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Activation of methyl halides bonds by electric fields: A Valence Bond Perspective

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DEDICATORIA

A todos quienes acumulan experiencia en base a caídas, esta fue una más. A mi yo del pasado por las decisiones tomadas, quizá ahora me equivocaría otra vez, es tarde para arrepentimientos.

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A Dios por traerme hasta aquí y permitirme dar vuelta. A mis padres por apoyarme en este rumbo que tomó el camino. A quien dio su tiempo para que este proyecto pudiera culminar con éxito. Al director de este proyecto por su paciencia y guía académica.

RESUMEN

En el presente trabajo, la activación de enlaces σ-polares inducidos mediante campos eléctricos externos es estudiada desde la perspectiva de la Teoría de Enlace de Valencia. Como ejemplos representativos del mecanismo de disociación en cuestión, se toman en cuenta los enlaces tipo C − X (X = Cl, Br, I) de haluros de alquilo, experimentando la acción de campos eléctricos homogéneos y heterogéneos orientados a lo largo del eje de enlace. Para todos los casos, el incremento de la fuerza del campo eléctrico tiene efectos similares: i) estabilización de la energía potencial a lo largo del camino de disociación, ii) disminución de la longitud de enlace de equilibrio (a bajos campos eléctricos), y iii) la transición de una ruptura homolítica, hacia una heterolítica cuando el enlace está sujeto a una gran magnitud de campo. Estas observaciones generales son explicadas a través del modelo de enlace de valencia el cual involucra el entrecruzamiento de curvas entre la estructura iónica y la covalente, luego de cierta magnitud de campo eléctrico.

Palabras clave: Teoría de enlace de valencia, Campos eléctricos externos, Haluros de alquilo, activación enlaces tipo-σ.

ABSTRACT

In the present work, the activation of polar σ-bonds induced by an external electric field (EEF) is studied from the Valence Bond theory perspective. As representative examples, the dissociation mechanism of C–X bonds (X = Cl, Br, I) of methyl halides, under the experience of a homogeneous as well as a heterogeneous field oriented along the bond axis is considered. For all cases, the increase in the electric field have similar effects: (i) the stabilization of the potential energy along the dissociation path, (ii) a decrease of the equilibrium bond length (at low EEFs), and (iii) the transition from a homolytic cleavage to a heterolytic one when the bond is subjected under a strong enough field. These general observations are explained through a Valence Bond model that involves the curve crossing between the ionic and the covalent structure after some field strength.

Keywords: Valence Bond, External Electric Fields, Alkyl–Halides, σ-bond activation

TABLA DE CONTENIDO

Activation of methyl halides bonds by electric fields: A Valence Bond Perspective

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Abstract

In the present work, the activation of polar σ-bonds induced by an external electric field (EEF) is studied from the Valence Bond theory perspective. As representative examples, the dissociation mechanism of C–X bonds (X = Cl, Br, I) of methyl halides, under the experience of a homogeneous as well as a heterogeneous field oriented along the bond axis is considered. For all cases, the increase in the electric field have similar effects: (i) the stabilization of the potential energy along the dissociation path, (ii) a decrease of the equilibrium bond length (at low EEFs), and (iii) the transition from a homolytic cleavage to a heterolytic one when the bond is subjected under a strong enough field. These general observations are explained through a Valence Bond model that involves the curve crossing between the ionic and the covalent structure after some field strength.

Keywords: Valence Bond, External Electric Fields, Alkyl–Halides, σ-bond activation

1. Introduction

Alkyl halides or halo–alkanes are hydrocarbon derivatives in which one or more C–H bonds have been substituted by C–X bonds (X = F, Cl, Br, I) [1]. Mixed compounds are also known, being the most representative examples the chlorofluorocarbon (CFCs) compounds that have been suggested as important depletion agents of the ozone layer [2]. Halo–alkanes have a variety of applications in different industrial activities since they can be used as: refrigerants, foaming agents, solvents, propellants, extinguishing agents and chemical reagents [3]. Besides, a particular group of perfluorinated–alkanes (i.e. perfluorooctanate acids PFAS and sulfonates PFOS) have their most important application in the semiconductor manufacturing industry, and they are considered indispensable for the development of new technologies [4]. The great variety of applications that make use of halo–alkanes have led to their mass production and consumption, which in turn, have generated an overload and accumulation of halo–alkanes in aquatic, terrestrial and aerial systems [5, 6]. Moreover, these family of compounds have been catalogued as hazardous contaminants due to their ability to bioaccumulate in macro–organisms and their possible potential as carcinogens [7]. As a result of the aforementioned environmental issues and negative health effects, the Stockholm Convention of the United Nations classified these

