

## ON THE DISSOCIATION CHARACTERISTICS OF $\text{H}_2\overset{+}{\text{C}}\text{OH}$ IONS AND THEIR PARTICIPATION IN THE $\text{H}_2$ -CATALYSED ISOMERISATION OF $\overset{+}{\text{C}}\text{OH}$ TO $\overset{+}{\text{H}}\text{CO}$

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### ABSTRACT

Experiments and ab initio molecular orbital theory calculations on the dissociation characteristics of  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  have shown that it could act as an intermediate in the  $\text{H}_2$ -catalysed isomerisation of  $\overset{+}{\text{C}}\text{OH}$  to  $\overset{+}{\text{H}}\text{CO}$ . The rate-determining energy barrier was the addition reaction  $\text{H}_2 + \overset{+}{\text{C}}\text{OH} \rightarrow \text{H}_2\overset{+}{\text{C}}\text{OH}$  and not the latter's dissociation to  $\overset{+}{\text{H}}\text{CO} + \text{H}_2$ . No evidence was obtained for the participation of the oxoniomethylene cation,  $\overset{+}{\text{H}}\text{COH}_2$ , in the reaction  $\text{H}_2\overset{+}{\text{C}}\text{OH} \rightarrow \overset{+}{\text{H}}\text{CO} + \text{H}_2$ . For the dissociation reaction  $\text{H}_2\overset{+}{\text{C}}\text{OH} \rightarrow \overset{+}{\text{H}}\text{CO} + \text{H}_2$  it was found from calculations that the reaction centre lies towards the carbon atom, in agreement with recent interpretations of secondary isotope effects. The associated transition state has a very short lifetime ( $10^{-14}$  s). It was also found that rearrangement of (singlet)  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  to singlet  $\text{H}_3\overset{+}{\text{C}}\text{O}$  is energetically prohibited. Isomerisation into triplet  $\text{H}_3\overset{+}{\text{C}}\text{O}$ , although energetically possible, is too slow to compete with fragmentation, thus explaining the observation that the hydroxylic hydrogen atom always appears in the  $\text{H}_2$  molecule.

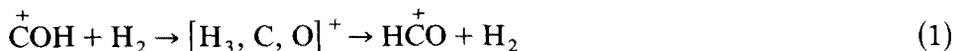
### INTRODUCTION

The ions  $\overset{+}{\text{H}}\text{CO}$  and  $\overset{+}{\text{C}}\text{OH}$  have attracted considerable attention in recent years because of their significance as ions observed in interstellar space [1].

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Experiments by Illies et al. [2] and by Burgers et al. [3–5] have clearly identified  $\overset{+}{\text{COH}}$  as a stable species in the gas phase. In agreement with high level ab initio molecular orbital theory calculations [6], the ion was found to isomerise partially to  $\overset{+}{\text{HCO}}$  at energies below the dissociation limit to  $\text{H}^+ + \text{CO}$ , the fragmentation of lowest energy requirement, 108 kcal mol<sup>-1</sup> above  $\overset{+}{\text{COH}}$ . The heats of formation ( $\Delta H_f^0$ ) of  $\overset{+}{\text{HCO}}$  and  $\overset{+}{\text{COH}}$  have most recently been measured by McMahon and Kebarle [7],  $\Delta H_f^0[\overset{+}{\text{HCO}}] = 194$  kcal mol<sup>-1</sup> and  $\Delta H_f^0[\overset{+}{\text{COH}}] = 230$  kcal mol<sup>-1</sup>. The difference in these heats of formation (36 kcal mol<sup>-1</sup>) is in good agreement with the ab initio calculations of DeFrees et al. [8] (33 kcal mol<sup>-1</sup>) and Nobes and Radom [6] (37 kcal mol<sup>-1</sup>). Note that the earlier experimental value for  $H_f^0[\overset{+}{\text{COH}}] = 220$  kcal mol<sup>-1</sup> [3] has been shown to be too low and corresponded to energy-rich  $\overset{+}{\text{HCO}}$  ions [9].

With respect to their observation in space and their origin from the reaction of  $\text{H}_3^+$  with CO, a difficulty exists in regard to the observed interstellar abundance,  $[\overset{+}{\text{COH}}] < 0.003 [\overset{+}{\text{HCO}}]$  [1] and the laboratory result of Illies et al. [2],  $[\overset{+}{\text{COH}}] = 0.1\text{--}0.01[\overset{+}{\text{HCO}}]$ . One way to account for the low interstellar abundance of  $\overset{+}{\text{COH}}$  is that this ion can be catalytically converted to its thermodynamically more stable isomer by reaction with molecular hydrogen.



