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RRKM and direct MP2/6-31G(d,p) quasiclassical trajectory study of the H₂ elimination in the photodissociation of vinyl chloride at 193 nm

Jesús González-Vázquez [a], Emilio Martínez-Núñez [b], Saulo Vázquez [b,*],
Jesús Santamaría [a], Luis Bañares [a]

[a] *Departamento de Química Física, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain*
[b] *Departamento de Química Física, Facultad de Química, Universidad de Santiago de Compostela, Qumica Fsica,
Avda de las Ciencias sn, Santiago de Compostela E-15782, Spain*

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Abstract

RRKM calculations and MP2/6-31G(d,p) quasiclassical trajectories (QCT) were performed to investigate the H₂ elimination in the photodissociation of vinyl chloride at 193 nm. The kinetic study involved nine elementary steps and the QCT investigation was made for the relevant reaction channels. The trajectories were initiated at the transition states using a microcanonical, quasiclassical normal-mode sampling. Comparison between the calculated product energy distributions and the available experimental data is discussed. Overall, the present results (RRKM and QCT) suggest that the direct three-center elimination, which may occur via two similar transition states, is the dominant mechanism for H₂ production.
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1. Introduction

Vinyl chloride (VCl, C_2H_3Cl) is a prototypical system for studying molecular eliminations in saturated olefins. The photodissociation dynamics of VCl has been extensively investigated during the last decades, and a brief history of this subject is reported in a previous Letter of ours [1].

The elimination of HCl, H₂, H and Cl (^2P_J) have all been identified as primary dissociation products in the 193 nm photodissociation of VCl. Except atomic chlorine, all these photofragments are expected to be produced entirely on the electronic ground state (see [2,3], and references therein). Riel and Morokuma [4] have investigated the dissociation of vinyl chloride using ab

initio methods. The reaction channels leading to molecular hydrogen elimination, and a channel leading to HCl that involves the common intermediate 10, are depicted in Fig. 1. A more complete potential energy diagram obtained by MP2/6-31G(d,p) geometry optimizations and single point QCISD(T)/6-311+G(d,p) energy calculations for the HCl and H₂ eliminations is given in Fig. 4 of [4]. In the present Letter, the nomenclature used to name the structures follows that of Riel and Morokuma [4], and hereinafter each channel will be referred to by the name of its relevant transition state. Channels B3 and B4 are three-center eliminations to give chlorovinylidene (9) and H₂. The corresponding (classical) recombination barriers are very small, about 5 and 3 kcal/mol, respectively (≈7 and 6 kcal/mol with the zero-point energy corrections) [4]. Intermediate 9 may experience a subsequent isomerization (via H (B31) or Cl (B32) migration) to chloroacetylene (Cl—C≡C—H) by surmounting small energy barriers. Channel C12 first
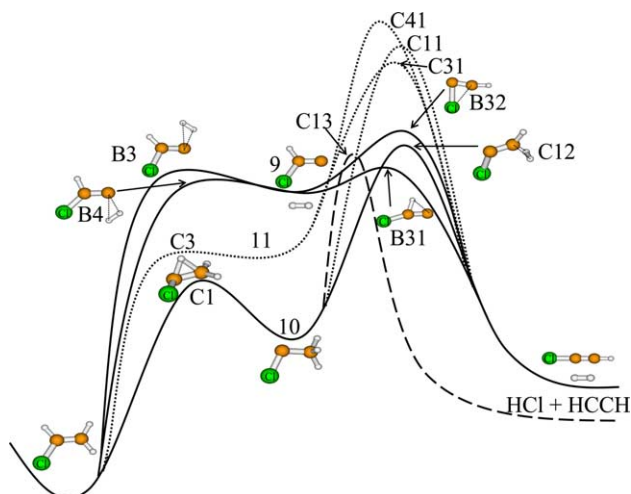

Fig. 1. Schematic potential energy diagram showing the channels considered in the kinetic analysis. Solid lines represent the channels studied by quasiclassical trajectories.

involves an H migration through transition state C1 to give chloroethylidene (10), and then a three-center H_2 elimination (through transition state C12) to give chloroacetylene and H_2. From intermediate 10, H_2 may be formed through transition state C11 (see [4] for details). Also from 10, HCl may be obtained through transition state C13, which is a bit lower in energy than C12. Finally, molecular hydrogen may be also produced by two channels (C31 and C41) initiated with a Cl migration through transition state C3 (see [4] for more details).