compounds as Persistent Organic Pollutants (POPs), exhorting governments, especially from developed countries, to take the necessary measures to regulate their production, use, and disposal [8] with the purpose of creating strategies to mitigate their negative impact. One of the desired actions is to develop an effective and efficient treatment method. The encapsulation of halo–alkanes in meso- and micro-porous materials [9] and their advanced reduction–oxidation (REDOX) treatment by means of physicochemical techniques [10, 11] can be mentioned as well–known standard methods. Back in 1969, Schrauzer and Deutsch reported on the carbon–halogen bond dissociation mediated by Vitamin B_{12}, where the authors suggested that the super-reduced form of Cobalamin, $Co^I Cbl$ acts as a nucleophile specie capable to attack a halogenated carbon atom to activate the C–X bond [12]. Regarding this previous study, recent theoretical efforts have been conducted in our group to evaluate the potential of $Co^I Cbl$ to cleavage different C–X bonds. Cortés-Arriagada et al. [13] theoretically studied the particular case of the C–F bond dissociation [14, 15] in presence of $Co^I Cbl$ structures, where the results suggested that the coordination of dimethylbenzimidazole (DMB) nucleotide at the lower axial position to the central cobalt atom increases its nucleophilicity, thus the presence of the lower ligand reduces the activation energy barrier, and facilitates the C–F bond cleavage. The latter study was extended by Terán et al. [16] where the C–X bond with X= Cl, Br, or I, cleavage mediated by $Co^I Cbl$, and its related compound Cob[I]aloxim, $Co^I Cbx$ was theoretically described. The results showed that DMB-$Co^I Cbx$ can be envisaged as a reliable model to describe the C–X cleavage process occurring in presence of Vitamin B_{12} (i.e. $Co^I Cbl$). Moreover, it was showed that the polarization $C^{\delta+}$–$X^{\delta-}$ is the determining factor in the bond dissociation mechanism, in agreement with leaving group ability of these halides.

Besides of the above–mentioned, one of the major findings of the latter studies is that the Co^I present in both $Co^I Cbl$ and $Co^I Cbx$ acts as a highly polarizing ion capable of promoting the charge separation of polar bonds [16]. Thus, the effect of the metal ion can be envisaged as an "external electric field" acting on the different C–X bonds to promote their polarization. In this context, the control of chemical reactions by means of the application of oriented EEFs has been suggested as a novel catalytic method [17, 18, 19, 20, 21, 22, 23]. It is worth to mention that the mechanism of some enzymatic systems[22, 24] are based on the latter idea. Taking this into consideration Rincón and his collaborators considered an EEF as an agent capable to activate non-polar covalent bonds, considering for this effects the stretching of σ H–H and C–H bonds of molecular hydrogen and methane in the presence of both, a homogeneous EEF and a heterogeneous one, created by a source constituted by point charges [25]. Therefore, it is of paramount interest to gain insights on the activation of polar bonds under the experience of EEFs. In the present document, is studied the cleavage of C–X (X = Cl, Br, I) σ-polar bonds of methyl halides (CH_3Cl, CH_3Br, CH_3I) under the influence of EEFs is thoroughly studied from the Valence Bond perspective [26, 27, 28], as a continuation of our previous works.

