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Mediators for hydrogenation of carbon monoxide: theoretical study of addition of H_2 to HCO^+ in the presence of CO or H_2O

Åse Marit Leere Øiestad, Einar Uggerud*

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

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Abstract

Relevant parts of the potential energy surfaces of the title reaction systems (CH_3O^+, $C_2H_3O_2^+$, and $CH_5O_2^+$) have been explored using quantum chemical models (MP2/6-31G(d,p) and G2). The results of the calculations demonstrate that the barrier for hydrogenation drops significantly when a third molecule (CO or H_2O) can act as a proton acceptor during the critical H–H bond heterolytic dissociation step, thereby avoiding the tight transition state found for the direct reaction. (Int J Mass Spectrom 201 (2000) 179–185) © 2000 Elsevier Science B.V.

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1. Introduction

Quantum chemistry has developed rapidly during the last decades. As the combined result of improvement of computer algorithms, increased availability and efficiency of computers, and development of user-friendly program interfaces, quantum chemical model calculations have become common in almost all subdiciplines of chemistry. Reliable and accurate models of small and medium-sized molecules can be obtained efficiently. Because theoretical calculations are extremely useful for interpreting experimental data, the interplay between quantum chemistry and ion chemistry has been very fruitful, and it has been going on for a long time. Correspondingly, precise experimental data from ion chemical studies have also been of great importance for evaluating the performance of quantum chemical methods.

Modern ion chemical instrumentation is very expensive, and it is sometimes difficult to achieve the experimental conditions needed to fully test out a chemical idea. In these cases quantum chemical calculations may be of great help, and a well-founded decision on how to set up a suitable experiment can be made on the basis of the predictions given by the calculations. In addition a totally new paradigm for chemical research has been created, because information and insight not available from any easily conducted experiment is available from theoretical models.

Hopefully, the present subject is illustrative and appropriate. We have a long standing interest in hydrogenation/dehydrogenation chemistry, both due to the simple and fundamental nature of the reactions, and their economic significance. The important indus-

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* Corresponding author. E-mail: einar.uggerud@kjemi.uio.no

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trial process of hydrogenation of carbon monoxide to give formaldehyde,

$$CO + H_2 \rightarrow CH_2O \quad (1)$$

is practically thermoneutral ($\Delta H^0 = +2$ kJ mol^{-1}), but has an unfavourable critical energy of $E_0 = 346$ kJ mol^{-1} [1,2]. For this reason it is usually conducted in the presence of a transition metal catalyst [3]. It would be of both fundamental theoretical interest and of industrial significance if the reaction could be carried out under different conditions than those used in the current process. Acidic catalysis could be one alternative. Upon protonation of the carbon (the alternative, protonation on the oxygen, gives rise to a higher energy route for hydrogenation as demonstrated by deuterium labeling [4–6]),

$$HCO^+ + H_2 \rightarrow CH_2OH^+ \quad (2)$$

the critical energy is reduced to $E_0 \approx 220$ kJ mol^{-1} [4–6], which still is quite unfavourable, but is nevertheless motivating for further investigation. On the other hand, upon protonation the reaction becomes exothermic by $\Delta H^0 = -115$ kJ mol^{-1}. Our own experimental and theoretical ion chemical studies have revealed that the barriers of H_2 addition reactions are strongly susceptible to changes in the electron configuration and density of the atomic centre to which the addition takes place [6]. Introduction of a nearby substituent may have a dramatic effect. In addition, direct H_2 addition often leads to extremely tight transition structures, as in the case of reaction (2). We would expect that a less tight transition structure is accompanied by a drop in the critical energy. This could be achieved if the heterolytic cleavage of H_2 which is necessary for the reaction to take place is mediated by a third molecule.

2. Methods

Quantum chemical calculations were carried out using the program system GAUSSIAN 94 [7]. The methods used were Møller-Plesset perturbation theory to second order (MP2) [8] with the 6-31G(d,p) basis set [9], and the compound G2 method [10].