We have recently studied the HCl elimination from VCl by quasiclassical trajectory (QCT) calculations, and good agreement with experiment was found for product energy distributions [1,5]. Our study corroborated that the three-center HCl elimination mostly occurs in concert with isomerization of vinylidene to acetylene, which had been proposed previously by Huang et al. [6] in order to explain the observed nonstatistical distributions of product translational energies. On the other hand, our results predicted that the four-center channel produces rotationally hot HCl molecules while low rotational states of HCl are essentially populated when vinyl chloride dissociates through the three-center channel. This result is at odds with a previous conclusion inferred from fully resolved vibration–rotation emission spectra of HCl and simple theoretical models [7].

As far as the molecular hydrogen elimination is concerned, He et al. [2] measured the nascent rotational state distributions of H_2 photoproducts in the first five vibrational levels. They also measured the maximum and average translational energies for some of the rovibrational levels of H_2 by using magic angle Doppler spectroscopy. They found that the translational energy of the fragments plus the internal energy of H_2 exceed the available energy for a direct three-center mechanism.
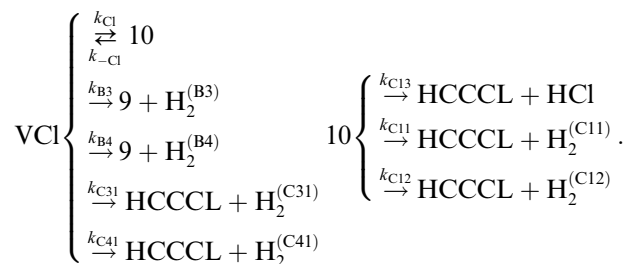
Accordingly, and based on the ab initio calculations of Riel and Morokuma [4], they concluded that the mechanism most consistent with their experimental data is H migration followed by H_2 elimination from chloroethylidene. The authors also suggested a minor contribution from direct three-center eliminations.

More recently, Blank et al. [3] investigated the photodissociation of VCl at 193 nm by using photofragment translational spectroscopy. The large average translational energy measured in their experiment for the H_2 elimination (18 ± 2 kcal/mol) [3] appeared to be inconsistent with the small barrier for recombination of H_2 + :CCHCl. Accordingly, they suggested that direct three-center H_2 elimination may occur concertedly with isomerization of chlorovinylidene (structure 9 in Fig. 1) to chloroacetylene, in a way similar to that proposed for the HCl elimination. The main mechanism for H_2 elimination suggested previously by He et al. [2] would also lead to a large translational energy release.

In this Letter, we will try to elucidate the preferred mechanisms for H_2 elimination from VCl at 193 nm with the aid of RRKM and direct MP2/6-31G(d,p) trajectory calculations. We computed product energy distributions for the relevant channels (those depicted in Fig. 1 by solid lines) and compared them with the available experimental information. The trajectories were started at the transition states using microcanonical initial conditions. This is a reasonable assumption even though the process of internal conversion may lead to some selectivity of the vibrational modes excited and, since the lifetime is short at 193 nm of excitation, intramolecular vibrational energy redistribution may not be complete before VCl decomposes.