2. Models, methods and computational details

Even if the details of the methodology has already been treated in previous works [29, 30, 25], a brief summary of the theory is presented in the following for clarity. According to Pauling [31], the electron pair bond can be described using a Valence Bond (VB) wave-function containing three contributions: one covalent structure, $\Psi(A \cdot\cdot B)$, and two ionic structures, $\Psi(A^- B^+)$ and $\Psi(A^+ B^-)$. Following this idea, the resonant states are described by the following wave–function:

$$\Psi_{VB}(A - B) = C_1\Psi(A \cdot \cdot B) + C_2\Psi(A^-B^+) + C_3\Psi(A^+B^-) \tag{1}$$

The relative values of the coefficients C_1, C_2, and C_3, allows the A–B bond to be classified as: pure covalent, pure ionic, or a mixed state. On the other hand, the A–B bond wave-function according to the GVB theory [32] can be described by a combination of two Slater determinants, where each one of the terms is constituted by a product of a set of double occupied orthogonal core orbitals, the bonding σ and the anti-bonding $\sigma*$ Natural Molecular Orbitals [32]

$$\Psi_{GVB}(A - B) = C_I det|\{core\}\,\sigma\overline{\sigma}| + C_{II} det|\{core\}\,\sigma^*\overline{\sigma^*}| \tag{2}$$

note that the bar over the spin-orbital distinguishes the spin coordinate. Moreover, the classical Valence Bond wave–function can be also approximated using the semidelocalized Coulson-Fisher type pair of orbitals, instead of Natural Molecular Orbitals:

$$\Psi_{GVB}(A - B) = N_{GVB}[det|\{core\}\,\phi_a\overline{\phi_b}| + det|\{core\}\,\phi_b\overline{\phi_a}|] \tag{3}$$

where N_{GVB} is the normalization constant:

$$N_{GVB} = \frac{1}{\sqrt{2(1 + S_{ab}^2)}}$$

and, where S_{ab} is the overlap integral between ϕ_a and ϕ_b that can be estimated as:

$$S_{ab} = \frac{\sigma_1 - \sigma_2}{\sigma_1 + \sigma_2}$$

Here, σ_1 and σ_2 are the occupation numbers of the molecular orbitals (ϕ_a and ϕ_b respectively), and they must obey the sum rule $\sigma_1^2 + \sigma_2^2 = 1$. In order to compute the coefficients of each contribution (C_1–C_3), the Coulson-Fisher pair orbitals must be expressed in terms of the "fully localized hybrid orbitals" a and a' belonging to the molecular part A (methyl fragment), and b and b' belonging in the molecular part B (halide fragment) [25]:

$$\phi_a = C_{aa}a + C_{ba}b'$$

$$\phi_b = C_{bb}b + C_{ab}a'$$

By including these expressions into Eq. 3, a wave–function in terms of covalent and ionic contributions can be obtained as:

$$\begin{aligned}
\Psi_{GVB}(A - B) \quad = \quad & N_{GVB}\Big(C_{aa}C_{bb}\left[det|(core)\,a\bar{b}| + det|(core)\,b\bar{a}|\right] + \\
& +C_{ab}C_{ba}\left[det|(core)\,a\bar{b'}| + det|(core)\,b'\bar{a'}|\right] + \\
& +C_{aa}C_{ab}\left[det|(core)\,a\bar{a'}| + det|(core)\,a'\bar{a}|\right] + \\
& +C_{bb}C_{ba}\left[det|(core)\,b\bar{b'}| + det|(core)\,b'\bar{b}|\right]\Big)
\end{aligned}$$

As a result, two terms associated to the covalent part are obtained: the first one depends on the orbitals a and b and has coefficient $C_1^1 = N_{GVB}C_{aa}C_{bb}$, while the second one depends on a' and b' and has coefficient $C_1^2 = N_{GVB}C_{ab}C_{ba}$. The ionic contributions to the wave–function are $\Psi(A^-B^+)$

and $\Psi(A^+B^-)$ and have coefficients $C_2=N_{GVB}C_{aa}C_{ab}$ and $C_3=N_{GVB}C_{bb}C_{ba}$, respectively. The coefficients of localized hybrid orbitals in the Coulson-Fisher pair orbitals (C_{aa}, C_{ba}, C_{ab}, C_{bb}) can be approximated as follows:

