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Ab Initio SCF Study of HCO_2H, HCO_2H^-, and HCO_2H^+. Application to the Decomposition of Formic Acid on Titanium Dioxide

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An ab initio SCF study of the acid HCO_2H and the HCO_2H^- and HCO_2H^+ species, the limiting forms which could be obtained when HCO_2H is in the presence of electron donors or acceptors, leads to an understanding of the mechanism of the catalytic decomposition of formic acid on these different centers.

INTRODUCTION

The results of kinetic experiments on the catalytic decomposition of formic acid on TiO_2 have shown that electron-donor centers promote the dehydration reaction, whereas electron-acceptor centers have no catalytic activity in this reaction (*1*). EPR confirmed the existence of a Ti^{3+}–HCO_2H bond at the surface of TiO_2 (*1*). NMR provided structural detail about the species $(HCO_2H)^{-\epsilon}$ chemisorbed on the electron-donor centers by giving the value of the electronic charge $-\epsilon$ transferred from the solid and the deformation angle of this species relative to the initial planar structure (*2*).

We thought that it would be interesting to seek confirmation of the interpretation of the various experimental data by an ab initio SCF study of the acid HCO_2H and the HCO_2H^- and HCO_2H^+ species, the limiting forms which could be obtained when HCO_2H is in the presence of electron donors or acceptors. In particular, the electron distribution in the latter should lead to an understanding of the mechanism of the catalytic decomposition of formic acid on these different centers.

METHOD

The calculations were carried out with the Gaussian 70 series of programs (*3*) and the STO-3G minimal base set (*4*), using the Roothaan hamiltonian (*5*) for the closed shell systems (singlet) and the unrestricted Nesbet hamiltonian (*6*) for the open shell systems (doublet). Analyses of the charge density and the bond indices were performed by the Mulliken method (*7*).

RESULTS

1. Molecule HCO_2H

We have adopted the standard geometry of the molecule (*8*) (Fig. 1). The atomic functions are defined by the axes depicted in Fig. 1. For convenience, all the atoms are numbered (Fig. 2).

We have determined the molecular orbitals. The energies E corresponding to those which are occupied range from −20.2964 to −0.3490 a.u. The only ones which are of interest to this study are the π-MO (No. 12), which is the last occupied one, whose equation is

$$\pi\text{-MO-12} = 0.30\, p_y^{C(1)} + 0.61\, p_y^{O(2)} - 0.72\, p_y^{O(4)}; \quad E_{12} = -0.3490 \text{ a.u.}$$

and the unoccupied antibonding π^*-MO (No. 13) whose equation is

$$\pi^*\text{-MO-13} = 0.84\, p_y^{C(1)} - 0.72\, p_y^{O(2)} - 0.32\, p_y^{O(4)}; \quad E_{13} = +0.3037 \text{ a.u.}$$

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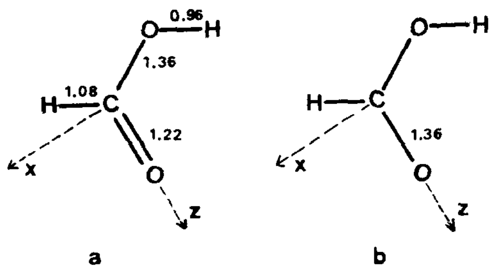

FIG. 1. Geometry of molecule (a) and ions (b).

The form of these two MO indicates that they can overlap with the Ti *d*-orbitals, both in reactions involving electron donation to Ti^{4+} (filled π-MO-12) or electron capture from Ti^{3+} (empty π^*-MO-13). Moreover (Fig. 2), the two oxygen atoms are negatively charged (-0.26 and -0.33 a.u. for the C=O and C—OH group oxygens, respectively) while the hydrogen and carbon atoms are positively charged. Finally, the Mulliken bond indices are 0.43, 0.30, 0.27, and 0.375 for the C=O, C—OH, O—H, and C—H bonds, respectively.