Using ab initio molecular orbital methods, DeFrees et al. [8(a)] calculated two potential energy surfaces for this reaction. The first was a low-energy pathway not involving stable intermediates, whereas the second involved  $\text{H}_2\overset{+}{\text{COH}}$  and  $\text{HCOH}_2^+$  as possible intermediate species. For the first reaction [see Fig. 2 in ref. 8(a)], an energy barrier of 10 kcal mol<sup>-1</sup> relative to  $\text{COH} + \text{H}_2$  was calculated, but recent work by Wagner-Redeker et al. [10] indicated that the barrier height for this reaction was very small (< 1 kcal mol<sup>-1</sup>). These results account well for the small interstellar abundance of  $\text{COH}^+$ ; the whole question was re-analysed by Jarrold et al. [11] in 1986, bringing theory and experiment into close agreement for the low-energy isomerisation pathway.

For the reaction that proceeds via the stable intermediates  $\text{H}_2\overset{+}{\text{COH}}$  and  $\text{HCOH}_2^+$  [see Fig. 3 in ref. 8(a)], an activation energy of 86 kcal mol<sup>-1</sup> relative to  $\overset{+}{\text{COH}} + \text{H}_2$  was calculated for reaction (1). The corresponding transition state appears in the fragmentation of the  $\text{HCOH}_2^+$  isomer to yield

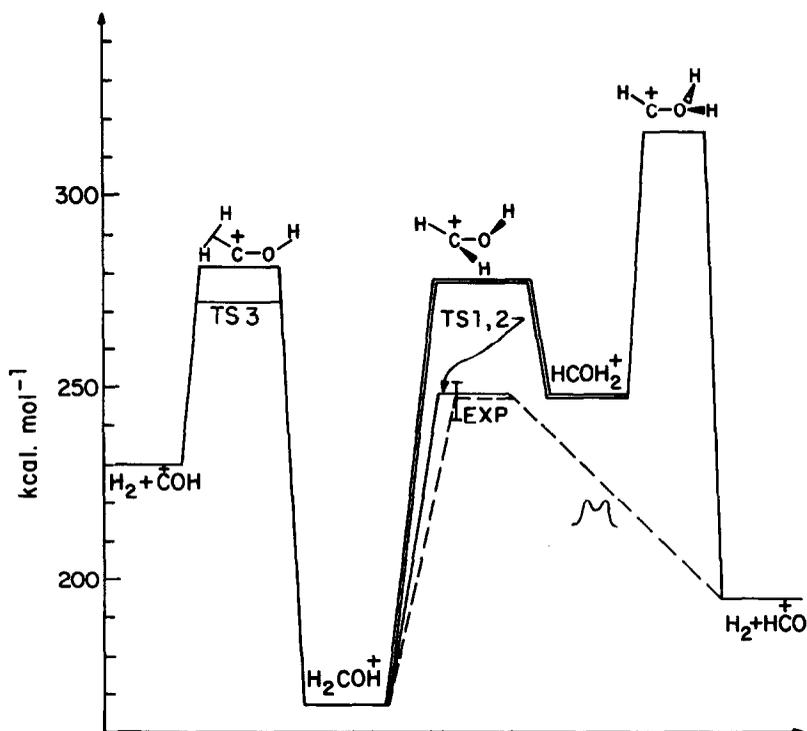


Fig. 1. Energy diagram for  $[\text{H}_3\text{C}, \text{O}]^+$  ions. —, Calculations of DeFrees et al. [8]; ---, Nobes et al. [5]; - - -, from AE of metastable peak; TS1, TS2 this work. Metastable peak shape as indicated.

$\text{HCO}^+ + \text{H}_2$ . It lies  $149 \text{ kcal mol}^{-1}$  above the lowest energy isomer,  $\text{H}_2\overset{+}{\text{C}}\text{OH}$ ,  $\Delta H_f^0 = 169 \text{ kcal mol}^{-1}$  [12,13] and  $166 \text{ kcal mol}^{-1}$  [14,15]. The isomerisation reaction  $\text{H}_2\overset{+}{\text{C}}\text{OH} \rightarrow \text{HCOH}_2^+$  involved a lower-lying transition state which was also studied by Nobes et al. [16]. The results of these calculations, shown in Fig. 1, indicated that  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  ions with internal energies slightly in excess of the minimum energy required for fragmentation should produce  $\text{COH} + \text{H}_2$ . Also, loss of  $\text{H}^+$  from such ions may be even more energetically favourable because the dissociation limit  $\text{H}_2\overset{+}{\text{C}}\text{O}^+/\text{H}^+$  is slightly lower in energy than the transition state separating  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  and  $\overset{+}{\text{C}}\text{OH}/\text{H}_2$  (assuming that there is no barrier for the  $\text{H}_2\overset{+}{\text{C}}\text{O}^+/\text{H}^+$  recombination reaction, see below).

