

**QUENCHING OF THE  $^3P$  AND  $^1P$  STATES OF Mg BY ACETYLENE  
AND POSSIBLE FORMATION OF VINYLIDENE.  
A THEORETICAL AB INITIO SCF CI STUDY**

Patrick CHAQUIN, Alain SEVIN and Aristotelis PAPAKONDYLIS

*Laboratoire de Chimie Organique Théorique (URA 506), Université Paris VI, 4, Place Jussieu, 75252 Paris Cedex 05, France*

Received 5 October 1989

Physical and chemical quenching of  $^3P$  and  $^1P$  states have been studied by theoretical ab initio SCF CI methods. The singlet and the triplet are attractive, yielding  $C_{2v}$  triangular  $\pi$  exciplexes. No secondary minimum corresponding to an open form has been found on the singlet surface, whereas the triplet surface exhibits a very shallow secondary minimum corresponding to a  $\sigma$  complex. Physical quenching is expected to be efficient for both states. The initial energy of the singlet system is large enough to induce a hydrogen transposition yielding vinylidene magnesium, which, in turn, can easily undergo a C–Mg rupture and produce vinylidene. This channel might compete with an insertion reaction of Mg into a C–H bond.

## 1. Introduction

Molecule–metal atom (in ground or excited states) reactions have been studied for a long time in the gas phase [1], and more recently in low-temperature matrices. Matrix experiments have shown that metal atoms like Al [2], Cu [3], Ag [3,4], Au [3,5] can give either  $\pi$  or  $\sigma$  complexes with acetylene, while the reaction with Na [6] yields a vinylidene complex through hydrogen migration. Several theoretical studies of such complexes have been carried out [7]. Moreover, the hydrogen migration has been studied in  $\sigma$  complexes of Li, Be, B, Na, Mg [8], and Al [8,9]. Breckenridge and Umemoto [10] measured the quenching cross section of  $^1P$  Mg by a variety of hydrocarbon compounds, among which acetylene, in the gas phase. Contrary to saturated hydrocarbons, acetylene does not produce MgH during the quenching process [11].

We present here an exploratory study of the reactivity with acetylene of Mg atom, especially in its lowest singlet and triplet ( $3s^13p^1$ ) excited states,  $^1P$  and  $^3P$ . We particularly focused our attention on the approach of the reactants and the formation of exciplexes, and the possible evolution towards vinylidene complexes as well as insertion of the metal into a C–H bond.

dene complexes as well as insertion of the metal into a C–H bond.

## 2. Calculation methods

The SCF step was achieved using the MONSTER-GAUSS series of programs [12]. The Davidson RHF Hamiltonian [13] was used for doublet species and radical pairs; the closed-shell Roothaan–Fock Hamiltonian [14] was used for the other cases. Two methods of calculations were used.

*Method I.* After 6-31G [15] level SCF calculation, a space of about 100 selected configurations was diagonalized. This method provides exploratory runs and semiquantitative potential energy surfaces (PESs).

*Method II.* The 6-31G\*\* [15] SCF step was followed by a Møller–Plesset [16] second-order (MP2) treatment using the CIPSI method [17]: a set of 100 to 150 reference configurations was taken as a basis for the multireference perturbation scheme involving  $10^6$  to  $10^7$  terms according to the state under scrutiny. This method affords reliable energy values for the crucial points (reactants, products, exciplexes, and transition states).

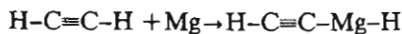
Owing to the size of the system, the structure optimizations were carried out at the SCF level with the

gradient technique of the MONSTERGAUSS program, thus some uncertainty remains regarding these geometries. Nevertheless, in the important case of the  $C_{2v}$  singlet exciplex 4 (see fig. 5 below), the structure has been optimized from a grid of about 20 points using method I (limited CI).

