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Halogen-Abstraction Reactions from Chloromethane and Bromomethane Molecules by Alkaline-Earth Monocations

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ABSTRACT:

The reactions, in gas-phase, between alkali-earth monocations (Mg^+ , Ca^+ , Sr^+ , Ba^+) and CH_3X ($\text{X}=\text{Cl}$, Br) have been theoretically studied. The stationary points on the Potential Energy Surfaces were characterized at Density Functional Theory level on the framework of the mPW1K functional with the QZVPP Ahlrichs's basis sets. A complementary kinetics study has also been performed using conventional/variational microcanonical transition state theory. In the reactions of Mg^+ with either chloro- or bromomethane the transition structure lies in energy clearly above the reactants rendering thermal activation of CH_3Cl or CH_3Br extremely improbable. The remaining reactions are exothermic and barrierless processes, thus carbon-halogen bonds in chloro- or bromomethane can be activated by calcium, strontium or barium monocations to obtain the metal halogen cation and the methyl radical. The Mulliken population analysis for the stationary points of the Potential Energy Surfaces supports a "harpoon"-like mechanism for the halogen-atom abstraction processes. An analysis of the bonding situation for the stationary points on the Potential Energy Surface has also been performed in the framework of the Quantum Theory of Atoms in Molecules.

1. Introduction

The study of reactions in gas-phase provides the opportunity to research the intrinsic reaction mechanism avoiding disturbing effects arising from the presence of the solvent. In particular, the study of the interaction between metal cations and alkyl halides has attracted attention in the last two decades. In addition to their importance in different areas of chemistry such as organometallic chemistry,¹ biochemistry,² and atmospheric chemistry,³ these gas-phase reactions allow to analyze the possible selective metal-mediated activation of carbon-hydrogen and carbon-halide bonds.

In the last years, numerous experimental works have been reported including gas-phase reactions of metal cations with halogenated methanes. Development of ion sources and modern mass spectrometric techniques has led to a variety of thermodynamic, kinetic, and mechanistic information about gas-phase ion-molecule reactions. Mass spectrometers have proven to be powerful tools for studying the kinetics, mechanisms, and product distributions of gas phase bimolecular reactions. To study ion-molecule reactions, under highly controlled conditions, different mass-spectrometric techniques, such as selected-ion flow tubes (SIFT),^{4,5} guided ion beam (GIB),⁶ and ion cyclotron resonance (ICR)⁷ have been developed.

Alkyl halides are interesting substrates for reactions with metal cations, as they provide an opportunity for competition between C-H and C-X bond activation. In particular, methyl halides, CH_3X (X= F, Cl, Br), have substantial dipole moments ($\mu=1.8471 \text{ D}^8$ (CH_3F), 1.88 D^9 (CH_3Cl) and 1.81 D^9 (CH_3Br)) so are amenable to electrostatic deceleration and trapping and the different polarity of the C-X bond might contribute to interesting reactive features. In fact, the strength of the C-X bonds in halogenated compounds is directly related to their dissociation ability and the energetically accessible pathways available for their primary processes. Besides this intrinsic interest, chloromethane and bromomethane have an unquestionable relevance in atmospheric chemistry because they are involved in various catalytic atmospheric reaction cycles responsible for the depletion of the ozone layer.

The reactions between methyl fluoride and different monocations have been studied extensively in the past few years (see below), mainly because they provide insight into carbon-fluorine bond activation. Another interesting topic regarding reactions between monocations and halocarbons concerns the mechanism through which these reactions

proceed. Basically, two different mechanisms have been proposed: (a) single-electron transfer (SET), namely, “harpoon”-like mechanism, and (b) insertion-elimination mechanism.^{10,11} The main evidence supporting the “harpoon”-like mechanism is, in principle, the inverse correlation between the second ionization energy (SIE) of the metal and the efficiency of the reaction.

In an exhaustive study reported in 2006, Zhao *et al.*¹ carried out a systematic analysis of the gas-phase reactions of CH₃F with 46 different atomic cations, including 29 transition-metal and 17 main-group cations, using an inductively coupled plasma/selected-ion flow tube tandem mass spectrometer (ICP/SIFT). In these reactions, different channels were observed depending essentially on the atomic monocation considered.

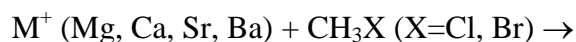
Some years ago, Harvey *et al.*¹² carried out both an experimental and theoretical study of the mechanism of the reaction of Ca⁺ with fluoromethane. From that study the authors pointed out that a “harpoon”-like mechanism seems to operate in this reaction. However a correlation between SIEs and reactivity was not found. The authors concluded that the mechanism through which metal-mediated activation of carbon-halide bonds takes place is not fully understood.