2. Methods

Microcanonical rate constants were computed for the nine elementary steps involved in the elimination of H_2, including the elimination of HCl from intermediate 10 (see Fig. 1):

$$\text{VCl}\begin{cases} \overset{k_{C1}}{\underset{k_{-C1}}{\rightleftarrows}} 10 \\ \overset{k_{B3}}{\rightarrow} 9 + H_2^{(B3)} \\ \overset{k_{B4}}{\rightarrow} 9 + H_2^{(B4)} \\ \overset{k_{C31}}{\rightarrow} \text{HCCCL} + H_2^{(C31)} \\ \overset{k_{C41}}{\rightarrow} \text{HCCCL} + H_2^{(C41)} \end{cases} \quad 10\begin{cases} \overset{k_{C13}}{\rightarrow} \text{HCCCL} + \text{HCl} \\ \overset{k_{C11}}{\rightarrow} \text{HCCCL} + H_2^{(C11)} \\ \overset{k_{C12}}{\rightarrow} \text{HCCCL} + H_2^{(C12)} \end{cases}.$$

In the above processes we considered that VCl leads directly to H_2 + HCCCl through C31 and C41, which is a reasonable approximation because the stability of intermediate 11 is only of 0.01 kcal/mol [4]. This scheme leads to the following two kinetic equations:

$$\begin{pmatrix} d[VCl]/dt \\ d[10]/dt \end{pmatrix} = \begin{pmatrix} -(k_{Cl} + k_{B3} + k_{B4} + k_{C41} + k_{C31}) & k_{-Cl} \\ k_{Cl} & -(k_{C13} + k_{C11} + k_{C12} + k_{-Cl}) \end{pmatrix} \begin{pmatrix} [VCl] \\ [10] \end{pmatrix}.$$

The solutions of this system were subsequently used to get the relative yields of H_2 formed from the different channels at $t \to \infty$. Previously, the microcanonical rate constants for the nine elementary steps were calculated using the well-known equation of RRKM theory

$$k(E) = \frac{\sigma W^{ts}(E)}{h\rho(E)},$$

where σ is the reaction path degeneracy, $W^{ts}(E)$ the total number of states at the transition state with energy less than or equal to E, and $\rho(E)$ the density of states at the reactant. In this work, $W^{ts}(E)$ and $\rho(E)$ were evaluated by direct count of vibrational states using a program [8] based on the Beyer–Swinehart algorithm [9]. The data employed in these calculations comprised QCISD(T)/6-311+G(d,p)//MP2/6-31G(d,p) results of Riel and Morokuma [4] for energy barriers and MP2/6-31G(d,p) frequencies obtained in this work.

For the direct QCT calculations, the MP2/6-31G(d,p) level of theory was used because it gives a good balance between accuracy and computational cost. As shown in the work of Riel and Morokuma [4], the energetics of the H_2 elimination channels (in particular for the exit channel regions) predicted at the MP2/6-31G(d,p) level are in reasonably good agreement with the more accurate, single point QCISD(T)/6-311+G(d,p) data using the MP2/6-31G(d,p) optimized geometries. The trajectories were initiated at transition states B3 and B4 by using a microcanonical, quasi-classical normal mode sampling described in detail elsewhere [10,11]. Each ensemble consisted of 300 trajectories run at an available energy corresponding to a photon excitation of 193 nm. Using the QCISD(T) energetics and the scaled MP2 zero-point energies of [4], this excitation energy corresponds to 68.1 kcal/mol above the B3 (classical) energy, and to 69.7 kcal/mol above the B4 energy. The trajectories were integrated by the Hessian based method [12] implemented in GAUSSIAN 98 [13] with a step-size of 0.25 amu$^{1/2}$ bohr. Products were considered fully separated when the lowest distance between atoms located on different fragments reached a value of 8 bohr. Therein the distributions of product internal and recoil translational energies were computed. The products' translational energy distributions were fitted by using the method of Legendre moments [14], and the H_2 rotational and vibrational quantum numbers were calculated by the Einstein–Brillouin–Keller (EBK) quantization of the action integral [15–17].

3. Results and discussion

The RRKM results of Fig. 2 indicate that the most probable reactive channels resulting in H_2 formation at 193 nm (148.1 kcal/mol) are, by far, B3 and B4, while channels involving hydrogen or Cl migration (C11, C12, C31 and C41) have little probability to occur. Particularly, the relative abundance of H_2 produced by channels B3 and B4 accounts for 95% of the total (with a relative ratio B3:B4 of 45:50), and that produced by channel C12 amounts 4%. Therefore, our kinetic results show that direct H_2 three-center eliminations are the dominant mechanisms of molecular hydrogen formation, and that a small fraction of H_2 molecules is produced through channel C12, which involves an H migration as a first step.