2. *Limiting Cationic Form* $(HCO_2H)^+$

We adopted the planar configuration for this study and assumed a $C-O^{(2)}$ distance of 0.136 nm (*8*). It should be noted first of all that the MO spin orbital which contains the unpaired electron corresponds roughly to the analytical form of the π-MO-12 of the neutral species:

$$\pi\text{-MO-}12\alpha = 0.19\, p_y^{C(1)} - 0.55\, p_y^{O(2)} + 0.81\, p_y^{O(4)};$$
$$E_{12\alpha} = -0.7703 \text{ a.u.}$$

The O–H and C–H bond indices change very little on going from the neutral form to the cationic form $(HCO_2H)^+$. The $C-O^{(2)}$ bond index decreases markedly from 0.43 to 0.29 while that of C–OH increases from 0.30 to 0.35. This increase is due to a fairly large decrease in the electronic charges on C and $O^{(4)}$ atoms in favour of the bond between them from 0.26 to 0.41 and -0.33 to 0.17, respectively. Consequently, when HCO_2H loses an electron, the C–OH bond is not weakened. Rupture of this bond cannot therefore be catalysed by chemi-

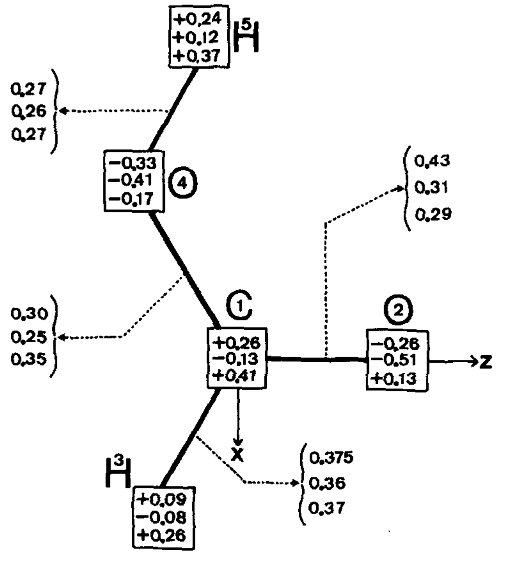

FIG. 2. Bracketed values are Mulliken indices and values in boxes are the charges at the atoms in HCO_2H, HCO_2H^-, and HCO_2H^+.

TABLE 1

Calculated Spin Densities for $HCOOH^-$ and $HCOOH^+$

Atom		AO	Spin density	
			$HCOOH^-$	$HCOOH^+$
1	C	1*s*	5.395×10^{-5}	-1.300×10^{-4}
1	C	2*s*	5.918×10^{-2}	-3.341×10^{-2}
1	C	$2p_x$	2.410×10^{-2}	-3.628×10^{-2}
1	C	$2p_y$	0.487	-6.398×10^{-2}
1	C	$2p_z$	1.323×10^{-2}	-5.186×10^{-2}
2	O	1*s*	4.495×10^{-5}	4.785×10^{-5}
2	O	2*s*	1.331×10^{-2}	2.309×10^{-2}
2	O	$2p_x$	2.805×10^{-3}	0.968
2	O	$2p_y$	0.478	9.996×10^{-2}
2	O	$2p_z$	-2.469×10^{-2}	4.710×10^{-2}
3	H	1*s*	-5.703×10^{-2}	3.491×10^{-2}
4	O	1*s*	-3.026×10^{-6}	-7.760×10^{-6}
4	O	2*s*	-1.310×10^{-3}	-1.203×10^{-3}
4	O	$2p_x$	-1.383×10^{-2}	1.908×10^{-2}
4	O	$2p_y$	3.360×10^{-2}	-3.585×10^{-2}
4	O	$2p_z$	-1.397×10^{-2}	2.997×10^{-2}
5	H	1*s*	-1.911×10^{-3}	2.165×10^{-4}

sorption of HCO_2H on electron-acceptor centers.