$$C_{aa} = \frac{\sigma_1^{1/4} \sum_{x=1}^{k} C_{x_1} + \sigma_2^{1/4} \sum_{x=1}^{k} C_{x_2}}{\sigma_1^{1/4} + \sigma_2^{1/4}} \tag{4}$$

$$C_{ab} = \frac{\sigma_1^{1/4} \sum_{x=1}^{k} C_{x_1} - \sigma_2^{1/4} \sum_{x=1}^{k} C_{x_2}}{\sigma_1^{1/4} + \sigma_2^{1/4}} \tag{5}$$

$$C_{ba} = \sqrt{1 - C_{aa}^2} \tag{6}$$

$$C_{bb} = \sqrt{1 - C_{ab}^2} \tag{7}$$

here, the summations of eq. 4 and 5 contain the values of the atomic orbital coefficients from the methyl fragment (x=first coefficient to k=the last coefficient), in the σ (C_{x1}) and $\sigma*$ (C_{x2}) molecular orbitals. The weight of each structure is calculated using the Coulson-Chirgwin formula [33]:

$$\omega_I = \sum_K C_I C_K S_{KI}$$

The latter methodology is used to analyze the bond cleavage C–X (X = Cl, Br, I) present in the simplest alkyl halides (i.e., CH_3Cl, CH_3Br, CH_3I), under the influence of two types of EEFs, namely: i) a homogeneous EEF aligned along the bond axis [34, 25, 35], with a strength varying from 0.02 to 0.05 a.u. and varied in 0.01 a.u. steps (1 a.u. = 5.14×10^{11} V/m) oriented in two fashions (i.e. positive and negative *see below*) ; and ii) a heterogeneous EEF created by placing point charges of different sign separated by 10 Å along the bond axis, considering charges between 1.2 e and 2.0 e increased by 0.2 e steps. In this case, the field is also oriented in both positive and negative fashions. The activation process is simulated by computing the energy of each system at different values of interatomic distance, varied from an initial point R_i to a final one R_f in ΔR = 0.1 Å steps. The equilibrium geometry at each point is computed with all internal coordinates free, but the C–X bond, while considering a C_{3v} symmetry.

In this study, the stretched bond is considered the active one, and in order to localize these orbitals, the bonding and anti-bonding orbitals are combined in the symmetry information used in the SCF initial guess. It has to be pointed out that for this kind of systems, the results computed by CASSCF(2,2) are completely equivalent to those obtained by a multiconfigurational method such as the GVB (N) (N=1: perfect-pairing strong orthogonalization) level of theory. The calculations were conducted by employing the GAUSSIAN 09 suit of programs [36], using in all cases the LanL2DZ basis set [32]. In asymmetric bonds, as the C–X one, the energy behavior depends on the field orientation. Here, the field aligned along the C-X bond, is referred to as positive if stabilizes the X^+CH3^- ionic structure of the methyl halide; whereas, is considered as negative if stabilizes the X^-CH3^+ one (Fig. [1]).
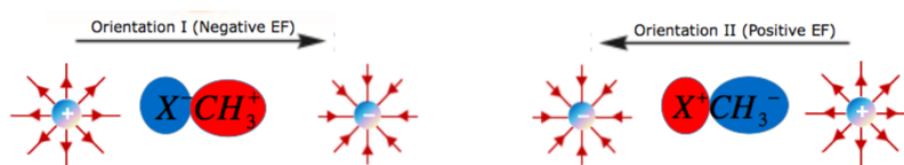
Figure 1: Schematic view of Electric Fields' orientation