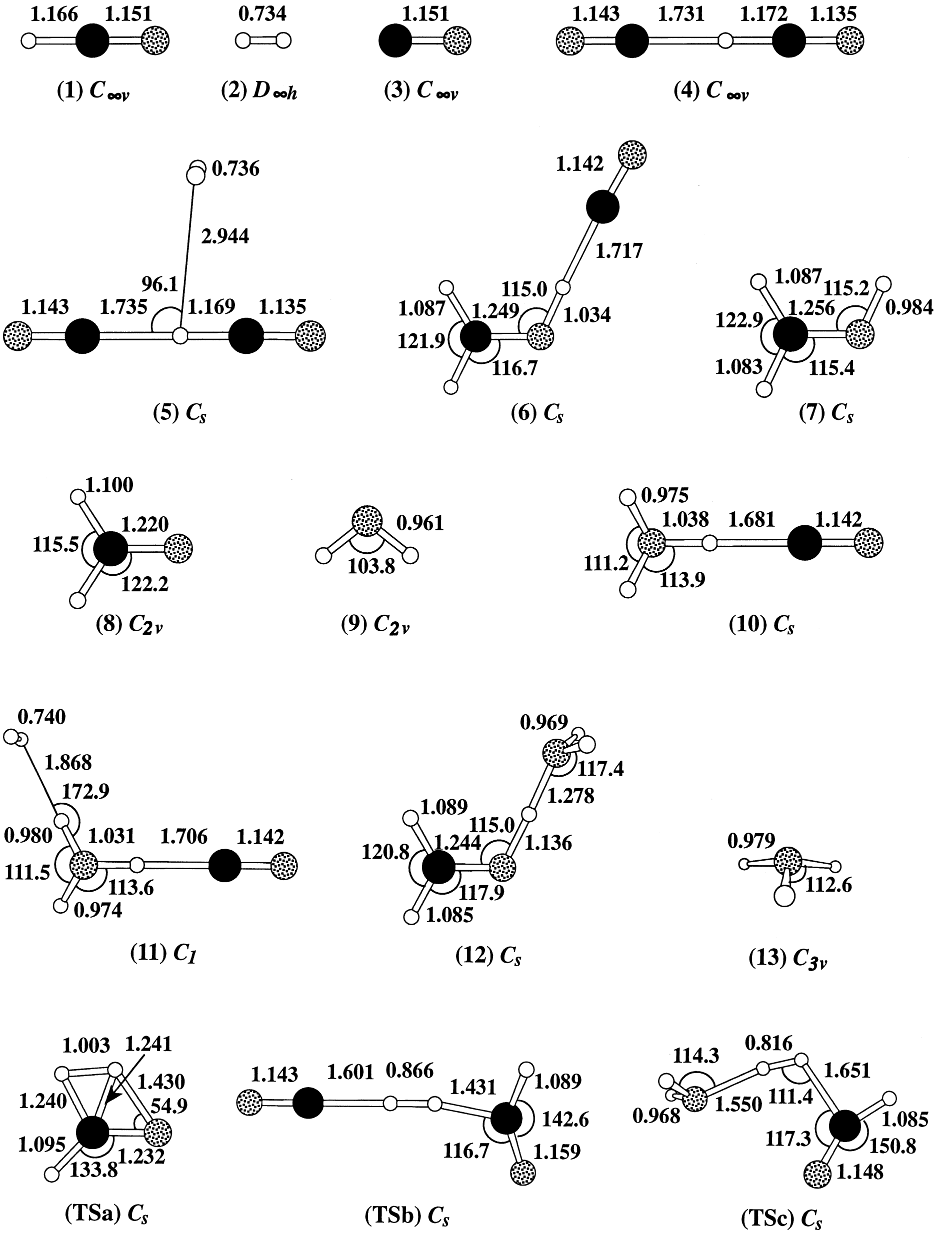
All relevant critical points (reactants, transition structures, intermediates, and products) of the potential energy surface were characterized by complete optimization of the molecular geometries [MP2/6-31G(d,p)]. Harmonic frequencies were obtained by diagonalizing the mass-weighed Cartesian force constant matrix, calculated from the analytical second derivatives of the total energy (the Hessian). Harmonic frequencies obtained in this manner were used to calculate the zero point vibrational energies (zpves). Total energies were calculated by including the MP2/6-31G(d,p) zero point vibrational energies scaled by a factor of 0.9608 [11]. For the G2 method the built-in scale factor was used.

3. Results and discussion

The most relevant geometric data of the molecular structures discussed here are shown in Fig. 1. The energy data are given in Table 1.