In order to confirm Harvey *et al.*¹²'s assertions, we performed a theoretical study of the reaction between methyl fluoride and calcium monocation,¹³ One of the main conclusions of our study was to emphasize the importance of the “outer” and “inner” transition states located on the Potential Energy Surface (PES) to control the kinetics of the process. Thus, the correlation, or lack of correlation, between reaction rate constants and SIEs of the metal might be rationalized in terms of a two transition state model.

This initial research was later complemented by including other alkaline-earth monocations¹⁴ in our study. Calculations suggested that these reactions seem to proceed through a “harpoon”-like mechanism, but further work, including other metal cations, was necessary to support the validity of the mechanistic findings reported. Recently, and, in order to get insight into selectivity and mechanism of carbon-fluorine bond activation of fluoromethane, we have extended our research to different first-row transition metal monocations (Sc⁺, Ti⁺, V⁺, Zn⁺),¹⁵ and main fourth-period monocations (Ga⁺, Ge⁺, As⁺, Se⁺).¹⁶ In the case of first-row transition metal monocations we found theoretical evidence for a “harpoon”-like mechanism for the fluorine-atom abstraction process that operates via electron transfer from the transition metal cation to the CH₃F

substrate in the transition structure. However, we did not find the expected relationship between the SIEs of the metal and the efficiency of the reaction. We just found such a correlation for the “inner” rate constant. Finally, regarding the main-fourth-period monocations study, we suggest that besides a “harpoon”-like mechanism, the possibility of an insertion-elimination process seems to play an important role in the cases where an oxidative addition was electronically plausible.

Although reactions between methyl fluoride and different monocations have been studied extensively, reactions including chloro- and bromomethane have received relatively little attention. Following this line of inquiry and in order to complete our previous studies, in this paper we present a theoretical analysis of the effect of the halide on reactivity of alkali-earth metal monocations with monosubstituted halogenated methanes:



Thermodynamical, kinetical and mechanistic implications of the results will be examined. In addition, we will characterize the molecular mechanism of these reactions from the redistribution of the electron density along the stationary points in the framework of the Mulliken population analysis (MPA) and making use of the Bader's Quantum theory of Atoms in Molecules (QTAIM).¹⁷

It is important to stress that the results reported in this work do provide a full mechanistic prediction on the studied processes in the sense that we fill the gap between quantum calculations and kinetics prediction (directly comparable with experimental data) by employing an appropriate theoretical kinetics model. In other words, the predicted rate constants should be, according to our previous work,¹³⁻¹⁶ in reasonable good agreement with the corresponding experimental values when available.

2. Computational methods

As in our previous kinetics studies,¹³⁻¹⁶ we have explored the PESs for the reactions between M^+ (Mg, Ca, Sr, Ba) and CH_3X (X=Cl, Br) at the Density Functional Theory (DFT) level. In particular, we have chosen the second-generation modified-Wang-1-parameter method for kinetics (mPW1K) functional¹⁸ which has previously proved its ability to describe PESs of reactions between analogous systems and gives accurate barrier heights.¹⁹ This functional is based on a modified version of the Perdew-Wang

gradient-corrected exchange functional by Adamo and Barone²⁰ and the Perdew-Wang gradient-corrected correlation functional. Regarding basis sets, we have employed Ahlrichs' quadruple- ζ quality (QZVPP) basis sets.²¹ For Sr and Ba, inner shell electrons are modeled by effective core potentials (ECPs) that reduce the number of basis functions and, more importantly, account for scalar relativistic effects.²¹

Geometric parameters have been computed using a tight convergence criteria and an ultrafine grid for numerical calculations. For each stationary point, we have calculated vibrational frequencies and zero-point energy (ZPE) corrections within the harmonic approximation at the mPW1K/QZVPP level of theory. The nature of the stationary points on the PESs has been determined by the number of negative eigenvalues of the analytical Hessian (zero in local minima and one in first-order saddle points). To explore the connections between transition-state structures and adjacent minima the intrinsic reaction coordinate (IRC)²² has been used.

ZPEs and thermodynamic functions were determined by using the statistical thermodynamic formulation of partition functions within the ideal gas, rigid rotor and harmonic oscillator models. A temperature of 298.15 K and a pressure of 1 atm have been assumed. Quantum and thermodynamics calculations were carried out with the GAUSSIAN 09 package of programs²³.

The molecular mechanism of the reactions studied in the present work, was characterized from the redistribution of the electron charge density, $\rho(r)$, along the reaction path connecting the stationary points, in the framework of the Bader's Quantum Theory of Atoms in Molecules (QTAIM)¹⁷. This model based on quantum mechanics and physical observables allows also a rigorous characterization of the nature of the bonding in the different species involved in the PESs of these reactions.