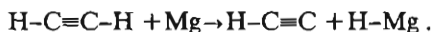
### 3. Results and discussion

#### 3.1. Approach of reactants and exciplex formation

Fig. 1 summarizes the main model approaches of Mg and acetylene (in its non-relaxed geometry) providing a basis for a discussion of the various physical and chemical quenching processes. Each of these paths is connected to a typical evolution of the system: paths a and b lead to the formation of  $\pi$  and  $\sigma$  complexes respectively; path c yields the insertion product following



and path d yields the abstraction reaction



Figs. 2 and 3 display the PESs for the  $C_{2v}$  approach of acetylene (without relaxation) and Mg in its low-lying singlet and triplet states respectively. The  $^1,^3P$  lowest states of Mg ( $3s^1 3p^1$ ) are split into three components of  $A_1$ ,  $B_1$  and  $B_2$  symmetry. The stabilization of the  $B_2$  PES can be interpreted from two complementary points of view. In perturbation terms, the

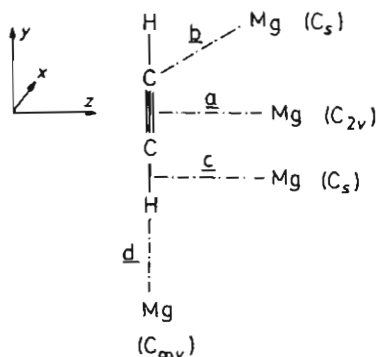


Fig. 1. Model approaches of Mg and acetylene.

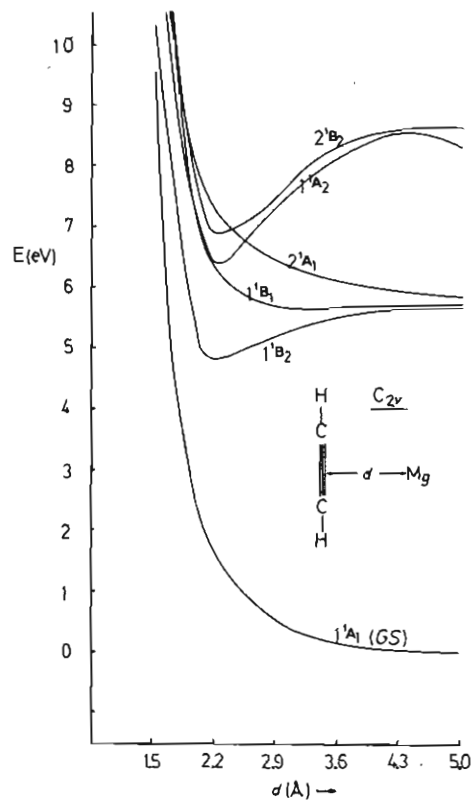


Fig. 2. Semiquantitative calculated singlet  $C_{2v}$  PESs for Mg+acetylene (method I).

excited electron is stabilized in the  $p_y$  atomic orbital (AO) of Mg through overlap with the empty  $\pi^*$  MO of acetylene having the same symmetry. From another point of view, Nikitin's charge transfer (CT) model [18] is accurate for such a system where the  $C_2H_2\text{-Mg}^+$  PESs lie at about 10 eV above the ground state (GS) at infinite separation of the ions. This energy can be experimentally evaluated from the ionization energy of Mg (7.64 eV) [19] and the existence of a  $\pi^*$ -shape resonance of acetylene in the 2.6 eV region [20]. According to Nikitin's model, the CT PESs ( $A_2$  and  $B_2$ , singlet and triplet arrangement of both radical ions), which are strongly stabilized when the separation of ions decreases, give rise to several avoided crossings with the lower PESs of the same symmetry. As an end result, all PESs of  $A_2$  and  $B_2$  symmetry exhibit a potential energy well. The depth of the well along a given PES depends on the asymp-

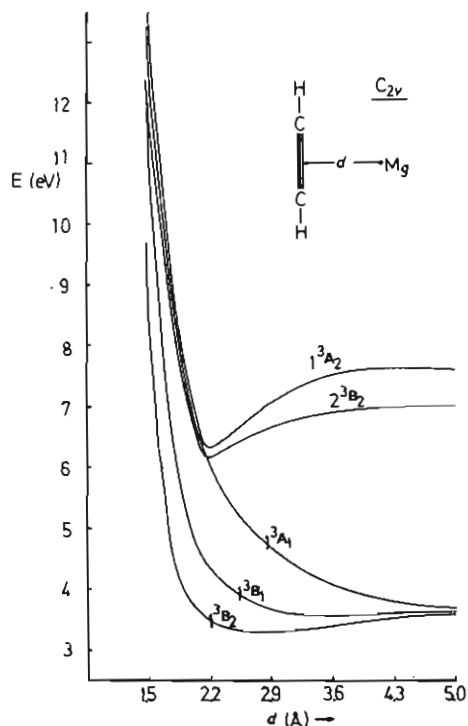


Fig. 3. Semiquantitative triplet  $C_{2v}$  PESs for Mg+acetylene (method I).