3. Results and Discussion

3.1. Methyl Chloride

Fig. [2] presents the potential energy curves calculated by stretching the C–Cl bond from R_i = 1.20 Å to R_f = 4.0 Å under the effect of both the homogeneous ([2a]) and the heterogeneous ([2b]) EEFs. In Fig. [2a] and Fig. [2b] two behaviors are clearly distinguished at the EEF magnitude low and high limits: (i) the homolytic dissociation with a barrier when the EEF is absent, and (ii) an almost barrierless heterolytic dissociation at high values of the EEFs. The latter behavior is similar to the activation process of the H–H and the C–H bonds reported in a previous work [25] for molecular hydrogen and methane, respectively. However, in the present case a barrierless process was observed to occur at smaller strengths of the EEFs. In the case of the H–H and the C–H bonds, the barrierless activation mechanism was observed to occur at EEF values above 0.1 a.u.; whereas, in the case of the the C–Cl bond, the barrierless process occurs at values between 0.02 and 0.03 a.u. in the homogeneous EEF. Moreover, at values of the homogeneous EEF smaller than 0.03 a.u., the potential energy curves do not change qualitatively with respect to the non-EEF case. Fig. [2a] shows that, as the field strength grows, the value of the potential energy minimum lowers as well as the equilibrium bond length decreases slightly, from approximately 1.91 Å, when no field is applied, to 1.81 Å at 0.02 a.u. For the EEF strength of 0.03 a.u., the potential energy profile changes qualitatively, exhibiting an almost marginal maximum. On the other hand, for larger EEF values the curve minimum decreases to give rise a barrierless cleavage, that means, there is not noticeable minimum. For the heterogeneous EEFs (Fig. [2b]), the curves obtained placing charges larger than 1.2 e exhibit a decrease of the minimum along the interatomic distance. Furthermore, a defined equilibrium bond length is not observed, since the activation process is barrierless.
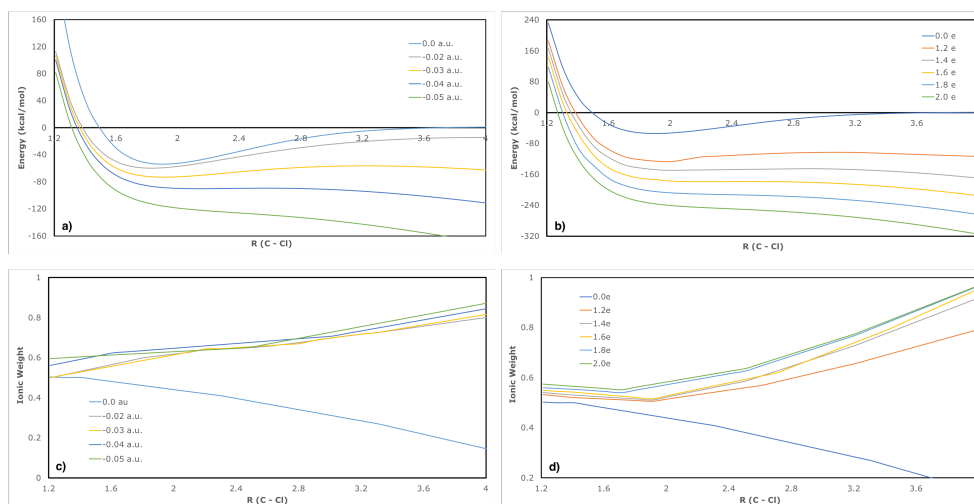
Figure 2: Methyl Chloride (CH_3Cl) Potential Energy Surfaces. a) Under Homogeneous Electric Field. b) Under a Electric Field created by dipole charges. Methyl Chloride (CH_3Cl) Ionic Weights. c) C–Cl stretching inside a negative homogeneous field. d) C–Cl stretching inside an electric field created by a dipole of charge.