The fragmentation of  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  has been studied in some detail [17–22]. It has been shown [18,19,22] that  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  loses  $\text{H}_2$  unimolecularly in the  $\mu\text{s}$  time frame and that a large amount ( $> 30 \text{ kcal mol}^{-1}$ ) of the ion's internal

energy appears as translational energy of the products, showing the existence of a barrier for the reverse reaction.

In view of the above arguments, we were prompted to re-investigate the unimolecular chemistry of gaseous  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  ions and have found that a relatively low-energy pathway is available whereby  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  eliminates  $\overset{+}{\text{H}}\overset{+}{\text{C}}\text{O}$  instead of  $\overset{+}{\text{C}}\text{OH}$ . This was confirmed by ab initio calculations, which also led to the clarification of the associated reaction mechanisms.

## EXPERIMENTAL

All experiments were performed on an AEI-MS902S or a VG-ZAB-2F mass spectrometer. Experimental conditions and appropriate references are given in the text. In the double collision experiment  $\text{H}_2\overset{+}{\text{C}}\text{OH} + \text{He} \rightarrow [\text{H}, \text{C}, \text{O}]^+ \rightarrow \text{mass selection} \rightarrow [\text{H}, \text{C}, \text{O}]^+ + \text{He} \rightarrow \text{C}^+, \text{HC}^+$ , interference peaks were observed: the signals corresponding to  $\text{C}^+$  and  $\text{HC}^+$  showed weak shoulders at field strengths 40–60 V higher than those calculated for  $\text{C}^+$  and  $\text{HC}^+$ . From inspection of the peak shapes, it was concluded that the quoted peak height ratio  $\text{C}^+/\text{CH}^+ = 0.5$  is an upper limit. The origin of these interference signals is probably the following: to eliminate the detection of *metastably* formed  $\overset{+}{\text{H}}\overset{+}{\text{C}}\text{O}$  ions from  $\text{H}_2\overset{+}{\text{C}}\text{OH}$ , the ionising electrons' energy was reduced until the peak disappeared, Helium was then admitted to the first field-free region to induce the  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  ions to decompose. However, under these conditions, the ions exiting the ion source will contain unfragmented molecular ions  $\text{CH}_3\text{OH}^+$  and so  $^{13}\text{CH}_3\text{OH}^+$  ions will also be present in the first field-free region. The latter will be partially decomposed by collision with He, losing  $\text{H}_2$  and  $\text{H}^+$  and producing  $m/z$  30 ions which will be transmitted by the magnet at an apparent mass of 27.3, close to that of the  $[\text{H}, \text{C}, \text{O}]^+$  ions formed from  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  (27.1). These  $m/z$  30 ions  $[\text{H}, ^{13}\text{C}, \text{O}]^+$  will in turn produce, upon collisional activation in the second field-free region,  $m/z$  13 and  $m/z$  14. At an accelerating voltage of 8000 V, these ions will have kinetic energies ca. 50 V higher than  $m/z$  12 and  $m/z$  13 formed from  $[\text{H}, ^{12}\text{C}, \text{O}]^+$ .

## RESULTS AND DISCUSSION

The transition state energy for the reaction  $\text{H}_2\overset{+}{\text{C}}\text{OH} \rightarrow [\text{H}, \overset{+}{\text{C}}, \text{O}] + \text{H}_2$  was assessed experimentally as follows. The precursor ion was made by the dissociation of ionised methanol. The latter ion, however, undergoes two competing fragmentations to produce  $[\text{H}, \text{C}, \text{O}]^+$  ions [5] via consecutive