In the context of the QTAIM model two limiting types of interactions can be identified: shared interactions and closed-shells interactions²⁴. In a shared interaction, typical of covalent compounds, the nuclei are bound as a consequence of the lowering of the potential energy associated with the concentration of electronic charge shared between the nuclei; this is reflected in relatively large values of $\rho(r)$ at the critical point and negative values of the Laplacian, $\nabla^2\rho(r)$. The second limiting type of atomic interaction is that occurring between closed-shell systems, such as those found in ionic bond or van der Waals molecules for instance. In these interactions, $\rho(r)$ is relatively

low in value and the value of $\nabla^2\rho(r)$ is positive. Nevertheless, between these limiting types there is a whole spectrum of intermediate interactions. It should be noted that for elements with more than half-filled valence shells, a lack of the expected density accumulations along the bonds can be found.^{25,26} Typical examples are the F–F bond in the F_2 molecule and the O–O bond in H_2O_2 .

The total energy density $H(r)$ is another useful property to characterize the degree of covalence of a bond. It is defined as the sum of the potential energy density, $V(r)$ and the gradient kinetic energy density $G(r)$ at a critical point. If $H(r)$ is negative in value, the system is stabilized by the accumulation of electronic charge in the internuclear region, which is a typical characteristic of a covalent interaction.²⁷ When the value of $H(r)$ is positive, depletion of electronic density from the internuclear region takes place, a characteristic of ionic interactions and van der Waals systems.²⁷ We can also quantitatively analyze the covalent character of an interaction by taking into account the $|V(r)/G(r)$ ratio. The value of this relationship is greater than 2 in covalent interactions, smaller than 1 for non-covalent interactions and between 1 and 2 for partially covalent bonds.

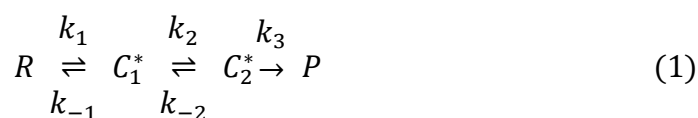
Total electron densities were obtained at mPW1K/QZVPP level. In all calculations, we assessed the accuracy of the integration over the atomic basin (Ω) by the magnitude of the corresponding Lagrangian function, $L(\Omega)$, ($-(1/4)$ times the atomic integral of the Laplacian of the electron density), which, in all cases, was lower than 10^{-4} a.u. The topological analysis of electron charge density was performed for each stationary point on the PESs using the Keith 's AIMAll package²⁸ including standard thresholds.

Bearing in mind the experimental data available on the CH_3F reactions, we have focused on the $M^+ + CH_3X$ primary products. Other channels involving the formation of HX , H_2 or MH products have not been considered in the present work.

The PESs for the reactions considered in this study could be represented by a three steps scheme. The first step corresponds to a barrierless interaction between the metal monocation (M^+) and the halogen atom of the halomethane molecule (CH_3X) giving a stable intermediate C_1 . In the second stage, intermediate C_1 converts to insertion complex C_2 via a first order saddle point transition structure, TS_2 . Finally, from intermediate C_2 , the formation of products (methyl radical and MX^+) takes place, through a barrierless process. A simplified scheme of the energy profile for the $M^+ + CH_3X$ reactions is shown in Figure 1.

For kinetics determinations, we have used a model proposed by Mozurkewich and Benson,²⁹ and based on the Rice-Ramsperger-Kassel-Marcus (RRKM) theory, for calculating rate constants of bimolecular reactions with negative activation energies and curved Arrhenius plots. These reactions can be mechanistically explained by assuming that an intermediate complex is formed and the rate-determining step involves a tight transition state with a rather small or negative potential energy relative to the reactants. The main assumption in Mozurkewich and Benson model²⁹ is that the pressure is low enough so the intermediates do not undergo any subsequent collision (collisionless regime with the total energy E and total angular momentum J conserved).

The general scheme for these reactions studied in the present work can be depicted by:



where R and P stand for reactants and products, respectively, and C_1^* , C_2^* represent “hot” intermediates.

All the molecular systems included in the PESs were treated as prolate symmetry top rotors since they exhibit rotational constants fulfilling $A_i > B_i \approx C_i$. The rotational energy levels were computed in terms of the J and K quantum numbers:

$$E_i(J, K) = J(J + 1)B_i + (A_i - B_i)K^2 \quad (2)$$

The J quantum number is conserved during the reaction, nevertheless the K -rotor is treated as active³⁰⁻³² when computing the sum of states ($W_i(E, J)$ functions).