Regarding the ionic weight, defined as the sum of C_2 and C_3 according to the eq. [2], (Fig. [2c] and Fig. [2d]), it is observed that, for any strength value of the two types of EEF, it tends to increase from 0.50 to 0.94 (on average for homogeneous and heterogeneous EEFs) along the C–Cl bond coordinate. The latter increment is not smooth as a discontinuity is observed at bond distances about 1.81 and 1.91 Å for the homogeneous and heterogeneous EEFs, respectively. Moreover, for the strongest values of the two EEFs (Fig. [2c] and Fig. [2d]), the discontinuity occurs before the equilibrium interatomic distance, and the ionic weight grows up to 0.99 which indicates an almost complete ionic behavior of the bonding fragments, being $Cl^-CH_3^+$ the dominating ionic structure, favored with the 99 % of the total value, implying that as one increment the distance form the equilibrium, the regime of dissociation changes from homolytic to heterolytic. The latter can be explained considering the ionization potential of the fragments, which is 9.84 eV [37] for methyl radical, whereas the value of the Cl atom is 12.97 eV [38]. By observing these differences, it is clear that the $Cl^-CH_3^+$ can be considered as the most stable structure at the dissociation limit. In contrast, for the non-EEF case, the ionic weight decreases almost constantly, suggesting a predominant character of the covalent fragment in the VB wave–function. The latter behavior shows that the presence of the EEFs stabilizes the ionic structure in a way that they become the predominant one at the stretching bond limit. Furthermore, the decrease potential energy minimum's depth implies a larger resonance energy between the covalent and the ionic structures (Fig. [2a]). Due to the increase of the resonance energy and the ionic weight as a function of the EEF magnitude, the interatomic equilibrium distance is also affected, being shorter at weak EEFs magnitudes (or larger at stronger EEFs) than the value associated to the non-EEF case. It is important to note that this observation is in favorable agreement with the results previously reported by Papanikolaou and Karafiloglou [17] whom affirmed that "in general a σ–bond with non-negligible polarity, if the electric field decreases (or increases) the difference of the weights of the two principal ionic structures, then the bond length decreases (or increases, respectively)". Using the assumption that in the presence of an EEF, the energy gap between the

covalent and the ionic states is reduced by a factor that involves the product of the EEF strength times the charges of the ionic species and the bond distance, and taking into consideration that the charge of the ionic species can be considered constant, the curve-crossing point (in Bohrs) is approximated by the value of the covalent-ionic gap (in Hartree) divided by that of the field strength (in a.u.). If the covalent-ionic gap is taken as the sum of the methyl ionization potential (IE) plus the chlorine electron affinity (EA), which is 13.44 eV, the approximated crossing-point would be below 8.64 Å for a 0.03 a.u. EEF.

3.2. Methyl Bromide and Methyl Iodine

The activation of the CH_3Br and CH_3I bonds (Fig.[3] and [4], respectively) is discussed using as point of reference the results obtained for the CH_3Cl system. For the studied bonds, the following similarities are to be noted: (i) in all cases, a transition between a barrier homolytic activation at low EEFs to a barrierless heterolytic dissociation at high EEFs is observed for both the homogeneous and the heterogeneous EEFs. For CH_3Br and CH_3I these transitions occurs at EEF values between 0.02 and 0.03 a.u., being common to the chlorine methyl system. For the heterogeneous case, the barrierless process is observed to occur for charges larger than ≥1.2 e as also observed in the CH_3Cl case. (ii) For low EEFs, there is a decrease in the binding energy and the internuclear distance (from 2.07 to 1.87 Å for CH_3Br and from 2.22 to 2.12 Å in CH_3I). (iii) The CH_3Br and CH_3I tend to be more ionic than the CH_3Cl even at short distances, being this in consistency with the much better ability of the these atoms as leaving groups. (iv) The ionic weights are very similar for all the field values. Solely at the non-EEF, a different behavior is observed.