total energy difference between this PES and the CT PES. When this difference is weak (e.g.  $2^1B_2$ , fig. 2), the crossing occurs at large acetylene-metal separation ( $d$ ) and the electronic energy strongly decreases while nuclear repulsion remains weak. On the contrary, for lowest PESs ( $1^3B_2$ , fig. 3), the crossing with CT occurs at a smaller  $d$  value for which the nuclear repulsion becomes important. This is the reason why the minimum is much less marked in the triplet than in the corresponding singlet surfaces. A complete discussion of diabatic processes, including the calculation of diabatic PESs will be published later on [21].

The singlet PESs for a  $C_s$  approach (path b) are displayed in fig. 4. The angle Mg-C-C ( $120^\circ$ ) has been chosen such that it roughly corresponds to that expected in a possible  $\sigma$  complex. No significant minimum is observed. Both other model approaches (paths c and d), which are not reported, exhibit monotonous PESs for the lowest states arising from  $^3P$  and  $^1P$  states of Mg.

In conclusion, using a first approximation of the

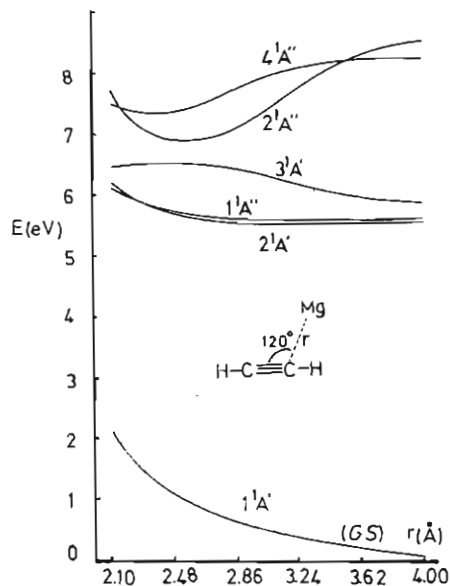


Fig. 4. Semiquantitative singlet  $C_s$  PESs for Mg+acetylene (method I).

reaction coordinates, i.e. a single approach, with no relaxation of acetylene, the only attractive PESs correspond to the  $C_{2v}$  geometry.

We will now examine in more detail the exciplexes originating from the lowest triplet and the lowest singlet of Mg.

**Triplet exciplex.** In a first step, the triplet  $1^3B_2$  exciplex geometry was optimized, at SCF 6-31G\*\* level, within the  $C_{2v}$  point group, yielding structure 1 of fig. 5. When the system is allowed to lower its symmetry from  $C_{2v}$  to  $C_s$ , structure 2 (fig. 5) is obtained. Nevertheless, after MP calculation, 1 is found at a lower energy than 2, at 1.21 eV below the asymptotic energy of  $Mg(^3P) + C_2H_2(GS)$ . A  $\sigma$ -type exciplex (structure 3, fig. 5) has been found at 0.34 eV above the preceding  $\pi$ -type one. Its optimized structure agrees very well with Morokuma's calculations at the 3-21G SCF level [8]. These two minima are separated by a very weak energy barrier (0.09 eV above 3, structure TS1, fig. 5).

