Theoret. Chim. Acta (Berl.) 48, 215–221 (1978)

THEORETICA CHIMICA ACTA

Vertical Proton Affinities of CH_2O and CH_2OH^+ in Their Ground Singlet, Excited Triplet and Ionized Doublet States

Otto P. Strausz

Department of Chemistry, University of Alberta, Edmonton, Canada

Cornelia Kozmutza and Ede Kapuy

Physics Institute, Technical University, Budapest, Hungary

Michael A. Robb

Queen Elizabeth College, London, England

Giannoula Theodorakopoulos and Imre G. Csizmadia

Department of Chemistry, University of Toronto, Toronto, Canada

Vertical proton affinities were calculated with closed and open shell direct SCF-MO methods for the ground, excited triplet and ionized doublet states of CH_2O and CH_2OH^+.
The computed gas phase basicity of CH_2O follows the order: $CH_2O(^1A_1) > CH_2O^*(^3A_1 \text{ or } ^3A_2) > CH_2O^+(^2B_2 \text{ or } ^2B_1)$.

Key words: Proton affinities of CH_2O and CH_2OH^+

It is common knowledge that the colour of acid base indicators and the spectral characteristics of carbonyl and other lone pair-containing chromophores are markedly influenced by protonation and hydrogen bonding [1, 2]. The $n \rightarrow \pi^*$ transitions are known to exhibit a hypsochromic shift and the $\pi \rightarrow \pi^*$ transitions, a bathochromic shift. These phenomena were interpreted in terms of a one-electron model giving the following order for stabilization of orbitals upon protonation [3]: $n > \pi^* > \pi$. In contrast to this, *ab initio* SCF-MO studies [4] carried out on saturated systems, namely, ground state and protonated methanol and the methoxy ion, showed that the occupied and virtual MO levels are stabilized to similar extents in the course of successive protonation.

For this reason it appeared to be desirable to undertake an *ab initio* study of

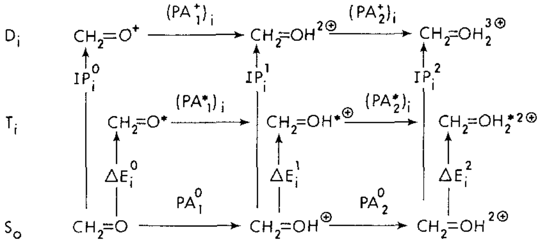

Fig. 1. Interrelationship of protonated and unprotonated formaldehyde in the ground, singlet, low-lying excited triplet and ionized doublet states

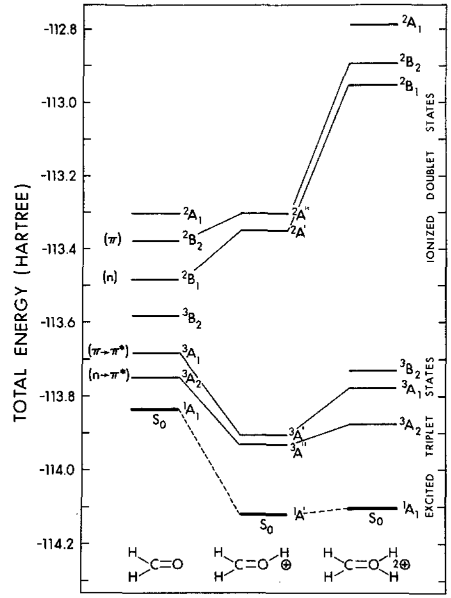

Fig. 2 Variation of state energies of formaldehyde upon protonation

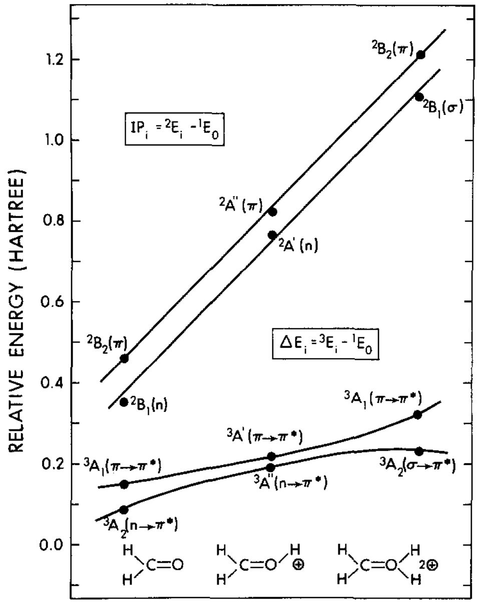

Fig. 3. Variation of *S–T* excitation energy, ΔE_i, and molecular ionization potential, IP_i, of formaldehyde upon protonation