3.1. Without mediator

The reverse of reaction (2)—loss of dihydrogen from protonated formaldehyde—is a well studied gas phase reaction [4,5,12–17]. The computed potential barrier for reaction (2) of $E_0 = 238$ kJ mol^{-1} (Fig. 2) is reflected by a translational energy release of 150 kJ mol^{-1} for the reverse reaction. In Fig. 1 the geometry of the corresponding transition structure (**TSa**) is reproduced. It is evident from this structure that the 1,2-addition of H–H is not symmetrical with respect to the C–O bond. At a first glimpse it appears as if the H_2 molecule adds to the carbon atom in a 1,1 fashion. Closer analysis of this reaction type—qualitative consideration of correlation between basicity and barrier height [6]—reveals that this is only correct for the first phase, in which the H_2 molecule is polarized and partially broken, and thereby activated. Upon passage of the TS this activation leads to bond dissociation, so that the hydride part moves to the



(1) $C_{\infty v}$ (2) $D_{\infty h}$ (3) $C_{\infty v}$ (4) $C_{\infty v}$

(5) C_s (6) C_s (7) C_s

(8) C_{2v} (9) C_{2v} (10) C_s

(11) C_1 (12) C_s (13) C_{3v}

(TSa) C_s (TSb) C_s (TSc) C_s

Fig. 1. Structures of the stationary points [MP2/6-31G(*d*,*p*)] with indication of the most important geometrical parameters.

electrophilic carbon atom, and the proton part moves to the most basic oxygen.

We have recently presented a general explanation, based on frontier orbital theory, to the fact that this and related H_2 additions have substantial barriers, while others have zero or small barriers [6]. As an example, addition of H_2 to the methyl cation, CH_3^+, gives CH_5^+ directly with no barrier. In this case the electronic structure of the molecule makes it an ideal electron acceptor by having an empty carbon p_z

Table 1
Total energies from ab initio calculations.

Structure	MP2/6-31G(d,p)[a] (Hartrees)	G2 (0 K)[b] (Hartrees)
HCO^+ (**1**)	−113.248 42	−113.401 10
H_2 (**2**)	−1.147 57	−1.166 36
CO (**3**)	−113.016 58	−113.177 50
$[OCH^+ \cdots CO]$ (**4**)	−226.290 31	−226.598 27
$H_2[OCH^+ \cdots CO]$ (**5**)	−227.437 60	−227.765 02
$[CH_2OH^+ \cdots CO]$ (**6**)	−227.470 27	−227.804 94
CH_2OH^+ (**7**)	−114.429 59	−114.607 76
CH_2O (**8**)	−114.157 17	−114.338 92
H_2O (**9**)	−76.198 76	−76.332 05
$[OC \cdots H_3O^+]$ (**10**)	−189.514 85	−189.791 53
$H_2[OC \cdots H_3O^+]$ (**11**)	−190.663 23	−190.961 59
$[CH_2OH^+ \cdots OH_2]$ (**12**)	−190.685 55	−190.984 49
H_3O^+ (**13**)	−76.472 19	−76.591 93
TSa	−114.297 78	−114.476 90
TSb	−227.391 76	−227.726 03
TSc	−190.597 98	−190.899 06

[a] The included zero point energy is scaled by (0.9608) E_{zpv}[MP2/6-31(d,p)].

[b] The built-in scale factor for the included zero point energy is used.

orbital. Substitution of two of the methyl hydrogens by a double bonded oxygen—a good p-electron donor—has a dramatic effect. The HCO^+ ion has no empty p orbital as a result of electron donation from oxygen, and H_2 addition is severely hampered, as discussed previously.

Our idea is that the presence of a third molecule may lower the barrier for hydrogenation (1) by serving as an electron accepting buffer in the critical phase of the reaction and (2) to open up the unfavourable four membered ring of **TSa**, thereby providing a less tight transition structure. In this work we chose to consider two potentially promising candidates, namely water and carbon monoxide.

3.2. With carbon monoxide

Upon introduction of one CO molecule to the reaction system, the barrier for hydrogenation becomes markedly lower. The critical energy for the overall reaction

$$HCO^+ + H_2 + CO \rightarrow CH_2OH^+ + CO \qquad (3)$$

is seen to be only $E_0 = 50$ kJ mol^{-1} (Fig. 2). Compared to **TSa**, the position of transition structure **TSb** is significantly more early on the reaction coordinate. This is seen by inspection of the geometrical parameters displayed in Fig. 1, and is a precise indicator of the influence of CO. It is evident that the H–H bond is activated by polarization in the same way as in reaction (2), with the hydride part pointing toward HCO^+ and the proton part towards CO. There is, however, a significant difference. In order to achieve the necessary activation of H_2 in the naked system, the supermolecule had to adopt the extremely unfavourable and tight geometry of **TSa**. This is almost completely avoided in **TSb**.