Taking the above results into account, we first performed direct MP2/6-31G(d,p) trajectories in order to compute product energy distributions for the B3 and B4 channels. In particular, the translational energy distributions $P(E_t)$ are depicted in Fig. 3. As can be seen, both channels predict very similar $P(E_t)$, with average translational energies of 17.0 and 16.9 kcal/mol for B3 and B4, respectively. The total average translational energy, weighted by the B3:B4 branching ratio of 45:50, is 16.95 kcal/mol, which agrees with the experimental result of 18 ± 2 kcal/mol [3]. However, the experimental data of Blank et al. [3] may be uncertain because the average translational energy reported in the text of their Letter is not consistent with the corresponding translational distribution depicted
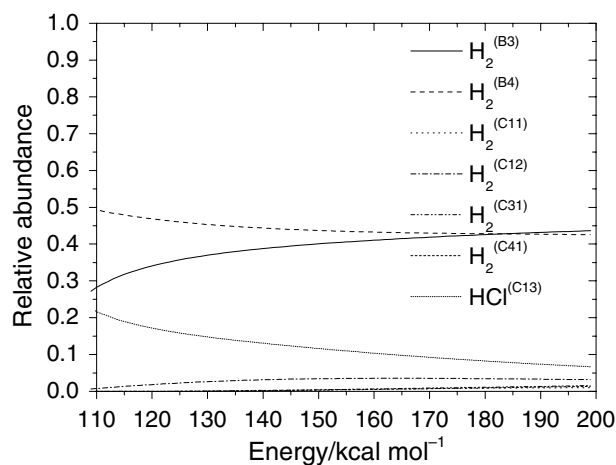

Fig. 2. Relative abundances of H_2 for the photodissociation of VCl at 193 nm obtained by RRKM calculations (see text).
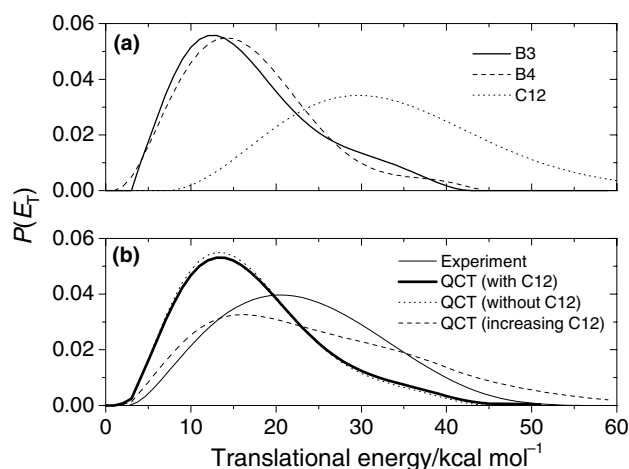
Fig. 3. (a) Translational energy distributions calculated for channels B3, B4 and C12. (b) Total distributions obtained as weighted contributions from the B3 and B4 and C12 channels (see text) along with the experimental $P(E_t)$ of Blank et al. [3] (solid line). In all cases, the distributions are normalized to unit area.

in Fig. 6 of that Letter [1]. In fact, it is apparent that the average translational energy extracted from that figure, reproduced in Fig. 3b of this Letter, for the purposes of comparison (solid line), is significantly larger than 18 kcal/mol. The distribution of Blank et al. [3] is not in accordance with our total translational distribution obtained as a weighted sum of the B4 and B3 contributions (dotted line in Fig. 3b).