formaldehyde, the simplest unsaturated system that has only one site of protonation. The proton affinity associated with the first protonation of ground state formaldehyde has been investigated theoretically [5–7] and experimentally [8] before, but similar studies on the higher states of formaldehyde are lacking.

In the present article we wish to report the results of direct SCF calculations[1] on the singlet ground state, some low-lying triplet excited states and ionized doublet

---

[1] The molecular orbitals were expanded in terms of a double zeta basis set. These basis functions were contracted from a set of primitive GTF according to Veillard, Theoret. Chim. Acta (Berl.) **11**, 441 (1968). The molecular integrals were evaluated and the closed shell SCF computations (Rev. Mod. Phys. **23**, 69 (1951)) were performed using a modified version (Chem. Phys. Letters **10**, 631 (1971)) of the POLYATOM 2 system (Program No. 199, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana). The open shell SCF programs were written by M. A. Robb. All computations were carried out on a CDC 7600 computer at the University of London using fixed molecular geometries. The coordinates [5] used for all three species in bohr atomic units are as follows.

	x	z
H_1	-1.7854978	-2.3801381
H_2	$+1.7854978$	-2.3801381
C	0.0	-1.3492803
O	0.0	$+0.9373158$
H_3	$+1.5825752$	$+1.8510158$
H_4	-1.5825752	$+1.8510158$

(all y coordinates are identically zero).

Table 1. Molecular orbital energies of formaldehyde, mono- and di-protonated formaldehyde

H_2CO		H_2COH^+		$H_2COH_2^{2+}$	
Orbitals	ε_i (a.u.)	Orbitals	ε_i (a.u.)	Orbitals	ε_i (a.u.)
11 $3b_1$	+ 0.1918	11 $9a'$	− 0.0450	11 $3b_1$	− 0.2966
10 $6a_1$	+ 0.1516	10 $8a'$	− 0.0945	10 $6a_1$	− 0.3539
9 $2b_2(\pi^*)$	+ 0.1082	9 $2a''(\pi^*)$	− 0.1960	9 $2b_2(\pi^*)$	− 0.4851
8 $2b_1(n)$	− 0.4475	8 $7a'(n)$	− 0.8289	8 $2b_1(\sigma)$	− 1.1902
7 $1b_2(\pi)$	− 0.5358	7 $1a''(\pi)$	− 0.9145	7 $1b_2(\pi)$	− 1.3132
6 $5a_1(n)$	− 0.6449	6 $6a'(n)$	− 1.0163	6 $5a_1(\sigma)$	− 1.3616
5 $1b_1$	− 0.7133	5 $5a'$	− 1.0931	5 $1b_1$	− 1.5362
4 $4a_1$	− 0.8746	4 $4a'$	− 1.2551	4 $4a_1$	− 1.6290
3 $3a_1$	− 1.4266	3 $3a'$	− 1.8259	3 $3a_1$	− 2.2202
2 $2a_1$	−11.3598	2 $2a'$	−11.6916	2 $2a_1$	−12.0021
1 $1a_1$	−20.5966	1 $1a'$	−20.9698	1 $1a_1$	−21.3645

(hole) states of formaldehyde as well as its mono- and d-protonated forms. This makes it possible to analyze the pattern[2] of *S–T* excitation energies and ionization potentials. From these results we can also calculate the gas phase proton affinities of the unprotonated and mono-protonated species of the ground state, the low lying excited triplet and ionized doublet states. The interrelationship of these species and the definition of relative energies are illustrated schematically in Fig. 1.