Despite the quite favourable critical energy, it is important to recognize that there are two important factors which in practice will hinder efficient reactivity. First, although reaction 3 is calculated (G2) to be exoergic by $\Delta E = -105$ kJ mol^{-1}, this is mainly the result of the difference in proton affinity between carbon monoxide and formaldehyde. To establish a true catalytic cycle, the highly unfavourable proton transfer from formaldehyde to carbon monoxide would have to be included at the end of the reaction scheme in Fig. 2. Second, the simultaneous collision of three molecules in the configuration of **TSb**, is a highly unlikely event. Instead a two step gas phase termolecular reaction must be formulated

$$HCO^+ + H_2 + CO \rightarrow [OCH^+ \cdots CO]\,(\mathbf{4}) + H_2 \qquad (4)$$

$$[OCH^+ \cdots CO]\,(\mathbf{4}) + H_2 \rightarrow [CH_2OH^+ \cdots CO]\,(\mathbf{6}) \qquad (5)$$

Due to the binding energy of complex 4, the efficient critical energy of reaction (at high pressures) increases to $E_0 = 102$ kJ mol^{-1}.

A very interesting issue arises from a closer inspection of the energy diagram of Fig. 2. When the diagram is read from right to left, the total reaction corresponds to dehydrogenation through hydride abstraction:

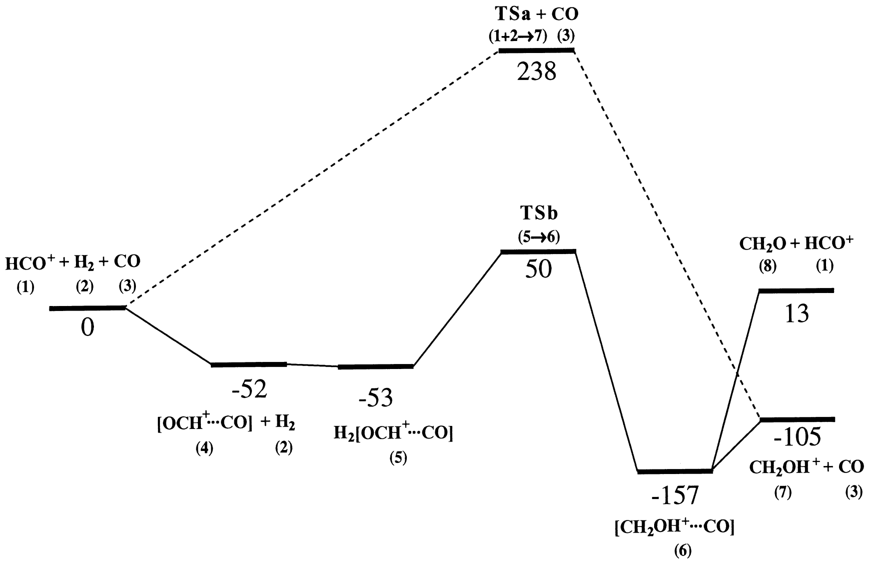


Fig. 2. Schematic potential energy diagram [MP2/6-31G(*d,p*)] for the carbon monoxide mediated route for hydrogenation of the formyl cation. The dotted line indicates the nonmediated reaction.

$$HCO^+ + CH_2O \rightarrow HCO^+ + CO + H_2 \qquad (6)$$

This reaction is exoergic by 13 kJ mol^{-1}, implying an autocatalytic route for dehydrogenation of formaldehyde! The barrier of 37 kJ mol^{-1}, is of course a point of consideration, and seems to be slightly too high for an efficient gas phase reaction. Quantum mechanical tunneling probably does allow the reaction to proceed with less energy than this. However, the most obvious obstacle to autocatalytic dehydrogenation is the existence of the competing proton transfer

$$HCO^+ + CH_2O \rightarrow CH_2OH^+ + CO \qquad (7)$$

This barrierless and highly exoergic reaction will soon deplete the HCO^+ population, and thereby practically hinder utilisation of the elegant autocatalytic route.

Blanchette et al. have investigated structures and reactivity of $C_2H_3O^+$ isomers [18]. Not unexpected, but of great interest and relevance to the present study, they reported that metastable $^+CH_2OCHO$ (*m/z* 59) gives rise to CH_2OH^+ ions (*m/z* 31), but that there is no sign of HCO^+ (*m/z* 29), and the corresponding process including **TSb**.

3.3. With water

The calculated energy level diagram is displayed in Fig. 3. It shows that the termolecular gas phase reaction

$$HCO^+ + H_2 + H_2O \rightarrow CH_2OH^+ + H_2O \qquad (8)$$

has practically no barrier [the values are $E_0 = 1$ kJ mol^{-1} for G2, and $E_0 = -8$ kJ mol^{-1} for MP2/6-31G(*d,p*)]. Water is seen to strongly promote reaction. The noncyclic transition structure, **TSc**, is characterized by being even earlier than **TSb**, which is exactly as expected taking the lower barrier into consideration. The H–H bond which is broken during reaction is 0.816 Å in **TSc**, 0.866 Å in **TSb**, and 1.003 Å in **TSa**. These values should be compared to 0.734 Å for an intact H_2 molecule.