losses of  $\text{H}^\cdot$  and  $\text{H}_2$  or  $\text{H}_2$  and  $\text{H}^\cdot$ , respectively, and thus an appearance energy (AE) of the  $[\text{H}, \text{C}, \text{O}]^+$  ions generated in a mass spectrometer's ion source may not correspond to the desired fragmentation route. However, the secondary process may be selectively monitored via the appropriate metastable peak. The AE of the metastable peak  $\text{H}_2\overset{+}{\text{C}}\text{OH} \rightarrow [\text{H}, \text{C}, \text{O}]^+ + \text{H}_2$  was obtained by a comparative method [23] using the MS902S mass spectrometer,  $\text{AE} = 15.1 \pm 0.1$  eV. With  $\Delta H_f^0[\text{CH}_3\text{OH}] = -48$  kcal mol $^{-1}$  [24] and  $\Delta H_f^0[\text{H}^\cdot] = 52$  kcal mol $^{-1}$  [25], the threshold energy is calculated to be 248 kcal mol $^{-1}$ , well above the thermochemical dissociation limit for  $\text{H}\overset{+}{\text{C}}\text{O} + \text{H}_2$  (194 kcal mol $^{-1}$ ) and  $\overset{+}{\text{C}}\text{OH} + \text{H}_2$  (230 kcal mol $^{-1}$ ). Next, the collisional activation (CA) mass spectrum of the metastably generated  $[\text{H}, \text{C}, \text{O}]^+$  ions was recorded (ZAB-2F mass spectrometer) and was found to be identical to reference  $\overset{+}{\text{H}}\text{CO}$  ions [3]. Therefore  $\overset{+}{\text{C}}\text{OH}$  is not produced unimolecularly in the rate constant range of from ca.  $10^4$  to  $10^{6.5}$  s $^{-1}$ , mean rate constant  $10^{5.5}$  s $^{-1}$  [26]. The activation energy for this reaction relative to  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  (using  $\Delta H_f^0 \text{H}_2\overset{+}{\text{C}}\text{OH} = 167$  kcal mol $^{-1}$ ) is 81 kcal mol $^{-1}$ . This latter value is far below the previously mentioned ab initio value (149 kcal mol $^{-1}$ ) and so it must be concluded that  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  loses  $\text{H}_2$  via a route not considered by DeFrees et al. [8(a)].

$\text{H}_2\overset{+}{\text{C}}\text{OH}$  ions fragmenting at much higher rate constants ( $> 10^7$  s $^{-1}$ ) produce a mixture of  $\overset{+}{\text{C}}\text{OH}$  and  $\overset{+}{\text{H}}\text{CO}$ . This was shown by observing the metastable peak  $\text{H}_2\overset{+}{\text{C}}\text{OH} \rightarrow \overset{+}{\text{H}}\text{CO} + \text{H}_2$  in the first field-free region of the ZAB-2F mass spectrometer and then reducing the ionising electrons' energy until  $\overset{+}{\text{H}}\text{CO}$  just disappeared. The  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  ions now leaving the source have insufficient energy to decompose unimolecularly by  $\text{H}_2$  loss. They were then induced to decompose by collision with He admitted to the first field-free region of the instrument. The structure of the resulting ions of  $m/z$  29,  $[\text{H}, \text{C}, \text{O}]^+$ , was then determined by transmitting them through the magnet and observing their collisionally induced decomposition in the second field-free region gas cell. The resulting CA mass spectrum, in which the  $m/z$  13 :  $m/z$  12 ratio was  $\leq 0.5$ , intermediate between that for  $\overset{+}{\text{H}}\text{CO}$  and  $\overset{+}{\text{C}}\text{OH}$ , 0.83 and 0.34, respectively, indicates that both  $\overset{+}{\text{H}}\text{CO}$  and (mainly)  $\overset{+}{\text{C}}\text{OH}$  are produced in the collision-induced decomposition of  $\text{H}_2\overset{+}{\text{C}}\text{OH}$ ,  $\overset{+}{\text{C}}\text{OH}$  via a reaction path of higher energy requirement (see Fig. 1) than that producing  $\overset{+}{\text{H}}\text{CO}$ . (The above ratio of 0.5 is an *upper limit*; see Experimental.). It has previously been reported [27] that the kinetic energy release for the collisionally induced loss of  $\text{H}_2$  is smaller than that for the metastable reaction and

it was suggested that excited  $\text{HCO}^+$  ions are produced in the collision encounter. The present results show that  $\text{COH}^+$  ions are produced.

It follows, therefore, (see Fig. 1) that the rate-determining energy barrier for the bimolecular reaction  $\text{COH}^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H}_2$  via stable intermediates, is the addition reaction  $\text{H}_2 + \text{COH}^+ \rightarrow \text{H}_2\text{COH}^+$  and not the latter's dissociation to  $\text{HCO}^+ + \text{H}_2$ . However, the conclusion of DeFrees et al. [8(a)] that there is no path via stable intermediates by which the reactants  $\text{H}_2 + \text{COH}^+$  can form the products  $\text{H}_2 + \text{HCO}^+$  without overcoming a large barrier, remains valid.

To elucidate the mechanism of  $\text{H}_2$  loss from  $\text{H}_2\text{COH}^+$ , we have performed ab initio calculations. It is known that the transition state for  $\text{H}_2$  loss cannot be symmetrical with respect to the positions of the H atoms, because the reaction is remarkably atom-specific [18,19,22], e.g.  $\text{D}_2\text{COH}^+$  ions generated by D loss from  $\text{CD}_3\text{OH}^+$  show only an intense metastable peak for loss of HD;  $\text{CDHOH}^+$  ions lose  $\text{H}_2$  and HD, the ratio of the metastable peaks is 2.0:1.