**Singlet exciplex.** The  $C_{2v}$   $\pi$  structure 4 (fig. 5) of the  $^1B_2$  exciplex has been optimized from a grid of points using method I. At the 6-31G\*\* RHF level, another minimum is found, corresponding to a  $\sigma$  complex 5. Nevertheless, (i) the barrier separating

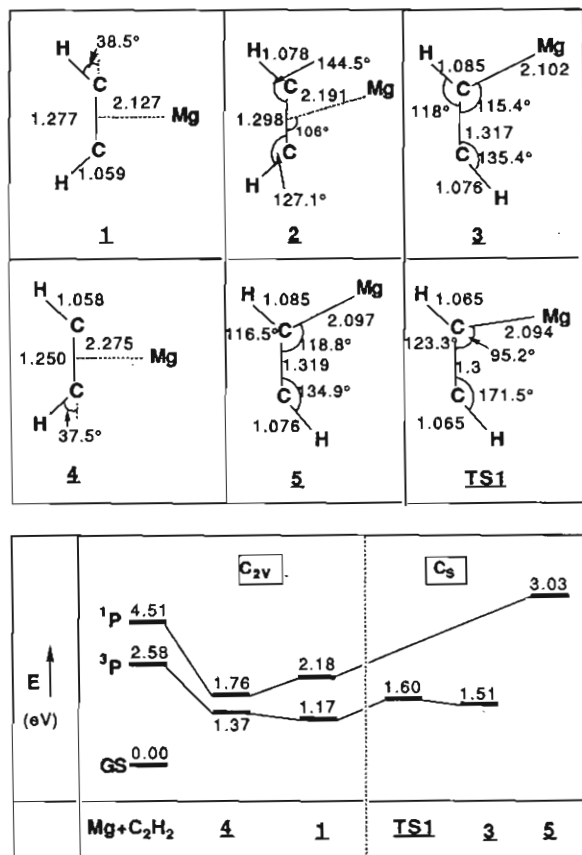


Fig. 5. Mg acetylene exciplexes arising from the lowest  $^3P$  or  $^1P$  states of Mg. The bondlengths are in Å; the energies are in eV with respect to  $Mg+C_2H_2$  at 5 Å ( $C_{2v}$ ). Absolute reference energy:  $-276.613276$  au.

these two exciplexes at the SCF level disappears at the MP level and the  $\pi$  structure 4 is found to be the most stable (2.75 eV below the energy of separated moieties); (ii) at method I level a monotonous PES links 4 and 5. So, we can expect for this system a unique  $\pi$ -type singlet  $B_2$  exciplex.

These results can be compared with those previously obtained with the related Mg- $N_2$  system. In the latter case a  $\pi$  exciplex of the same  $C_{2v}$  symmetry was found, with a stabilization of 2.46 eV (versus 1.88 eV in  $C_{\infty v}$  symmetry) with respect to the asymptotic  $N_2+Mg(^1P)$  energy value [22].

### 3.2. Physical quenching of the $1^3P$ and $1^1P$ states of Mg

The important stabilizations involved in the formation of both triplet and singlet exciplexes (1.21 and 2.75 eV, respectively) agree with a relatively high cross section of quenching, as found by Breckenridge and Umemoto. Since both triplet and singlet exciplexes have a preferential  $C_{2v}$   $\pi$ -type structure of  $B_2$  symmetry, the  $E$  to  $V$  energy transfer will preferentially occur through  $b_2$  vibrations. Indeed, the matrix element coupling the  $B_2$  state and the GS ( $A_1$ ),  $\langle A_1 | \partial/\partial Q | B_2 \rangle$  [23], is non-zero when the normal coordinate,  $Q$ , is of  $b_2$  symmetry.

Such deformations essentially correspond to the following three motions: in-plane out-of-phase C-H bending, out-of-phase C-H stretching, and in-plane  $C_2H_2$  "rotation" with respect to the Mg atom. These normal coordinates have been modeled by small deformations  $R_i$  (fig. 6), and the corresponding matrix elements have been calculated by a finite difference method of derivation [21]. Although the obtained values are only rough approximations (the  $R_i$  are not normal coordinates) they seem to indicate that one mode couples more strongly the two PESs. This coordinate ( $R_3$ ) corresponds to a rotation of acetylene with respect to the metal atom, and the corresponding matrix element is about three or four times greater than the other two. Since the transition probability is proportional to the square of this matrix element, the electronic energy transfer should be one order of magnitude more probable to rotational than to vibrational energy.