Despite the favourable barrier, an efficient gas phase reaction cannot be expected in this case for the same reasons as we outlined in the discussion of reaction (3).

The reverse of reaction (8) has previously been studied indirectly, and unintentionally, by an experimental and theoretical investigation of the unimolecu-

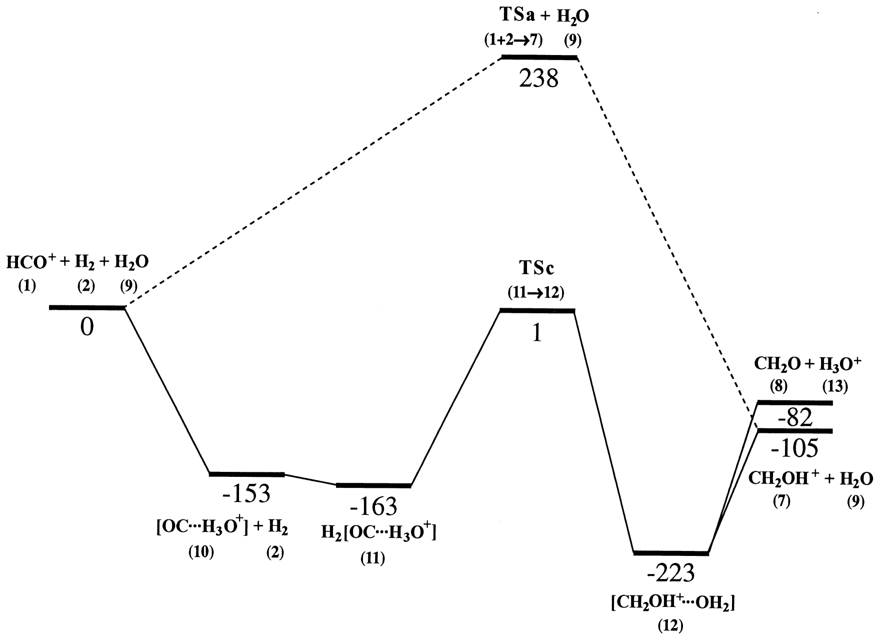


Fig. 3. Schematic potential energy diagram [MP2/6-31G(*d,p*)] for the water mediated route for hydrogenation of the formyl cation. The dotted line indicates the nonmediated reaction.

lar decomposition of protonated methyl hydroperoxide [19]. It was concluded that observation of HCO^+ (*m/z* 29) in the metastable ion spectrum of $[CH_3O_2H]H^+$ (*m/z* 49) ions is due to the following series of events (scheme simplified here):

$$CH_3O_2H_2^+ \rightarrow [CH_2OH^+ \cdots OH_2]$$

$$\rightarrow CH_2OH^+ + H_2O \rightarrow HCO^+ + H_2 + H_2O \quad (9)$$

A statistical mechanical analysis of the energy content of the intermediately formed CH_2OH^+ ions gave some support to this mechanism, which implies passage through **TSa**. On the basis of the present model we are now in the position to propose an alternative mechanism, in which the $[CH_2OH^+ \cdots OH_2]$ complex (**12**) does not dissociate in a two step process (loss of water followed by loss of dihydrogen), but instead rearranges directly via **TSc** to give the products $HCO^+ + H_2 + H_2O$. The critical energy of this mechanism is significantly lower than that of the reverse of Eq. (2), as seen from Fig. 3.

4. Concluding remarks

This work does not represent a broad and systematic study of factors that promote H–H activation and incorporation of dihydrogen in nonsaturated compounds. Despite this we are able to draw some conclusions on 1,1 and 1,2 hydrogenations. (1) In the examples we know, protonation of an unsaturated molecule generally lowers the energy barrier for hydrogenation [6]. (2) In the two examples studied here, and in two recently studied [20] proton induced hydride abstractions from ethylamine (gives H_2), the reaction barrier is reduced in the presence of a third molecule (mediator). It appears as if the reaction barrier becomes lower the more basic the mediator is. To which extent this is a general trend we do not know. (3) The more basic the mediator is, the more exoergic is the hydrogenation reaction. This is a trivial point. Unfortunately, however, this counteracts a favourable total reaction because the proton has to be transferred back from the basic mediator to the substrate in order to constitute a catalytic cycle.

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