## CALCULATIONS

Calculations were performed for the reactions



which were all assumed to proceed on the singlet surface. The final results were obtained using the standard 6-31G\*\* basis set [28,29]. Initially, the geometries were optimized using the SCF (RHF) [30,31] procedure. However, it was not possible to find a reasonable transition state for reaction (2). Therefore, electronic correlation effects were incorporated by using the complete active space self-consistent field (CASSCF) [32] procedure, which is a special version of the well-known multi-configuration SCF (MCSCF) method [33]. In a CASSCF calculation, one selects an active orbital space consisting of SCF occupied and virtual orbitals. Within this active space, all

excitations are allowed, leading to a full configuration interaction (CI) calculation for the active space chosen. The number of configurations in the CASSCF wave function increases rapidly with the number of active orbitals. In the present work, therefore, only those orbitals which directly participate in the reactions have been included in the active orbital set. In order to obtain energies of comparable accuracy, the number and symmetries of the active orbitals were kept the same for all points on each potential energy surface.

For the cases considered here, the dominant correlation effects are associated with the bonds which are broken or formed during the reaction. The dissociation of a single bond may be described adequately by using two active orbitals [34] and so the calculations for reactions (4) and (5) were performed using the  $\sigma$ -type orbitals. For reaction (2), the sensitivity of the results to the size of the active orbital space was investigated using the smaller 4-31G basis. The results indicated that this reaction is essentially a two-step process, i.e. first the OH bond in  $\text{H}_2\text{COH}^+$  is broken and then the  $\text{H}_2$  bond is formed. Similar calculations for reaction (3) indicated that qualitatively correct results for the corresponding transition state may be obtained by using an active space of two  $\sigma$ -type orbitals. From these arguments, it was concluded that the use of two active orbitals in the CASSCF calculations should be adequate for reactions (2)–(5). Note, however, that this does not imply that the wavefunctions used to describe the  $\text{H}_2\text{COH}^+$  reactant in these reactions are all identical. This may be seen by considering the near-degeneracy effect in the double CO bond [35], which will lead to significant mixing of  $\sigma$ -type with  $\pi$ -type active orbitals for non-planar conformations. Therefore, for reaction (2), the calculations for the  $\text{H}_2\text{COH}^+$  reactant were performed using either two  $\sigma$ -type or two  $\pi$ -type active orbitals. Reaction (6) was primarily considered for the purpose of comparing our results with reliable calculations available in the literature [16] and it was treated in the same way as the other reactions.

Since our program does not allow the full force constant matrix (Hessian) of the optimized structures to be evaluated with the CASSCF method, we have used the generalized valence bond (GVB) method [36] for the determination of the nature of the stationary points on the potential energy surfaces and for the evaluation of the zero point vibrational energy (ZPVE) corrections. As explained above, we have used only two active orbitals for the CASSCF wavefunctions and these functions are thus equivalent to a GVB wavefunction with one correlated orbital pair. Since the normal mode analysis needed for the ZPVE correction is rather expensive, we have used the 3-21G basis for this purpose. The harmonic frequencies were then obtained using 3-21G/GVB reoptimized structures and the ZPVE correc-

tions were obtained using a scaling factor of 0.9 in order to correct for basis set incompleteness and for the remaining correlation effects [37]. For all these calculations, the program system GAMESS [38] was used, which provides for analytical gradient geometry optimization and numerical force constant evaluation techniques for CASSCF and GVB calculations [39].

For the 6-31G\*\*/CASSCF optimized geometries, single-point multiple-reference single and double excitation CI calculations with two reference configurations (2-MRDCI) were performed, using the direct CI program of Saunders and van Lenthe [40]. In these calculations, the GVB equivalent of the CASSCF wavefunction was used as the reference function for generating