It should be noted that previous studies dealing with the effect of protonation on the optical properties of unsaturated heteroatom-containing molecules were restricted to ground singlet states and to singlet-singlet transitions. The range of investigation is extended here to include triplet and doublet species in their parent, mono- and di-protonated forms.

The orbital energies of the ground singlet state of $CH_2{=}O$, $CH_2{=}OH^+$ and $CH_2{=}OH_2^{2+}$ calculated by the closed-shell SCF methods are summarized in Table 1. The trend is similar to that observed earlier [4] for the saturated analogs methanol and protonated methanol.

The ground state total energies are given in Table 2 and the effect of protonation on these levels, illustrated in Fig. 2, is similar to that observed in the cases of H_2O, HF and Ne [9]. As expected, the $\pi \rightarrow \pi^*$ state is the second lowest excited triplet state in the unprotonated [10] and doubly protonated formaldehyde (both species belong to the C_{2v} point group) and in the monoprotonated species as well.

These state energies allow us to compute the excitation (1) and ionization (2) energies for the *i*'th triplet or for the *i*'th doublet state:

$$\Delta E_i = {}^3E_i - {}^1E_0 \tag{1}$$

$$IP_i = {}^2E_i - {}^1E_0 \tag{2}$$

---

[2] It is expected that the pattern will be quite reliable even if the actual values incorporate the difference in correlation energies as a systematic error.

Table 2. Molecular total energy values[a] computed by direct SCF methods[b]

State	H_2CO		H_2COH^+		$H_2COH_2^{2+}$	
	Orbitals	E (a.u.)	Orbitals	E (a.u.)	Orbitals	E (a.u.)
Ionized doublet	6 ($^2A_1$)	−113.3033	—[c]		6 ($^2A_1$)	−112.7894
	7 ($^2B_2$)	−113.3782	7 ($^2A''$)	−113.3037	7 ($^2B_2$)	−112.8941
	8 ($^2B_1$)	−113.4847	8 ($^2A'$)	−113.3559	8 ($^2B_1$)	−112.9521
Excited triplet	$6 \rightarrow 9$ ($^3B_2$) ($n \rightarrow \pi^*$)	−113.5813	—[c]		$6 \rightarrow 9$ ($^3B_2$) ($\sigma \rightarrow \pi^*$)	−113.7302
	$7 \rightarrow 9$ ($^3A_1$) ($\pi \rightarrow \pi^*$)	−113.6851	$7 \rightarrow 9$ ($^3A'$) ($\pi \rightarrow \pi^*$)	−113.9076	$7 \rightarrow 9$ ($^3A_1$) ($\pi \rightarrow \pi^*$)	−113.7787
	$8 \rightarrow 9$ ($^3A_2$) ($n \rightarrow \pi^*$)	−113.7508	$8 \rightarrow 9$ ($^3A''$) ($n \rightarrow \pi^*$)	−113.9321	$8 \rightarrow 9$ ($^3A_2$) ($\sigma \rightarrow \pi^*$)	−113.8746
Ground singlet	Closed shell	−113.8398	Closed shell	−114.1263	Closed shell	−114.1063

[a] All energy values are given in hartree a.u.

[b] The orbitals involved in the open shells are indicated in front of the total energy values and the state symmetries are shown in parentheses behind the total energy values.

[c] Only the lowest state in each irreducible representation has been computed by the open shell SCF.

These values are summarized in Table 3 in the columns labelled ΔSCF. The changes in these relative energies (obtained by the direct SCF method) during the course of protonation are illustrated in Fig. 3. It should perhaps be noted that neither the $^3(n \rightarrow \pi^*)$ nor the $^3(\pi \rightarrow \pi^*)$ energies vary linearly with protonation; the former gives a convex while the latter a concave curve and there is no intersection. The functional behavior of the ionization energies to the n-hole and the π-hole states is different from that of the excitation energies in that they vary almost in parallel

Table 3. Ionization potentials and S–T excitation energies obtained[a] with one-electron approximations as well as with direct SCF computations