As mentioned before, according to the present RRKM calculations, the contribution from channel C12 to the total H_2 production is small (4%). However, in order to explore the possible influence of this channel on the product energy distributions, we run further QCT calculations for this channel by using, in this case, a semiempirical AM1 Hamiltonian supplemented with specific reaction parameters (AM1-SRP). This approach demands substantially less CPU time than the MP2/6-31G(d,p) computations, although the details of the couplings and curvatures in the exit channel may not be recovered by the SRP fitting [18]. We employed AM1-SRP models in previous studies (see for example [1,19,20]) and so in this Letter, we will not enter into details. Here, suffice it to say that the reverse barrier for channel C12 calculated by the AM1-SRP model (53.8 kcal/mol) agrees with that predicted by our own QCISD(T)/6-311+G(2d,2p)//QCISD/6-311+G(2d,2p) calculations (53.9 kcal/mol). We run a total of 10 000 trajectories from transition state C12, initialized in the same way as for B4 and B3, and using an extensively adapted version of the GenDyn program [21]. The translational distribution for channel C12 (see Fig. 3a)

is broader and shifted towards higher energies as compared with those predicted for channels B3 and B4. The average translational energy obtained for channel C12 (33.5 kcal/mol) is much higher than the reported experimental value of 18 kcal/mol and, of course, than those obtained for channels B3 and B4. However, since the RRKM branching ratio of the C12 channel is very small, its contribution has almost no influence on the total $P(E_t)$, as can be seen in Fig. 3b (solid thick line).

If it is assumed that the experimental distribution of Blank et al. [3] (shown in Fig. 3b) is correct and that the dissociation occurs on the electronic ground state, the bad agreement found between the QCT and experimental translational energy distributions may indicate that something wrong is present in our model calculations. Disagreement may come from the relative yields calculated for the H_2 elimination channels. If we artificially increase the branching ratio of the C12 channel (specifically, 1:1.1:2 for B3:B4:C12) in such a way that the calculated average translational energy matches that obtained from the experimental distribution of Fig. 3b (≈ 23 kcal/mol), we obtain a new distribution (dashed line) which also differs significantly from the experimental one, as it is broader and much more asymmetrical. This seems to disregard this possibility as the major source of error. Perhaps a different mechanism of H_2 elimination is taking place, such as, for example, direct four-center elimination. We have searched for a possible four-center transition state but, as found by Riel and Morokuma [4], the optimizations led to structures associated to other channels. Another possible source of error may come from the sampling model used in the trajectory calculations, which would be very inaccurate if the actual distributions of molecular states at the transition states differ significantly from the statistical model. As indicated in the Introduction, the excitation process may lead (after internal conversion) to a nonstatistical distribution of molecular states at the reactant, which in turn, and because of the excitation energy is rather high, may result in nonstatistical dynamics if the reaction rates compete with the rate of intramolecular vibrational energy redistribution (i.e., apparent non-RRKM behavior as defined by Bunker and Hase [22,23]). Although this may be a plausible explanation, it is worth noting that similar calculations on the HCl elimination from VCl and on the HF and H_2 eliminations from fluoroethylenes gave translational energy distributions in good agreement with experiment [1,19,20].

On the other hand, if the experimental average translational energy of 18 ± 2 kcal/mol reported by Blank et al. [3] is correct, our results would suggest that the prediction of H_2 molecules produced almost exclusively via channels B3 and B4 is accurate. The present $P(E_t)$ resembles those obtained for the three-center HCl elimination in previous QCT calculations [1,5]. That is, even though the reverse barriers are quite small, the

[1] We asked Dr. D.A. Blank about this mismatch but unfortunately they did not keep the original data. Therefore, either the average value of 18 kcal/mol or the distribution of Fig. 6 in [3] or both are wrong.