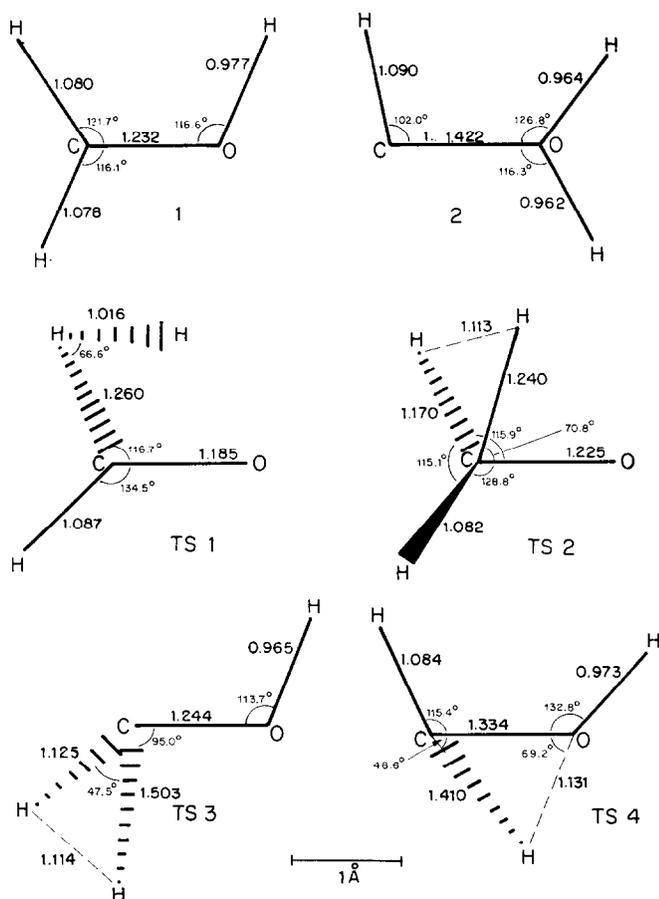


Fig. 2. Equilibrium and transition state structures for isomerisation and dissociation reactions on the  $[H_3, C, O]^+$  potential energy surface; 6-31G\*\*/CASSCF.

TABLE 1  
Calculated energies for the  $\text{H}_2\text{COH}^+$  surface

Species <sup>a</sup>	Symmetry of active orbitals	$E(\text{CASSCF})$ <sup>b</sup>	$E(\text{MRDCI})$ <sup>b</sup>	ZPVE <sup>c</sup>		$E_{\text{calc}}^{\text{Rel. d}}$	$E_{\text{exp}}^{\text{Rel. e}}$
				RHF	GVB		
$\text{H}_2\text{COH}^+$	$\pi$	-114.1910	-114.4730		26.5	0	
	$\sigma$	-114.1865	-114.4693	26.7		0	0 <sup>e</sup>
$\text{HCOH}_2^+$	$\sigma$	-114.0632					
TS1	$\pi$	-114.0306	-114.3201		18.5 <sup>f</sup>	89	
	$\sigma$	-114.0103	-114.3138	18.9 <sup>f</sup>		91	81
TS2		-114.0322	-114.3211		20.6	88	
TS3	$\sigma$	-114.0097	-114.2898		18.4	105	
TS4	$\sigma$	-113.9935					
$\text{HCO}^+ + \text{H}_2$	$\sigma$	-114.1177	-114.4086	18.1		30	27
$\text{COH}^+ + \text{H}_2$	$\sigma$	-114.0711	-114.3521	16.1		64	63
$\text{H}_2\text{CO}^{++} + \text{H}^{\cdot}$	$\sigma$	-114.0168	-114.2889	17.1		104	108
$\text{HCOH}^{++} + \text{H}^{\cdot}$	$\sigma$	-114.0086	-114.2807	17.0		110	115 <sup>g</sup>

<sup>a</sup> See Fig. 1 for the transition state geometries.

<sup>b</sup> 6-31G\*\* basis, energies in Hartrees.

<sup>c</sup> For those conformations for which the RHF method is expected to be insufficient, the GVB method was used (2 active orbitals). The ZPVE corrections are given in  $\text{kcal mol}^{-1}$ .

<sup>d</sup> Relative energies in  $\text{kcal mol}^{-1}$ , including ZPVE corrections (using a scaling factor of 0.9) with respect to the relevant  $\text{H}_2\text{COH}^+$  calculations.

<sup>e</sup>  $\Delta H_f^0(\text{H}_2\text{COH}^+) = 167 \text{ kcal mol}^{-1}$ .

<sup>f</sup> For the planar transition state TS1, two imaginary frequencies were found, indicating a non-planar transition state for reaction (2).

<sup>g</sup>  $\Delta H_f^0(\text{HCOH}^{++}) = 230 \text{ kcal mol}^{-1}$ .

all single and double excitations. The final results are shown in Table 1 and Fig. 2.