System	$IP_i = {}^2E - {}^1E_0$			$\Delta E_i = {}^3E_i - {}^1E_0$		
	Upper state	KT[b]	ΔSCF	Upper state	VO[c]	ΔSCF
$H_2COH_2^{2+}$	$^2A_1(\sigma)$	1.3616	1.3169	$^3B_2(\sigma \rightarrow \pi^*)$	0.4080	0.3761
	$^2B_2(\pi)$	1.3132	1.2122	$^3A_1(\pi \rightarrow \pi^*)$	0.4154	0.3276
	$^2B_1(\sigma)$	1.1902	1.1542	$^3A_2(\sigma \rightarrow \pi^*)$	0.2599	0.2317
H_2COH^+	$^2A''(\pi)$	0.9145	0.8226	$^3A'(\pi \rightarrow \pi^*)$	0.2854	0.2188
	$^2A'(n)$	0.8289	0.7705	$^3A''(n \rightarrow \pi^*)$	0.2358	0.1943
H_2CO	$^2A_1(n)$	0.6449	0.5365	$^3B_2(n \rightarrow \pi^*)$	0.3317	0.2585
	$^2B_2(\pi)$	0.5358	0.4616	$^3A_1(\pi \rightarrow \pi^*)$	0.2011	0.1546
	$^2B_1(n)$	0.4475	0.3551	$^3A_2(n \rightarrow \pi^*)$	0.1588	0.0889

[a] All values are given in hartree a.u.

[b] Calculated by Koopmans' Theorem.

[c] Calculated by virtual orbital method.

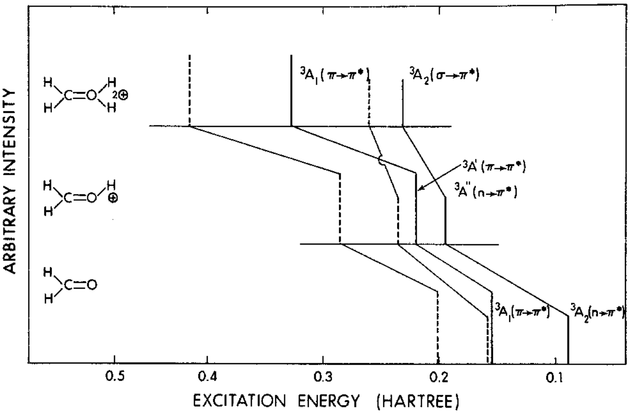

Fig. 4. Theoretical S–T absorption spectra of formaldehyde and its protonated forms. (Vertical broken lines represent the results of the calculations using the virtual orbital method. Vertical solid lines represent the results of the direct SCF calculations.)

and linearly with increasing degree of protonation. The linear variation of the ionized doublet hole states with protonation has also been observed in a series of ten-electron systems [11].

For comparison we calculated the relative energies, ΔE and IP, by the virtual orbital (VO) method (3) and by Koopmans' theorem (KT), Eq. (4).

$$\Delta E_i \equiv {}^3\Delta E_{1\to k} = (\varepsilon_k - \varepsilon_1) + J_{k1} \tag{3}$$

$$IP_i = -\varepsilon_i \tag{4}$$

These values are also included in Table 3.