distributions peak far away from zero (between 10 and 12 kcal/mol for the HCl elimination [1,5] and around 14 kcal/mol for the H_2 elimination), with average translational energies near 18 kcal/mol. In the case of the HCl elimination, our previous QCT calculations [1,5] confirmed that the three-center elimination occurs essentially in concert (although not synchronously) with the vinylidene → acetylene isomerization. Particularly, the average lifetimes for isomerization were calculated to lie between 37 and 70 fs, in rather good agreement with experiment (40–200 fs) [24]. For the H_2 elimination, Blank et al. [3] suggested a similar mechanism, based on the fact that the chlorovinylidene → chloroacetylene isomerization energies are rather low, too. In the present work we have checked this possibility by making an inspection of each individual trajectory. Specifically, an isomerization event was counted when either transition state B31 or B41 was surmounted. The calculations show that 70% of the total number of trajectories resulted in isomerization with an average lifetime of 24 fs, for a total average simulation time of 60 fs. Therefore, the present results support the suggestions of Blank et al. [3] that the three-center H_2 elimination from VCl takes place in much the same way as the three-center HCl elimination [1,3], and that the unexpectedly large translational energies arise from the concerted isomerization process, which allows some of its exothermicity to be released as relative translational energy of the photofragments.

He et al. [2] measured the translational energy for H_2 ($v = 2$, $J = 3$–11) + ClCCH by using magic angle Doppler spectroscopy. Their mean values obtained by ignoring $\mathbf{v} \cdot \mathbf{J}$ vector correlation are approximately in the range 20–23 kcal/mol. These mean kinetic energies could be up to 15% lower if vector correlation were appropriately taken into account in their analysis [2]. Using the RRKM branching ratios (45:50:4 for B3:B4:C12), our calculations predict an average translational energy of 15.4 kcal/mol for H_2 ($v = 2$, $J = 3$–11) + ClCCH, which is below the above range. The average value calculated for the C12 channel (28.5 kcal/mol) is significantly higher. A value of 20 kcal/mol for the average translational energy of H_2 ($v = 2$, $J = 3$–11) + ClCCH would be obtained if one uses B3:B4:C12 branching ratios of 1:1.11:0.65. Even in this case, the direct three-center eliminations would dominate the production of molecular hydrogen.

As far as the rotational energy distributions are concerned, Fig. 4 shows a comparison between the experimental [2] and QCT distributions for $v = 0$–4. The theoretical rotational distributions were normalized to the corresponding experimental ones for each vibrational level. The QCT results were obtained as a weighted contribution (45:50:4) from the B4, B3, and C12 channels. As seen in the figure, the agreement between theory and experiment is good. It is important to note that the distributions obtained for channel C12
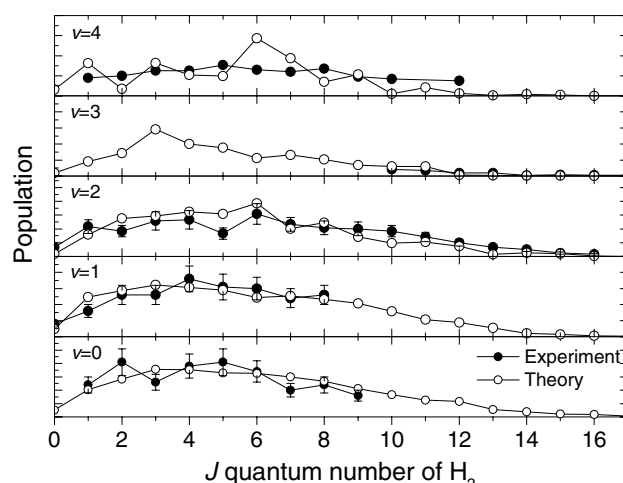

Fig. 4. Rotational distributions of H_2 ($v = 0$–4). The total theoretical distributions were calculated by using B3:B4:C12 branching ratios of 45:50:4. The ordinate is in arbitrary units, and the scales of the different panels do not indicate relative yields. The experimental distributions were taken from [2].

alone (not shown for simplicity) are also consistent with the experimental distributions, which prevented us from using this comparison to assess the importance of this reaction channel.

In summary, the results presented in this study suggest that the production of molecular hydrogen occurs mainly by direct three-center H_2 eliminations (via channels B3 and B4), rather than by elimination from chloroethylidene (formed by H migration) as concluded by He et al. [2], and that the large translational energy observed for H_2 + chloroacetylene arises basically from the concerted, nonsynchronous isomerization of chlorovinylidene to chloroacetylene as suggested by Blank et al. [3].

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