Following Tschuikow-Roux and co-workers,³³ the equilibrium concentrations of the intermediates, $[C_i(E, J)]_{eq}$, are related to total equilibrium concentrations, $[C_i]_{eq}$, by,

$$[C_i(E, J)]_{eq} = \frac{N_{C_i}(E, J) \cdot [C_i]_{eq} \exp[-(E - V_{C_i})/RT]}{Q_{C_i}} \quad (3)$$

where Q_{C_i} is the partition function of intermediate C_i with the center of mass motion factors out and V_{C_i} is the lowest energy of C_i . The steady-state concentration is related to it by means of,²⁹

$$[C_i(E, J)] = \frac{[C_i(E, J)]_{eq}}{1 + \frac{W_{i+1}(E, J)}{W_i(E, J)}} \quad (4)$$

It is easy to show³³ that starting from the definition,

$$k_{global} = \frac{1}{[R]} \sum_{J=0}^{\infty} \int_{V_{max}}^{\infty} dE \cdot k_3(E, J) \cdot [C_2(E, J)] \quad (5)$$

equations 3 and 4 lead to,

$$k_{global} = \frac{\left(\frac{2\pi\mu k_B T}{h^2}\right)^{-3/2}}{hQ_R} \sum_{J=0}^{\infty} \int_{V_{max}}^{\infty} dE \cdot W_1(E, J) \frac{W_2(E, J) \cdot W_3(E, J)}{W_2(E, J) \cdot W_3(E, J) + W_1(E, J)[W_2(E, J) + W_3(E, J)]} e^{-E/RT} \quad (6)$$

Where Q_R represents the product of the partition functions of reactants in which the center of mass motion partition function $(2\pi\mu k_B T/h^2)^{3/2}V$ has been factored out; T is the absolute temperature; R , k_B , and h are gas, Boltzmann and Planck constants, and μ is the reduced mass. V_{max} is the largest value from among the energy barrier associated to transition structures TS_i ($i=1-3$). The $W_i(E, J)$, ($i=1-3$) functions, that includes reaction symmetry factors, are the sum of states at energy lower than E and angular momentum J corresponding to the different transition structures TS_i ($i=1-3$). We have approached the convolution of the K -rotor into vibrational sums of states as:

$$W_i(E, J) = \sum_{K=0}^J W_i(E, J, K) = \sum_{K=0}^J g_{JK} W_i(E'_i, 0, 0) \quad (7)$$

where g_{JK} are the degeneracy associated to the JK rotational levels:

$$g_{JK} = \begin{cases} 2J + 1 & \text{if } K = 0 \\ 2(2J + 1) & \text{if } K > 0 \end{cases} \quad (8)$$

and $W_i(E'_i, 0, 0)$ includes the sum of active states with $J = K = 0$ and energies ranging from the transition state barrier TS_i and E'_i ($E'_i = E - E_i(J, K)$).

Sums of states, $W_i(E, J)$, were computed by means of the Forst algorithm³⁰ using the appropriate frequencies and inertia moments for the transition states.

We have applied the E, J -resolved microcanonical variational transition state theory (μ VTST) in its vibrator formulation^{34,35} for the process of formation of initial intermediate, C_1 , and the exit channel, where no transition structures (TS_1 and TS_3 respectively) were located. In these regions, we have constructed distinguished- reaction coordinate paths (DCPs).^{36,37} The points on the DCP were obtained by fixing one

internal variable as an approximate reaction coordinate, and minimizing energy with respect to all the other internal coordinates. In the exit channel, the DCP was constructed as the minimum energy structures found at 30 values of the M-C distance. However in the case of the entrance channel, the reactants interactions have very long range effects and we needed around 100 values of X-M distance to define each DCP.

Following on from our previous studies,¹³⁻¹⁶ we have adopted a three transition state model (3TS model). We have explicitly considered an “inner” (tighter) transition state located in the neighborhood of the first-order saddle point and an “outer” (looser) transition state (TS1) controlling the entrance channel, and the dissociation transition state.

A straightforward application of the steady-state hypothesis to the reaction scheme (1) leads to the 3TS canonical global rate constant:

$$k_{global}^{3TS} = \frac{k_1 k_2 k_3}{k_2 k_3 + k_{-1}(k_3 + k_{-2})} \quad (9)$$

When $k_3 \gg k_{-2}$, this expression reduces to the 2TS canonical global rate constant:

$$k_{global}^{2TS} = \frac{k_1 k_2}{k_2 + k_{-1}} \quad (10)$$

All kinetic constants were computed in the low-pressure limit by using our own software.¹³

3. Results and discussion

In this section we will present the thermochemical and kinetics results corresponding to the reactions of the different alkaline-earth monocations with each halomethane molecule. Then, the results achieved for the different halomethanes will be compared with our previous results on the $M^+(M=Mg-Ba) + CH_3F$ ¹⁴ reactions. Finally we will characterize the mechanism for the reactions studied by means of the Mulliken population analysis (MPA) and by a topological analysis of the electron density.