In the CH_3Br molecule, for 0.03 a.u. EEF there is potential energy barrier of 14.25 kcal/mol at a internuclear distance of 3.37 Å. In contrast to the heterogeneous EEF, the bond activation barrier occurs with a charge of 1.2 e, with an amount of about 12.28 kcal/mol, appearing at same internuclear separation as in the homogeneous case. However, the minimum energy depths diminish approximately between 84 and 202 % on average, respectively, in comparison to the values obtained for the homogeneous EEF case. This set of results indicate that for heterogeneous EEF considered here, the bond activation is larger as the bond is stretched. When the homogeneous EEF is applied (Fig.[3]c), the trend is clear to attain rapidly to almost 1, once the equilibrium has been overtaken for all magnitudes experienced, having a predominancy of ionic composition along the stretching, even reaching very similar values among the curves. The heterogeneous EEF case, as in the methyl chlorine molecule, has a slightly diminish in trend at the shortest distances, but once the minimum is found, shifts up to values near 1 as can be noticed in Fig. [3d]. These results lead us to conclude that the C–Br bond activation is larger for non-homogeneous fields, which could be understood by recalling that the EEF strength increases from the bond center along the bond axis. In spite of these differences in the potential energy curves, inspection shows that for both kinds of electric fields, the ionic weight behavior are similar. According to the simple electrostatic model explained in the last section, the covalent-ionic gap for CH_3Br is 13.2 eV, and the predicted curve-crossing point would be 8.55 Å.
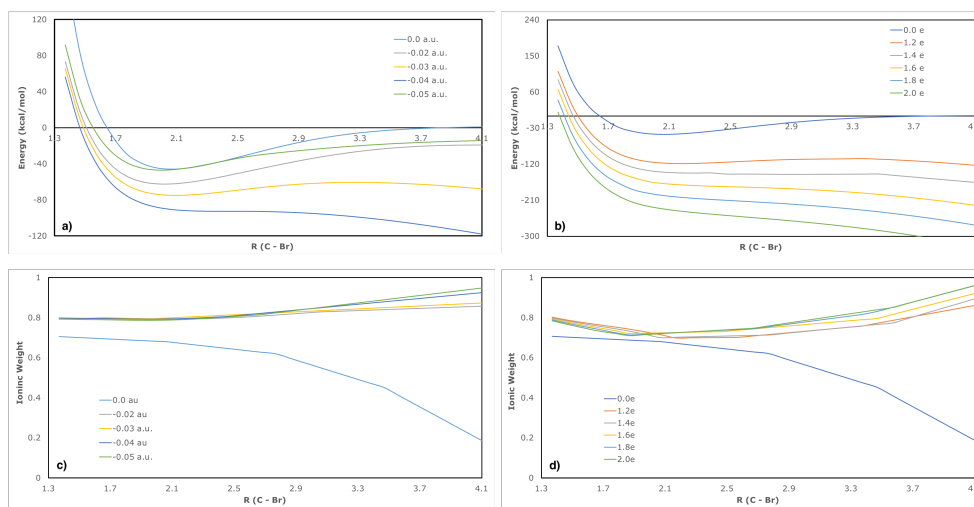
Figure 3: Methyl Bromide (CH_3Br) Potential Energy Surfaces. a) Under Homogeneous Electric Field. b) Under a Electric Field created by dipole charges. Methyl Bromide (CH_3Br) Ionic Weights. a) C–Br stretching inside a negative homogeneous field. b) C–Br stretching inside an electric field created by a dipole of charge.