3. *Limiting Anionic Form* $(HCO_2H)^-$

(*a*) *Planar form.* Firstly we have carried out a study of the anionic form on the assumption that it was planar (Fig. 2 and Table 1). In this case the π^*-MO spin orbital which contains the electron corresponds to the analytical form of the π^*-MO-13 of HCO_2H:

$$\pi\text{-MO-}13\alpha = 0.85\, p_y^{\mathrm{C}} - 0.59\, p_y^{\mathrm{O(2)}} - 0.42\, p_y^{\mathrm{O(4)}}; \qquad E_{13\alpha} = 0.2071 \text{ a.u.}$$

In comparison with the results for HCO_2H we observe that the overall negative charge on the atoms increases generally. The Mulliken indices of the O–H and C–H bonds are unchanged. In contrast, those of $C–O^{(2)}$ and C–OH decrease significantly; in particular, that of C–OH has the lowest value (0.25). Consequently, in $(HCO_2H)^-$ the C–OH bond is the easiest to break. This could explain the catalytic dehydration of HCO_2H on electron-donor centers.

Table 1 gives the calculated electron-spin densities. The principal densities are naturally π-type:

$$\rho^{\mathrm{C}}_{\pi^*(2p_y)} = 0.487 \qquad \text{and} \qquad \rho^{\mathrm{O(2)}}_{\pi^*(2p_y)} = 0.478.$$

We note that these two spin densities are nearly identical. This justifies our calculation of the overall electronic charge transferred from Ti^{3+} to HCO_2H on the basis of the NMR-determined value of $\rho_{\pi^*}{}^{\mathrm{C}}$ alone (*2*). This density $\rho_{\pi^*}{}^{\mathrm{C}}$ induces a spin polarisation along the σ bonds leading to contributions ρ_s on the *s* electrons of the order of 10^{-2}. The values associated with carbon and hydrogen atoms are of opposite sign and in this theoretical planar configuration of $(HCO_2H)^-$ the absolute values of $\rho_{2s}^{\mathrm{C(1)}} = 5.92 \times 10^{-2}$ and of $\rho_{1s}^{\mathrm{H(3)}} = 5.70 \times 10^{-2}$ are practically equal, in agreement with the theory of spin polarisation (*9*). The NMR signals of the hydrogen and the carbon of the CH group must be shifted downfield and upfield, respectively, relative to the corresponding position in HCO_2H, as is confirmed by the NMR results (*2*).

(*b*) *Nonplanar form.* We then determined the most stable geometric form of HCO_2H^- (optimisation in terms of energy minimum). More exactly, we considered only the variation of the $C–O^{(2)}$ distance and the out-of-plane angle α of the C–H bond relative to the theoretical planar position, all of the other parameters being fixed in the positions of the neutral molecule. Table 2 shows that the most stable configuration of $(HCO_2H)^-$ corresponds to a distance $d(C–O^{(2)}) = 0.129$ nm and an angle $\alpha = 28.5°$ (minimum total energy: -185.9560 a.u.). For $\alpha > 28.5°$ (cases not reported in Table 2) the values of the total energy are greater than this minimum whatever the reasonable distance of $d(C–O^{(2)})$. This value of α corresponds to the average bond angle of 118°, in agreement with the value obtained from the NMR of HCO_2H chemisorbed on electron-donor centers (*2*). The charges located on the atoms appear to be independent of the angle α ($\Delta q_i = 10^{-2}$ a.u.) for a given value of $d(C–O^{(2)})$. Also, for constant α, only q_{C} depends on $d(C–O^{(2)})$.

In the study of the planar structure we saw that electron capture by HCO_2H markedly decreases the energy of the two C–O bonds. However, the latter are very little affected by deformation of $(HCO_2H)^-$. The Mulliken index of C–OH, for example, decreases by 0.25 (for planar form) to 0.24 for the stablest form ($\alpha = 28.5°$).

Let us now consider the spin densities. The increase in α leads to higher $\rho_{2s}{}^{\mathrm{C}}$ and to lower $|\rho_{1s}^{\mathrm{H(3)}}|$. These results are also in complete agreement with those deduced from the NMR experiments which revealed that the absolute value of the carbon coupling constant ($a_{\mathrm{C}} = -13.330$ G) and that of hydrogen ($a_{\mathrm{H}} = 1.019$ G) are very different (*2*).