A. Energy results

Figure 2 depicts the structures of the stationary points on the PESs of the $M^+ + CH_3X$ ($M=Mg, Ca, Sr, Ba$; $X=Cl, Br$) reactions. The corresponding mPW1K/QZVPP optimized geometrical parameters are given in Table 1.

For all studied reactions, the first step corresponds to the formation of a rather stable encounter complex C_1 . The interaction potential between reactants is attractive for the whole range of $M\cdots X$ distances and no transition structure can be expected in this region of the PES. In all cases, the C_1 intermediate has C_s symmetry and exhibits similar geometrical disposition. In this intermediate, the $M-X-C$ angle is clearly distorted from linearity, the values ranging from 113.7° for the Mg^+ to 119.8° for Ba^+ , in their reactions with CH_3Cl . In the case of the reactions with CH_3Br the range of the computed values is around 5° (from 108.3° in Mg^+ to 113.5° for Ba^+). Regarding the $C-X$ distance, we observe that upon interaction the $C-Cl$ distance enlarges from 0.538 \AA in the case of Mg^+ to 0.428 \AA for Ba^+ with respect to that found in the isolated CH_3Cl reactant. However, in the bromomethane reactions, the $C-Br$ distance is almost identical in the C_1 complexes and in isolated CH_3Br . This suggests that the presence of M^+ does not perturb the geometrical parameters of the CH_3Br moiety in CH_3BrM^+ significantly, thus indicating that an ion-dipole description of bonding is appropriate for this species. As expected the $X-M$ bond distance increases when moving downwards in the group, ranging from 2.509 \AA (Mg^+) to 3.101 \AA (Ba^+) for the reactions with CH_3Cl and from 2.666 \AA (Mg^+) to 3.256 \AA (Ba^+) when the reactions are initiated by CH_3Br .

Once the C_1 complex is formed, the reaction proceeds through transition structure TS2. In all cases, the TS2 structures have C_s symmetry, however for magnesium monocation, the geometrical parameters are clearly different than those found for the remaining monocations. The $M\cdots X\cdots C$ angle is only 70.8° for the reaction of Mg^+ and CH_3Cl and it increases up to 152.0° for the reaction of Ca^+ and CH_3Cl . Consequently, while the $M\cdots C$ distance is just 2.671 \AA in TS2 for the reaction between Mg^+ and CH_3Cl it notably increases up to 4.552 \AA for the reaction of Ca^+ and CH_3Cl . However, despite these different values, in all cases the $M\cdots C$ distances are quite large, and thus suggesting that the alkaline-earth metal will interact solely with the halogen. The topological analysis of the electron density reveals that there is no bond critical point between the alkaline-earth metal and the halogen (see Tables 6 and 7 *vide infra*). In all reactions, the $M\cdots X$ distance in TS2 is slightly longer than this bond length in the

corresponding isolated MF^+ product. Consequently, it should be expected a late transition state for these processes.

Through transition structure TS2, intermediate C_1 transforms into intermediate C_2 . This complex has C_s symmetry, except for the $\text{Mg}^+ + \text{CH}_3\text{X}$ reactions where the C_2 complex shows C_{3v} symmetry. As expected the geometrical parameters of intermediate complex C_2 are quite close to that found in isolated products, since in all cases the $\text{M}\cdots\text{C}$ distances are large (ranging from 2.3 Å to 3.1 Å).

Table 2 summarizes the relative (with respect to the separate reactants) adiabatic potential energies ($\Delta U_0 = \Delta U + \text{ZPE}$) and the Gibbs free energies of the intermediates, transition state structures and products of the reactions studied in the present work. In Figure 3 we show a simplified picture of the PESs for these reactions.