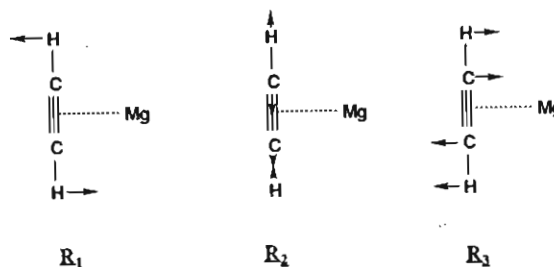


Fig. 6. Model deformations of the lowest  $C_{2v}$  Mg- $C_2H_2$  singlet exciplex. Calculated coupling with the GS,  $\langle \Psi_{exc} | \partial/\partial R_i | \Psi_{GS} \rangle$ , is: for  $R_1$  0.0330 au $^{-1}$ ; for  $R_2$  0.0248 au $^{-1}$ ; for  $R_3$  0.1147 au $^{-1}$ .

### 3.3. Chemical quenching of the $^3P$ and $^1P$ states of Mg

#### 3.3.1. Mg-vinylidene complex and vinylidene formation

Fig. 7 displays the calculated results for these reactions. The transition state (TS) for hydrogen transposition, **6**, along the lowest excited singlet surface was optimized at the RHF 6-31G\*\* level. Its structure is very close to that published by Morokuma [8] for the corresponding triplet state. Then MP calculations were performed (method II) on this structure for both singlet and triplet states. The hydrogen transposition requires an activation energy of 2.26 eV for the triplet state, and 2.22 eV for the singlet state above the corresponding  $\pi$  complex. For the singlet state, the TS is about 0.5 eV below the reactants at infinite separation, whereas, for the triplet, it lies 0.85 eV above the corresponding reactants. In other words,  $^1P$  Mg has energy enough to overcome

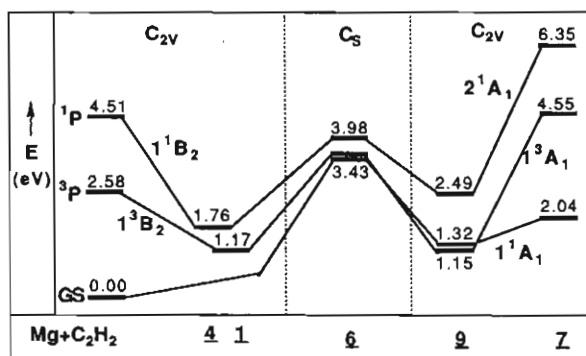
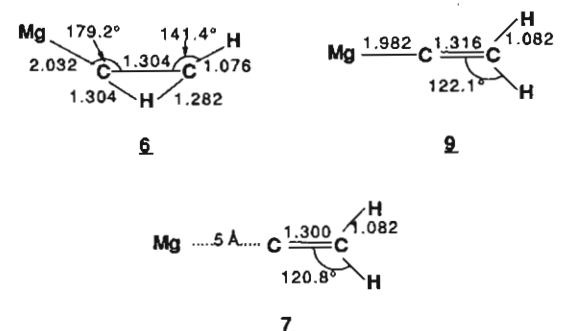


Fig. 7. Successive reactions yielding vinylidene. See also caption to fig. 5.

the barrier and yield vinylidene magnesium, while  $^3P$  Mg has not.

Regarding the first excited singlet state, a distinction can be made concerning the efficiency of the C<sub>s</sub> and C<sub>2v</sub> approaches, in yielding the H transposition reaction. The vibrational mode of the  $1^1B_2$  singlet of the  $\pi$  complex directly related to the reaction coordinate leading to  $2^1A_1$  Mg-CCH<sub>2</sub> must be of b<sub>2</sub> symmetry. From this point of view, a C<sub>s</sub> approach should favor such a vibrational mode in the  $\pi$  complex and yield the abovementioned reaction, while a C<sub>2v</sub> approach would be more advantageous for the a<sub>1</sub> symmetry modes of the resulting  $\pi$  complex. Moreover, a C<sub>s</sub> approach with a large kinetic energy could avoid the potential energy well of the  $\pi$  complex (compare figs. 2 and 4).

It is noteworthy that the GS of vinylidene magnesium **9** has been found to be triplet, but there is only a small gap (0.17 eV) between this state and the nearest singlet. This singlet state can easily yield Mg+CCH<sub>2</sub> (**7**) upon cleavage of the Mg-C bond, with a weak endothermicity ( $\approx 0.7$  eV by method II, none by method I), whereas the triplet GS is correlated with the high energy first triplet of these species.