### Loss of $\text{H}_2$ from $\text{H}_2\text{COH}^+$

For reaction (2), two transition states were located, viz. TS1 and TS2 in Fig. 2, both corresponding to formation of  $\text{HCO}^+ + \text{H}_2$ . The geometry of TS1 was calculated by restricting the optimization to planar structures ( $C_s$  symmetry), whereas TS2 was obtained by relaxing this constraint. According to the normal mode analysis, the planar structure TS1 has two imaginary frequencies. One of these corresponds to an out-of-plane distortion in the direction of the non-planar structure TS2, with a low frequency ( $|\omega| = 430 \text{ cm}^{-1}$ ), whereas the other corresponds to an in-plane distortion in the direction of the dissociation products, with a high frequency ( $|\omega| = 2560$

$\text{cm}^{-1}$ ). Since the true transition state should have only one imaginary frequency [41], this structure is not acceptable as the transition state for reaction (2). The non-planar structure TS2 has, indeed, only one imaginary frequency ( $|\omega| = 1260 \text{ cm}^{-1}$ ), which corresponds to motion along the dissociation coordinate for reaction (2) and it is slightly lower in energy than the planar structure TS1. Additional 6-31G\*\*/2-MRDCI calculations also showed that there is no barrier separating TS1 and TS2. We therefore conclude that the true transition state for reaction (2) is given by the non-planar structure TS2. However, inclusion of the ZPVE corrections leads to virtually the same energies for TS1 and TS2 relative to  $\text{H}_2\text{COH}^+$ . Therefore, the position of the migrating H atom in the activated complex for reaction (2) is *not well defined*. For internal energies slightly above the energy of TS2, this results in an effective saddle point region ranging from TS1 to TS2. The activation energy for reaction (2) is calculated as 89–90  $\text{kcal mol}^{-1}$  (6-31G\*\*/2-MRDCI/ZPVE).

For reaction (3), the transition state, TS3, is found to be planar (one imaginary frequency), analogous to the transition-state structure found for the reaction  $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$  [42]. The activation energy for this reaction is calculated as 105  $\text{kcal mol}^{-1}$  (6-31G\*\*/2-MRDCI/ZPVE). Thus, reaction (2) is the lowest in energy by which  $\text{H}_2\text{COH}^+$  can fragment. TS2 also lies well below the transition state, TS4, for the isomerisation reaction (6). This agrees with the experimental results from which it was concluded that the reaction of lowest energy requirement is loss of  $\text{H}_2$ . Where our calculations overlap with those of DeFrees et al. [8] and Nobes and Radom [6] the agreement is excellent [e.g. the calculated activation energies for reactions (3) and (6)].

The calculated activation energy for reaction (2) is about 8  $\text{kcal mol}^{-1}$  higher than the experimental value of 81  $\text{kcal mol}^{-1}$ . This may be due to three effects.

(a) Basis set incompleteness. The addition of extra polarisation functions may be expected to lower the barrier heights by several  $\text{kcal mol}^{-1}$  [42].

(b) Since the transition state is non-planar, we cannot separate  $\sigma$ - and  $\pi$ -type correlation effects. Therefore the restriction to two active orbitals may be too severe for the calculation of the activation energy for this reaction. Increasing the size of the active orbital space will probably lead to a lowering of the barrier.

(c) By analogy with the fragmentation of formaldehyde, the effective barrier for fragmentation in the metastable time frame may be lowered by hydrogen atom tunnelling [43]. Quantitative evaluation of this effect requires a more detailed investigation of the potential energy surface. However, assuming that the mass effects for both reactions are similar, the barrier

lowering may be estimated by comparing the imaginary frequencies corresponding to motion along the reaction path for these reactions. By approximating the barrier along the reaction coordinate by an inverted parabola and using  $\omega = 1260 \text{ cm}^{-1}$  (3.21G/GVB), we find that, for the  $\mu\text{s}$  time frame, the barrier for reaction (2) is lowered by 2–3 kcal mol<sup>-1</sup> by this effect. A similar effect may be expected for reaction (3) ( $|\omega| = 1100 \text{ cm}^{-1}$ ).

The transition state for reaction (2), viz. TS2, might be expected to attain the (singlet) methoxy cation structure of  $C_{3v}$  symmetry, which is unstable towards dissociation in  $\text{H}\overset{+}{\text{C}}\text{O} + \text{H}_2$ . However, additional calculations indicated that structures with  $C_{3v}$  symmetry are much higher in energy than either TS1 or TS2. The active participation of the methoxy structure must also be discarded on experimental grounds (viz. the labelling experiments discussed above), because the hydrogens are in equivalent positions in this species. Our results indicate that fragmentation from TS2 is very fast, i.e. it has a very short lifetime. This is reflected in the large amount of kinetic energy released (about 30 kcal mol<sup>-1</sup>). The recoil velocity,  $v$ , of the products may be calculated from  $T = \mu v^2/2$ , where  $T$  is the kinetic energy release and  $\mu$  the reduced mass. This leads to  $v = 1.15 \times 10^{14} \text{ \AA s}^{-1}$ . Thus, in a time lapse corresponding to one typical C–H vibration, the  $\text{H}_2$  and  $\text{H}\overset{+}{\text{C}}\text{O}$  moieties recoil by 1–2  $\text{\AA}$ , which is sufficient to lead to bond breaking.