Now, considering the Fig.[4a] when 0.03 a.u. are applied, the curve experiments a decrement of the bond activation barrier, regarding CH_3Br, until obtaining a value of 5.67 kcal/mol in this case, measured from the equilibrium geometry, to the internuclear distance at which the barrier maximum is located (3.02 Å); therefore this potential barrier has to be crossed. When the heterogeneous EEF is placed parallel to the bond axis (Fig.[4b]), the punctual charge 1.2 e, presents an energy barrier of 14.5 kcal/mol, being the greatest bond activation value among all the cases in the considered set of molecules, established between the minimum at 2.32 Å, and the maxima at 3.22 Å. The rest of charges ($\geq$ 1.4 e) the minimum energy positions turns virtually unattainable, the dissociation becomes barrierless, which indicates that for this case, the stabilization of the polar σ-bond ionic structure is larger. The wave–function is predominantly ionic in all the distances covered, except for the non-EEF case, which is essentially ionic at short distances, but as the interatomic length grow beyond the equilibrium geometry, becomes purely covalent at long-range separation exhibiting values around 0.85 up to almost 1.00 (Fig.[4c] and Fig.[4d]). The energy needed to form the ionic structure can be roughly estimated from the methyl radical IE plus the EA of the halogen, which yields 12.9 eV, and the estimated crossing point at 0.03 a.u. EEF would be 8.15 Å. Additionally, the methyl carbocation CH_3^+ is trigonal planar, while the methyl carbanion CH_3^- is pseudo-tetrahedral, and over dissociation, the carbanion inverts its structure [25]. These results allow us to understand why $I^-CH_3^+$ is the favored ionic structure upon electron transfer, correspondingly with the obtained numbers which show that the 99 % of the ionic value belongs to the $I^-CH_3^+$ fragment. These results are consistent with the statement exposed by Shaik et al.[18], who said that heteronuclear σ-bonds with small IE-EA values of the component fragments, or field magnitude is sufficiently strong , would elongate in an oriented EEF placed along the bond-axis making easier the dissociation to two ions; thus, the products will be ionic and highly stabilized by the field. Then, in Fig.[4] can be seen that as the EEF becomes higher, the weight of the $I^-CH_3^+$ structure grows and the covalent part gradually
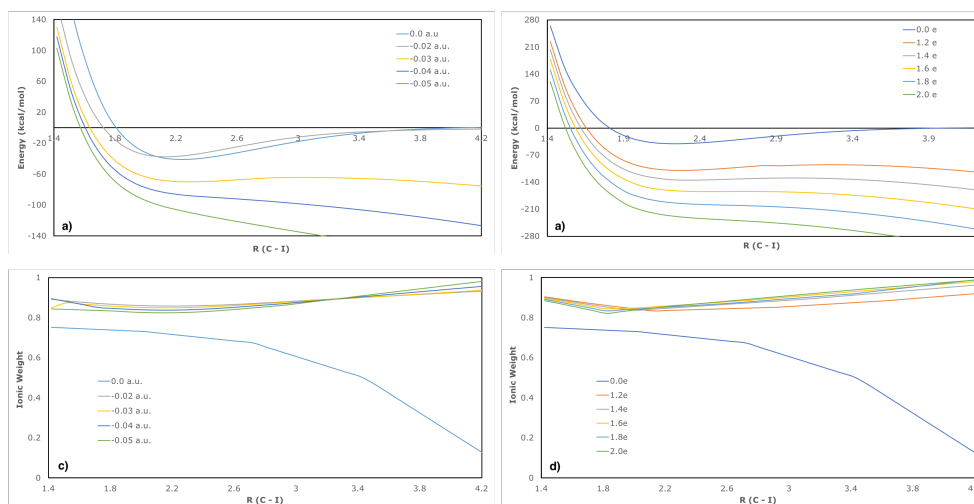
diminishes.

Figure 4: Methyl Iodine (CH_3I) Potential Energy Surfaces. a) Under Homogeneous Electric Field. b) Under a Electric Field created by dipole charges. Methyl Iodine (CH_3I) Ionic Weights. a) C–I stretching inside a negative homogeneous field. b) C–I stretching inside an electric field created by a dipole of charge.

4. Conclusions

In the present work we have studied the bond activation of the C–X present in methyl halides induced by electric fields oriented along the bond axis from a Valence Bond Theory perspective. Two kinds of static EEF have been applied, a homogeneous one as well as a heterogeneous one, the latter being generated by point charges of different sign placed along the bond axis, apart by 10.0 Å. For all cases, we observed two limiting behaviors: at non-EEF or very small EEFs a homolytic dissociation is observed with a barrier that slightly increase as the field grows, in contrast at large fields a heterolytic dissociation is obtained almost barrierless; this is the $X^-CH_3^+$ couples stronger with the EEF, and the C–X bonds become easier to activate, which indicates that the electron transfer occurs in such a way that the $X^-CH_3^+$ structure is favored over the $X^+CH_3^-$ one (X = Cl, Br, and I). In all cases, these results hold for both homogeneous and heterogeneous EEFs. Thus, this outcome may be considered as a general mechanism for bond cleavage under the experience of an electric field, as suggested by Rincón et al. [25]. The analysis of these results is complemented by carrying out the calculation of the ionic weights along the bond dissociation axis. Since the ionic bond structure stabilization, the EEF is larger than covalent structure, there is a decrease proportional to the EEF strength in the energy separation between the covalent and ionic structures potential curves. Thus, after some certain EEF magnitude is reached, the ionic structure potential energy crosses the covalent one. In all cases the coupling with the EEF is larger, and the crossing point occurs at very small EEF strengths, in contrast with the previous σ-bonds studies. We emphasize that this curve-crossing electron transfer mechanism may contribute to understand some of the reported results for covalent bond activation (polar or non polar) by means of external electric fields.

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