#### 3.3.2. Insertion into a C-H bond and formation of MgH

As usual in this type of reaction, we have to take into account two limiting model reaction coordinates (RC). The first one consists in a triangular approach of the C-H bond to be broken, yielding a bent form of the insertion product (approach c of fig. 1), which can either give MgH+C<sub>2</sub>H or H-Mg-C<sub>2</sub>H (**10**). The second mechanism, referred to as hydrogen abstraction, is a simple H transfer from acetylene to Mg atom via a linear approach of the reactants Mg...H-CCH (approach d, fig. 1).

Let us first examine the insertion reaction (fig. 8). The TS along the GS (TS2) has been optimized at the RHF 6-31G\*\* level, and the energies of the lowest triplet and singlet excited states, with the same geometry are reported. Starting from the triplet  $^3P$  Mg, the system requires at least 0.57 eV for reaching a "reactive" region, i.e. a geometry close to that of the TS of the GS (TS2). Moving along the first excited  $2^1A'$  singlet state surface, a minimum is encountered nearby this TS. But, as revealed by exploratory scans

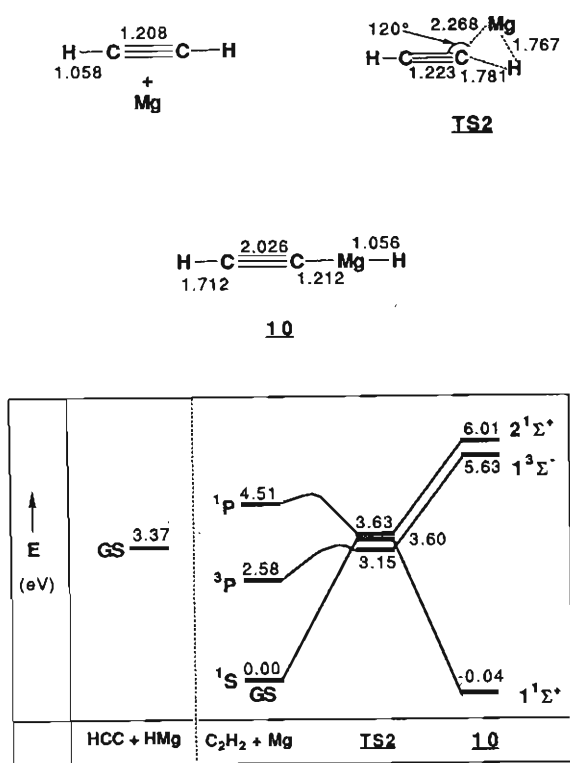


Fig. 8. Insertion of Mg atom into a C-H bond. See also caption to fig. 5.

using method I, an activation energy of about 0.5 eV is necessary before reaching this region.

No calculation was made concerning the direct end-on hydrogen abstraction for we believe that its major features can be extrapolated from previous calculations on  $\text{CH}_4 + \text{Mg}$  system [24,25]. In the latter system, an energy barrier of 1.5 eV is found on the lowest excited singlet state. The  $\text{MgH} + \text{CH}_3$  GS lies 2.87 eV above the reactants, so that the reaction is endothermic when starting from the lowest triplet  $^3P$  of Mg (2.57 eV calculated, 2.72 eV experimental [19]). Dealing with Mg and acetylene, the energy barrier on the singlet PES is expected to be at least of the same order of magnitude (1.5 eV) [25], since the C-H bond is more stable for acetylene (4.9 eV) than for methane (4.4 eV) [26]. Similarly, the endothermicity of the GS reaction can be evaluated to  $2.87 + 0.5 = 3.37$  eV, where 0.5 eV represents the C-H energy difference between acetylene and methane. The reaction remains exothermic starting from  $^1P$  Mg

(-1.13 eV), but with an important energy barrier ( $\geq 1.5$  eV) and rather endothermic starting from  $^3P$  Mg ( $\geq 1$  eV). In any case, the insertion mechanism will be preferred over direct abstraction. Let us recall that the same result was found dealing with  $\text{CH}_4 + \text{Mg}$  [24,25], in spite of steric hindrance, in the triangular approach, between Mg and other H atoms.