Regarding Table 2 results as a whole, we observe a similar energy profile for reactions of both halomethanes. Focusing on energetics of intermediate C_1 , as expected, the dissociation energies of M^+-XCH_3 adducts are quite low (ranging from around 14 kcal/mol in Sr^+ and Ba^+ reactions to 23 kcal/mol in Mg^+ reactions), thus suggesting weak electrostatic interactions between reactants. As expected the largest values were found for the reactions that include magnesium monocation and the lowest ones for the reactions of Sr^+ and Ba^+ . On the other hand, it should be noted that no significant differences were observed in the energetics of the C_1 encounter complexes when bromine substitutes to chlorine in the halomethane molecule. If we compare the energetics of C_1 and C_2 intermediates we observe that, except for the reactions initiated by magnesium monocation, intermediate C_2 is more stable than intermediate C_1 . The energy difference between the C_1 and C_2 isomers is around 27 kcal/mol for the reactions of Ba^+ . In the reactions of Ca^+ and Sr^+ these differences are around 18-19 kcal/mol whereas in the reactions of Mg^+ C_2 becomes less stable than C_1 . This tendency is closely related to the different halogen affinity showed by the alkaline-earth monocations. At mPW1K/QZVPP level, our predicted chlorine/bromine affinity for Mg^+ , Ca^+ , Sr^+ and Ba^+ are respectively: 70.51/62.05 kcal/mol, 101.67/90.48 kcal/mol, 100.49/89.57 and 111.64/100.66 kcal/mol.

Regarding energetics of the transition structure TS2, it can be seen that the transition structures for the insertion of M^+ into the carbon-halogen bond are below the entrance channel, except for Mg^+ . In this latter case, the transition structures are well above the

reactants ($\Delta U_0=11.77$ kcal/mol for the reaction with CH_3Cl and $\Delta U_0=9.53$ kcal/mol for the reaction with CH_3Br). Furthermore, in these reactions involving Mg^+ , the transition state connecting C_1 and C_2 is much higher in energy than reactants. Consequently, the thermal activation of both chloro- and bromomethane will be extremely improbable and the reactions should not progress beyond the C_1 adduct complex. It should be also noted that when bromine replaces chlorine in the reactions, the TS2 energy decreases for all reactions (from 2.24 kcal/mol in Mg^+ reactions to 4.19 kcal/mol in Ba^+ reactions). This behavior is related to the different polarity of the C-X bond in CH_3Cl and CH_3Br .

The processes of formation of products are clearly exothermic and exergonic, except for the reactions of Mg^+ . As expected the most exothermic (and exergonic) reactions are those initiated by barium monocation ($\Delta U_0=-34.68$ kcal/mol, for its reaction with CH_3Cl and $\Delta U_0=-34.43$ kcal/mol for the CH_3Br one). On the other hand, the reactions of Mg^+ with either CH_3Cl or CH_3Br are clearly endothermic and endergonic processes ($\Delta U_0=8.13$ kcal/mol, for the reaction with CH_3Cl and $\Delta U_0=5.80$ kcal/mol for CH_3Br). These results, together with the relatively high energetic barrier found, suggest that these reactions are not expected to proceed beyond the intermediate C_1 . Again, the exo- or endothermicity of the processes is directly related to the values of the chlorine/bromine affinity by the alkaline-earth monocations.

With regard to the relative adiabatic potential energies ($\Delta U_0 = \Delta U + ZPE$) and Gibbs free energies (ΔG) shown in Table 2, it can be seen that when the entropic factor is taken into account the products slightly stabilize (by around 1-2 kcal/mol) whereas intermediates and transition structures destabilize (by around 3-6 kcal/mol).

B. Kinetics results

Tables 3 and 4 summarize the calculated thermal rate constants, at a wide range of temperatures, for the reactions considered in the present work. The corresponding Arrhenius plots are shown in Figures 4 and 5. In both figure and tables we have collected the values of the global (2TS) rate constants and their main limiting components: k_{outer} , k_{inner} and k_{exit} in order to analyze the role played by the “outer”, “inner” and “exit” transition states in the global processes. As above mentioned, k_{inner} describes the limiting behavior of the global rate constant when the dominant bottleneck for the reaction is provided by the tighter “inner” transition state ($W_1(E,J)$, $W_3(E,J)$, $\gg W_2(E,J)$). When the looser “outer” transition state (in the entrance channel) controls the

rate constant we obtain $k_{\text{outer}}(W_2(E,J), W_3(E,J), \gg W_1(E,J))$. Finally k_{exit} describes the behavior of the rate constant when the exit dissociation channel controls the process.

As we have already noted, the reactions between magnesium monocation and either $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ are endothermic ($\Delta U_0=8.13/5.80$ kcal/mol) and have significant energetic barriers ($\Delta U_0=11.77/9.53$ kcal/mol). Thus the production of $\text{MgCl}^+/\text{MgBr}^+$ will be, *a priori*, likely precluded by this unfavorable thermochemistry. However in both reactions the endothermicity has a lower value than the energetic barrier, thus it should be expected that the exit channel does not play any significant role in the kinetics of these processes. In order to confirm this assertion, we have computed the “exit” component of the rate coefficients for these reactions. The Arrhenius plots for the reactions between Mg^+ and $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ (inset a in Figures 4/5) show the typical picture of those processes with positive activation barriers. As expected, both the “outer” and the “exit” components of the rate constant are very large compared to that found for the “inner” component, thus making the rate constant for the global process independent of both the entrance and exit channels. Note that in such conditions the 3TS global rate constant (equation (9)) reduces to the 2TS global rate constant (equation (10)). At 295 K our predicted rate coefficients for the reactions of Mg^+ with $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ have very low values, $k_{\text{global}}=4.89 \cdot 10^{-20}/4.89 \cdot 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, thus suggesting that the global processes cannot take place and the reactions will not proceed beyond the encounter complex CH_3XMg^+ .