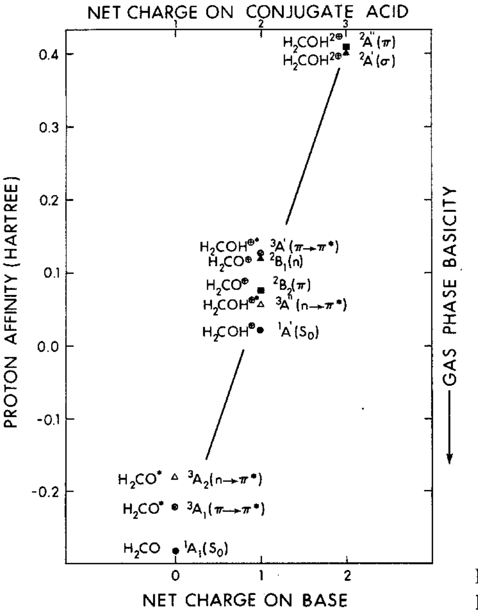

Fig. 5. Variation of proton affinity of formaldehyde with base net charge

Table 4. Proton affinity values for the low lying states of CH_2O and CH_2OH^+

System	Ground singlet state	Excited triplet states		Ionized doublet states	
		Transition	*PA*	Transition	*PA*
H_2CO	-0.2865[a, b]	$^3A_1 \rightarrow {}^3A'$ $(\pi \rightarrow \pi^*)$	-0.2224	$^2B_2 \rightarrow {}^2A''$ (π)	$+0.0745$
		$^3A_2 \rightarrow {}^3A''$ $(n \rightarrow \pi^*)$	-0.1812	$^2B_1 \rightarrow {}^2A'$ (n)	$+0.1288$
H_2COH^+	$+0.0231$	$^3A'' \rightarrow {}^3A_2$ $(n \rightarrow \pi^*)$	$+0.0575$	$^2A' \rightarrow {}^2B_1$ (σ)	$+0.4038$
		$^3A' \rightarrow {}^3A_1$ $(\pi \rightarrow \pi^*)$	$+0.1289$	$^2A'' \rightarrow {}^2B_2$ (π)	$+0.4096$

[a] Previously reported [5–7] theoretical values are: 0.2774, 0.2736, 0.3511.

[b] Experimental [8] value: 0.2565 ± 0.0048.

It is clear that these one-electron approximations overestimate the energy separations between states while the direct SCF method underestimates them. Clearly, the latter discrepancy is due to the difference in correlation energy between the ground singlet state ($^1E_{\text{corr}}$) and the excited triplet ($^3E_{\text{corr}}$) as well as ionized doublet ($^2E_{\text{corr}}$) states:

$$^1E_{\text{corr}} > {}^3E_{\text{corr}} \approx {}^2E_{\text{corr}} \tag{5}$$

However, it is expected that the *trend* in ΔE and IP upon protonation is revealed more accurately by the direct SCF method as compared to the one-electron approximations (VO and KT).

The trend in S–T absorption is illustrated in Fig. 4 in the form of a theoretical spectrum for all the computational methods used. A similar plot for the theoretical photoelectron spectra can also be drawn using the IP values summarized in Table 3.

Since there is no electron unpairing in the course of protonation the proton affinity (PA) values can be calculated with a greater reliability than the S–T excitation energy.

These values are tabulated in Table 4. The results clearly indicate that CH_2O is most basic in its electronic ground state (S_0), less basic in its excited triplet states (T_i), and that protonation in the ionized doublet states (D_i) is endothermic:

$$S_0 > T_i > D_i \tag{6}$$

Further inspection of the results shows how the computed PA value varies with the net charge of the molecule. The trend is clearly illustrated in Fig. 5.

Acknowledgement. The authors are grateful to the National Research Council of Canada for financial support.

References

1. Calvert, J. G., Pitts, J. N. Jr.: Photochemistry, p. 257. New York: John Wiley and Sons 1967
2. Jaffé, H. H., Orchin, M.: Theory and applications of ultraviolet spectroscopy, p. 188. New York: John Wiley and Sons 1962
3. Jaffé, H. H., Yeh, S. J., Gardner, R. W.: J. Mol. Spectry. **2**, 120 (1958)
4. Tel, L. M., Wolfe, S., Csizmadia, I. G.: J. Chem. Phys. **59**, 4047 (1973)
5. Tel, L. M., Wolfe, S., Csizmadia, I. G.: Intern. J. Quantum Chem. **7**, 475 (1973)
6. Hopkinson, A. C., Holbrook, N. K., Yates, K., Csizmadia, I. G.: J. Chem. Phys. **49**, 3596 (1968)
7. Ros, P.: J. Chem. Phys. **49**, 4902 (1968)
8. Harrison, A. G., Irko, A., van Raalte, D.: Can. J. Chem. **44**, 1625 (1966)
9. Daudel, R., Kozmutza, C., Kapuy, E.: Chem. Phys. Letters **36**, 555 (1975)
10. Langhoff, S. R., Davidson, E. R.: J. Chem. Phys. **64**, 4699 (1976)
11. Kozmutza, C., Kapuy, E., Robb, M. A., Daudel, R., Csizmadia, I. G.: J. Chem. Phys. (submitted)

Received August 8, 1975/ June 15, 1977/November 24, 1977