A further point worth noting is that the structure of the transition state for reaction (2) indicates that the reaction centre lies towards the carbon atom, whereas the structure considered by DeFrees et al. [8] has the centre towards the oxygen atom. Recently, Hvistendahl and Uggerud [22] concluded from extensive isotopic substitution experiments, that the reaction centre lies towards the carbon side of the C–O bond, in agreement with our calculations. Note that their conclusions were based on secondary isotope effects on the kinetic energy release; merely observing that the hydroxylic hydrogen atom is always in the  $\text{H}_2$  molecule cannot lead to a conclusion about the position of the reaction centre.

The triplet methoxy cation has been produced and identified [44]; it, too, loses  $\text{H}_2$  abundantly with a kinetic energy release of 30 kcal mol<sup>-1</sup>. However,  ${}^3\text{CH}_3\text{O}^+$  lies only  $\sim 5 \text{ kcal mol}^{-1}$  below its dissociation level and thus it should not be metastable (ab initio calculations [45] indicate that  ${}^3\text{CH}_3\text{O}^+$  lies ca. 92 kcal mol<sup>-1</sup> above (singlet)  $\text{H}_2\overset{+}{\text{C}}\text{OH}$ , in agreement with the above magnitude of the activation energy for  $\text{H}_2$  loss). Hence, it would appear that the slow fragmentation of  ${}^3\text{CH}_3\text{O}^+$  is spin-controlled, thus producing *metastable* ions. The reaction whereby excited singlet  $\text{H}_2\overset{+}{\text{C}}\text{OH}$  might rearrange into triplet  $\text{CH}_3\overset{+}{\text{O}}$  will also be slow and thus this reaction cannot compete with  $\text{H}_2$  loss from  $\text{H}_2\overset{+}{\text{C}}\text{OH}$ . This conclusion, too, is in agreement with the results of the labelling experiments.

### Loss of $H^\cdot$ from $H_2\overset{+}{C}OH$

Two pathways were considered, viz. O–H cleavage to produce  $H_2CO^+$  and C–H cleavage leading to  $HCOH^+$ . For both reactions, no saddle point could be located and hence the fragmentations have no well-defined transition state. The corresponding dissociation limits (see Table 1) are higher in energy than the transition state for  $H_2$  loss leading to  $HCO^+$  and this explains the absence of a metastable peak for loss of  $H^\cdot$ . Note that, according to the present calculations, the reverse reactions  $CH_2=O^{++} + H^\cdot \rightarrow H_2\overset{+}{C}OH$  and  $HCOH^{++} + H^\cdot \rightarrow H_2\overset{+}{C}OH$ , i.e. ion–radical recombinations, have no activation energies. We have proposed [46] that the exothermic addition of  $H^\cdot$  (or  $CH_3^\cdot$ ) to a heteroatom of an *even* electron cation will have a large barrier (ca. 1 eV). Evidently, this is not generally true for addition to an *odd* electron cation.

To summarize the present work.

(1) The reaction of lowest energy requirement of  $H_2\overset{+}{C}OH$  is loss of  $H_2$  to produce  $HCO^+$  with an activation energy of 81 kcal mol<sup>-1</sup> (experiment), 89 kcal mol<sup>-1</sup> (theory). The associated transition state was found to be non-symmetrical with respect to the hydrogen atoms.

(2) Singlet and triplet methoxy cations are not involved in the above fragmentation and  $HCOH_2^+$  is also not produced.

(3) At higher energies and higher rate constants,  $\overset{+}{C}OH$  is co-produced, in agreement with the calculations (see Fig. 1).

(4) The conclusion of DeFrees et al. that the reaction  $H_2 + \overset{+}{C}OH \rightarrow H_2\overset{+}{C}OH \rightarrow HCOH_2 \rightarrow H_2 + HCO$  will have a large barrier, remains unchanged, although the maximum barrier is now associated with the first step.

(5) The results are in agreement with earlier MINDO/3 calculations [19]. Unfortunately, no experimental method has yet been found to generate the ion  $HCOH_2^+$ . However, recent theoretical work by Koch et al. [47] has indicated that, for the doubly charged species,  $HCOH_2^{2+}$  is the thermodynamically most stable isomer. Gas-phase reduction of this ion might lead to the desired singly charged ion. It is predicted from theory that its unimolecular chemistry would be akin to that of energy-rich  $H_2\overset{+}{C}OH$  (see Fig. 1) and so loss of  $H_2$  would possibly lead to a bi-modal kinetic energy release and loss of  $H^\cdot$  should compete with this reaction.

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