There is one last point: $\rho_{1s}^{\mathrm{H(5)}}$ is -1.91×10^{-3} in the planar form of $(HCO_2H)^-$. The algebraic value of this spin density in-

TABLE 2

Influence of Geometry on Total Energy, Charges on Atoms, and Spin Densities

	Total energy, E_T (a.u.)	Angle α (°)	Distance d(C=O) (nm)	Charges located on the atoms					Spin density					
				$q^{O(2)}$	$q^{C(1)}$	$q^{H(3)}$	$q^{O(4)}$	$q^{H(5)}$	$\rho_\pi^{C(1)}$	$\rho_\pi^{O(2)}$	$\rho_{2s}^{C(1)}$ ×10²	$\rho_{1s}^{H(3)}$ ×10²	$\rho_\pi^{O(4)}$ ×10²	$\rho_{1s}^{H(5)}$ ×10³
HCOOH	−186.2019	0	0.122	−0.26	+0.26	+0.09	−0.33	−0.24	0	0	0	0	0	0
$HCOOH^+$	−185.9641	0	0.136	+0.13	+0.41	+0.26	−0.16	+0.37	−0.064	+0.100	−3.45	3.49	−3.58	0.21
$HCOOH^-$	−185.9424	0	0.136	−0.51	−0.13	−0.07	−0.41	−0.12	+0.487	+0.479	+5.92	−5.70	+3.36	−1.91
$HCOOH^-$	−185.9429	5	0.136	−0.51	−0.13	−0.08	−0.41	−0.12	+0.480	+0.481	+5.97	−5.48	+3.31	−0.90
$HCOOH^-$	−185.9443	10	0.136	−0.50	−0.13	−0.08	−0.41	−0.12	+0.464	+0.480	+6.20	−4.97	+3.21	0.45
$HCOOH^-$	−185.9466	25	0.124	−0.52	−0.06	−0.10	−0.42	−0.11	+0.376	+0.462	+7.81	−1.84	+2.51	9.28
$HCOOH^-$	−185.9467	10	0.132	−0.51	−0.11	−0.08	−0.41	−0.12	+0.460	+0.484	+6.12	−4.95	+3.09	0.64
$HCOOH^-$	−185.9517	20	0.132	−0.51	−0.11	−0.09	−0.41	−0.12	+0.406	+0.478	+6.93	−3.17	+2.79	5.30
$HCOOH^-$	−185.9531	25	0.128	−0.51	−0.08	−0.10	−0.41	−0.11	+0.373	+0.470	+7.56	−1.99	+2.55	8.55
$HCOOH^-$	−185.9545	25	0.130	−0.51	−0.09	−0.10	−0.41	−0.11	+0.371	+0.473	+7.45	−2.07	+2.57	8.24
$HCOOH^-$	−185.9560	28.5	0.129	−0.51	−0.09	−0.10	−0.41	−0.11	+0.347	+0.469	+7.81	−1.30	+2.43	10.31

creases with α. For example, it is $+10.31 \times 10^{-3}$ for the stablest configuration. This result is in agreement with theory which requires that in such a nonplanar structure the carbon directly induces a spin density on $H^{(5)}$ by hyperconjugation (*9*).

CONCLUSION

The wave mechanical study explains why dehydration of HCO_2H is facilitated by chemisorption of the molecule on electron-donor centers. When $(HCO_2H)^-$ if formed by the capture of an electron, all the bond energies decrease but most importantly those of the two C–O bonds. Moreover, the C–OH bond is the weakest and consequently the easiest to break.

The calculated electron spin density distribution is in complete agreement with the experimental results deduced from NMR. The two methods prove that when HCOOH is chemisorbed on an electron-donor center it loses its planar structure.

It might have been expected that the result would be similar when HCO_2H loses an electron by chemisorption on an electron-acceptor center. The above calculations prove the contrary: the C–OH bond index (0.35) is greater than that of the neutral form (0.30). This is due to the fact that, in this cationic form, the electronic charges are localized more between the atoms than on them. It is therefore impossible to catalyse the dehydration of formic acid in the presence of electron-acceptor centers.

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