#### 4. Conclusion: general survey of the $^3P$ and $^1P$ Mg reactivity

Though some uncertainty remains on the structures optimized at the SCF level, the calculations afford data on the ground of which the following semi-quantitative picture of the reactivity of the system can be proposed.

Starting from the triplet  $^3P$  state of Mg, the hydrogen abstraction reaction can be ruled out due to its endothermicity. The Mg-vinylidene complex formation requires an overall activation of 0.85 eV and the insertion reaction an activation of at least 0.57 eV. Both reactions thus appear unlikely, though not totally forbidden. An efficient physical quenching can be expected, with formation of  $\pi$  exciplex **1** (possibly in equilibrium with  $\sigma$  complex **2** in small amount), which could have a significant lifetime, since triplet-singlet GS conversion is expected to have a low rate in this case. Thus this exciplex could be trapped during matrix experiments and its phosphorescence would occur in the  $9000 \text{ cm}^{-1}$  region.

Dealing with singlet  $^1P$  Mg, the situation is more complex and would strongly depend on the experimental conditions. In the gas phase, i.e. when the possibilities of losing of internal energy are scarce, two reaction channels are to compete:

(i) A triangular approach of a C-H bond yielding a bent form of the insertion product  $\text{H-Mg-C}_2\text{H}$  (**10**), with internal energy enough to produce MgH through cleavage of the Mg-C bond. This process is diabatic (fig. 8) and depends, among others, on the efficiency of the excited state-GS conversion in the vicinity of the TS. In addition, it probably requires an activation of about 0.5 eV as suggested by exploratory scans.

(ii) The hydrogen transposition, yielding Mg-vinylidene complex in its lowest excited singlet state. This process occurs adiabatically, as shown in fig. 7.

Upon deactivation of the latter complex, the internal energy excess is sufficient to induce a further cleavage of the Mg–C bond.

In fact, both reactions suffer an efficient competition of the physical quenching via the strongly stabilized  $\pi$  complex; indeed, experimentally, no MgH production was detected by Breckenridge and Umemoto in spite of the rather high cross section of quenching. Nevertheless, the vinylidene formation cannot be a priori ruled out, since the formation of vinylidene–magnesium complex occurs on the same PES, and there is an excess of electronic energy with respect to the corresponding barrier. Moreover, in the absence of any trapping agent, the resulting vinylidene, which is a very labile species, undergoes a rapid transposition into acetylene [27]. Thus the overall process might be confused with physical quenching.

In the condensed phase, such as low-temperature matrices, one might expect to trap either the vinylidene complex with Mg, or one of its adducts with the matrix. On the other hand, the formation of the insertion product remains likely. Unfortunately, an efficient possibility of vibrational relaxation could indeed favor the trapping of the  $\pi$  exciplex, which constitutes a reactional "cul de sac".

In both condensed and gas phases we have to consider the possibility of intersystem crossing, for the energy of singlet structure 4 is very close to that of the triplet PES. This way, the emission of the triplet exciplex at rather large wavelength (about 1100 nm) might be observed. Let us recall that the Mg( $^3P$ ) phosphorescence at 516 nm has been observed by Ozin and co-workers [28] during the quenching of singlet Mg by CH<sub>4</sub> in matrix.