If we compare the results obtained for the two halomethanes considered in our study, we observe that the reaction will be faster when it involves CH_3Br rather than CH_3Cl . This result is mainly attributable to the lower energy barrier observed in the reaction including CH_3Br 9.53 kcal/mol (11.77 kcal/mol for CH_3Cl).

Let us now briefly make a comparison of these results and those obtained for the reaction of Mg^+ with CH_3F .¹⁴ The main difference concerns the implication of the exit channel in the control of the global reaction. Whereas in the reaction of Mg^+ with CH_3F , the products were located slightly higher in energy than the TS2 transitions structure, the opposite occurs in the reactions of either $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$. Thus, the dissociation channel will play a much more important role in the reaction of CH_3F than in the reactions studied here.

In contrast to the reactions of magnesium monocation, the Arrhenius plots for the $\text{Ca}^+ + \text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ reactions (inset b in Figures 4/5) show the typical behavior found

in barrierless processes. The global and “inner” rate constants decrease as the temperature increases and the “outer” component is practically constant in the whole range of temperatures considered. As expected the global rate constant is mainly controlled by the “outer” bottleneck especially at low temperatures. As the temperature increases both the “inner” and “outer” components became similar in importance. Our computed rate coefficients at 295 K are $k_{\text{global}}=1.72 \cdot 10^{-9}/2.74 \cdot 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

In the reactions of calcium monocation the magnitude of the rate constants raises as we move from fluoromethane to bromomethane as a direct consequence of the lowering of the energy barrier of the TS2 transition structure.

From Figures 4 and 5 (insets c and d) we can infer that, for the reactions of Sr^+ and Ba^+ with $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$, the global constants and their limiting components change with temperature as for prototypical barrierless processes. Kinetics of these reactions is mainly controlled by the “outer” bottleneck in the whole range of temperatures considered in our study. In the reactions of Sr^+ and $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$, the rate coefficients as computed at 295 K were $k_{\text{global}}=1.13 \cdot 10^{-9}/1.14 \cdot 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The 295 K our kinetics constants for the reactions initiated by barium monocation were $k_{\text{global}}=1.54 \cdot 10^{-9}/8.87 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

We should point out that in the equivalent reactions between Sr^+ and Ba^+ with CH_3F ¹⁴ the dominant contribution to the global constant was the “inner” component, except at very high temperatures where the “outer” bottleneck became competitive. This different behavior is reasonable since the energy of the TS2 transition structure is clearly below the reactants when both chlorine and bromine substitutes fluorine in the halomethane and, for these reactions the “outer” bottleneck fully controls the global rate constants.

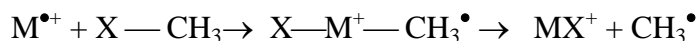
With regard to the efficiencies ($k_{\text{global}}/k_{\text{outer}}$), we observe that strontium and barium monocations show a much more active chemistry than magnesium monocation. The efficiencies are close to the unity in the reactions of Sr^+ and Ba^+ with CH_3Br whereas in the reaction of Mg^+ with CH_3Cl the efficiency, at 295 K, is as small as $3.82 \cdot 10^{-12}$. This behavior also agrees with our previous findings when studying the $\text{M}^+ + \text{CH}_3\text{F}$ reactions.¹⁴

C. Reaction Mechanisms

The reactions between metal monocations and halomethanes may evolve mainly through two different mechanisms^{38,39} namely single-electron transfer (SET) or “harpoon”-like mechanism:



and oxidative addition mechanism:



The results of our previous studies concerning the reactions of different monocations with fluoromethane¹³⁻¹⁶ suggested that the mechanism of the reaction could be determined by the structural disposition of the “inner” transition structure. In such a way, linear arrangements of the TS2 transition structure favor SET “harpoon”-like mechanisms whereas the oxidative addition mechanism could play an important role in reactions with ring arrangements of the TS2 transition state structures. It should be noted that even though an insertion-elimination mechanism always requires a nonlinear transition state structure the inverse is not true, and a nonlinear transition state structure does not always imply oxidative mechanism.

