P. Ros, *J. Chem. Phys.*, to be published.
[6] A. Henglein, *Adv. Chem. Ser.* 58 (1966) 63.
[7] H. F. Calcote and D. E. Jensen, *Adv. Chem. Ser.* 58 (1966) 291.
[8] H. Pritchard and A. G. Harrison, *J. Chem. Phys.* 48 (1968) 2827.
[9] C. C. J. Roothaan, *Rev. Mod. Phys.* 23 (1951) 69.
[10] E. Clementi and D. R. Davies, *J. Comput. Phys.* 1 (1966) 223.
[11] E. Clementi, *IBM Journal* 9 (1965) 2.
[12] S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293.
[13] W. J. Hehre, R. F. Stewart and J. A. Pople, *Faraday Symposium on Molecular Wave Functions*, paper 2, London (1968).
[14] E. B. Wilson, J. C. Decius and F. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
[15] *Interatomic Distances (and supplement) Special Publications nrs. 11 and 18*, Chemical Society, London (1958, 1965).
[16] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Comp., Princeton, New Jersey, 1951).
[17] B. J. Ransil, *Rev. Mod. Phys.* 32 (1960) 245.