## References

- [1] E.E. Nikitin, *Theory of Atomic and Molecular Processes in Gases* (Oxford Univ. Press, Oxford, 1974);  
K.J. Klabunde, *Chemistry of Free Atoms and Particles* (Academic Press, New York, 1980);  
W.H. Breckenridge, *Reactions of Small Transient Species* (Academic Press, New York, 1983) p. 157;  
W.H. Breckenridge and H. Umemoto, *Advan. Chem. Phys.* **L50** (1982) 325;  
I.V. Hertel, *Advan. Chem. Phys.* **L50** (1982) 475;  
C. Botcher, *Advan. Chem. Phys.* **42** (1980) 169.
- [2] P.H. Kasai, *J. Am. Chem. Soc.* **104** (1982) 1165;  
P.H. Kasai, D. McLeod Jr. and T. Watanabe, *J. Am. Chem. Soc.* **99** (1977) 3521.
- [3] J.H.B. Chenier, J.A. Howard, B. Mile and R. Sutcliffe, *J. Am. Chem. Soc.* **105** (1983) 788.
- [4] D. Cohen and H. Bash, *J. Am. Chem. Soc.* **105** (1983) 6980.
- [5] P.H. Kasai, *J. Am. Chem. Soc.* **105** (1983) 6704.
- [6] P.H. Kasai, *J. Phys. Chem.* **86** (1982) 4092.
- [7] V. Bonacic-Koutecky, private communication;  
C. Pouchan, *Chem. Phys.* **111** (1987) 87.
- [8] S. Sakai and K. Morokuma, *J. Am. Chem. Soc.* **91** (1987) 3661.
- [9] A.C. Scheiner and H.F. Schaefer III, *J. Am. Chem. Soc.* **107** (1985) 4451.
- [10] W.H. Breckenridge and H. Umemoto, *J. Chem. Phys.* **75** (1981) 698.
- [11] W.H. Breckenridge and H.J. Umemoto, *J. Chem. Phys.* **77** (1982) 4464.
- [12] J.S. Binkley, R.A. Whiteside, R. Krishnan, R. Seeger, D.J. DeFrees, H.B. Schlegel, S. Topiol, L.R. Kahn and J.A. Pople, *GAUSSIAN 80*, QCPE No. 368 (1978).
- [13] E.R. Davidson, *Chem. Phys. Letters* **21** (1973) 565.
- [14] C.C.J. Roothaan, *Rev. Mod. Phys.* **23** (1951) 69.
- [15] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees and J.A. Pople, *J. Chem. Phys.* **77** (1982) 3654;  
M.S. Gordon, J.S. Binkley, J.A. Pople and W.J. Pietro, *J. Am. Chem. Soc.* **104** (1982) 2997;  
W.J. Pietro, M.M. Francl, W.J. Hehre, D.J. DeFrees, J.A. Pople and J.S. Binkley, *J. Am. Chem. Soc.* **104** (1982) 5039.
- [16] C. Møller and M.S. Plesset, *Phys. Rev.* **46** (1934) 618.
- [17] B. Huron, J.P. Malrieu and P. Rancurel, *J. Chem. Phys.* **58** (1973) 5745;  
J.P. Malrieu, *Theoret. Chim. Acta* **62** (1982) 163;  
S. Evangelisti, J.P. Daudey and J.P. Malrieu, *Chem. Phys.* **75** (1983) 91.
- [18] A. Bjerre and E.E. Nikitin, *Chem. Phys. Letters* **1** (1967) 179.
- [19] C.E. Moore, *Atomic Energy Levels*, Vol. 1 (Natl. Bur. Stds., Washington, 1949).
- [20] R. Dressler and M. Allan, *J. Chem. Phys.* **87** (1987) 4510.
- [21] A. Sevin, A. Papakondylis, C. Giessner-Prettre and P. Chaquin, submitted for publication.
- [22] P. Chaquin and A. Sevin, *Chem. Phys.* **123** (1988) 351.
- [23] T.S. Lee, *J. Am. Chem. Soc.* **99** (1977) 3909, and references therein.
- [24] J.G. McCaffrey, R.A. Poirier, G.A. Ozin and I.G. Csizmadia, *J. Phys. Chem.* **88** (1984) 2898.
- [25] P. Chaquin, A. Sevin, A. Papakondylis and C. Giessner-Prettre, submitted for publication.
- [26] G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 3. *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, Princeton, 1966).
- [27] Y. Osamura, H.F. Schaefer III, S.K. Gray and W.H. Miller, *J. Am. Chem. Soc.* **103** (1981) 1904, and references therein;  
E.M. Evleth and A. Sevin, *J. Am. Chem. Soc.* **103** (1981) 7414.
- [28] J.G. McCaffrey and G.A. Ozin, *J. Chem. Phys.* **89** (1988) 1839, 1844;  
J.G. McCaffrey, J.M. Parnis and G.A. Ozin, *J. Chem. Phys.* **89** (1988) 1858.