Within the “harpoon-like mechanism another interesting point concerns the existence or not of an inverse relation between efficiency of a reaction and Second Ionization Energy (SIE) of the metal atom. From our previous studies¹³⁻¹⁶ we concluded that in reactions controlled by the “outer” transition state, no correlation between efficiency and SIE should be expected, and thus the SIE-rate coefficient relation should only operate for the “inner” component of the rate constant and not for the global process. It was also inferred that the SIE values should correlate with the energy difference between the TS2 transition structure, and the C_1 intermediate only when the $C_1 \rightarrow TS2$ step is basically an electron transfer process. To confirm such conclusions in the present case, we have determined atomic charges and spin densities of the metal, halogen and CH_3 moieties for the stationary points on the PESs in the framework of the Mulliken population analysis (MPA). Table 5 summarizes these data.

Table 5 shows that the positive charge on the alkaline-earth metal increases in value when we advance from C_1 to C_2 on the PESs. Similarly, the negative net charge on the halogen increases when passing from C_1 to C_2 through TS2. Regarding the spin

densities data it can be noted that in the intermediate C_1 , the metal moiety practically retains the unpaired electron of the isolated alkaline-earth metal. This metal spin density dramatically diminishes when moving from C_1 to C_2 . In parallel, the spin density of the CH_3 unit raises the same amount. Consequently our results from the MPA suggest a SET “harpoon”-like mechanism that operates through an electron transfer from the metal, M , to the CH_3X unit in the transition state structure TS2.

The SIE values, for the alkaline-earth metals, computed at mPW1k/QZVPP level, are: 349 kcal/mol (Mg^+), 272 kcal/mol (Ca^+), 253 kcal/mol (Sr^+) and 227 kcal/mol (Ba^+). On the other hand, the energy difference between intermediate C_1 and the transition state structure TS2 in the reactions between M^+ (Mg , Ca , Sr , Ba) and CH_3Cl/CH_3Br are: 33.43/31.26 kcal/mol (Mg^+), 13.27/10.29 kcal/mol (Ca^+), 12.9/9.56 kcal/mol (Sr^+) and 8.02/3.96 kcal/mol (Ba^+) (In these data the first value refers to the CH_3Cl reactions whereas the second one corresponds to reactions with CH_3Br). Thus, there is a clear correlation between SIE and $C_1 \rightarrow TS2$ energy barriers, strongly suggesting that charge transfer will be the main force operating between the fragments CH_3X and M^+ when reactants approach each other. On the other hand, no correlation between global rate constants and SIEs is found, because the “outer” transition state controls the global process.

In order to characterize the nature of the bonding in the stationary points of the PES we have performed a topological analysis of the electron charge in the context of the Bader’s Quantum Theory of Atoms in Molecules (QTAIM)¹⁷. The main results of the QTAIM analysis for the C_1 , TS2, and C_2 structures, are collected in Tables 5 and 6. For comparative purposes, we have included in the tables the local topological properties of the electronic charge density distribution for the CH_3Cl and CH_3Br reactants. In addition, the corresponding contour maps of the Laplacian of the electron density, including molecular graphs of electron density, are shown in Figure 5.

Within the QTAIM formalism, critical points on the one-electron density are identified. In the C_1 , TS2 and C_2 structures only (3,-1) bond critical points (BCP) were found. These correspond to a minimum value of $\rho(r)$ along the line connecting the nuclei and a maximum along the interatomic surfaces.

For each C_1 , TS2 and C_2 structures we have characterized five BCPs, namely one BCP between the alkaline-earth atom and the halogen atom, three BCPs between the

carbon atom and the hydrogen atoms, and one BCP corresponding to the bond between the carbon atom and the halogen atom, in the C_1 and TS2 structures. In C_2 structures the last BCP corresponds to the bond between the carbon atom and the alkaline-earth atom. It should be stressed that in the transition structures of the reactions of magnesium monocation, no BCP was found between carbon and metal atoms, and consequently no ring critical point appears, even though, *a priori*, the TS2 structure resembles a three-membered ring.

The local topological properties of the carbon-hydrogen BCPs are indicative of shared interactions: large values of electron density, negative values of its Laplacian, $|V(r)|/G(r)$ ratios greater than 2 and negative values of the total energy densities $H(r)$. It should be noted that there are two different types of C-H BCPs, one of them corresponds to the interactions between carbon and nonplanar hydrogens, and the other one is related to the carbon-planar hydrogen interaction. However, both C-H interactions show almost identical values of the local topological properties of the electronic charge density distribution and in tables 6 and 7 we have not made distinctions between the different hydrogen atoms.

Regarding overall halogen-metal BCPs, it can be inferred that the properties of the electron densities are compatible with closed-shell interactions: all have low values of electron density, positive values of its Laplacian ($\nabla^2\rho(r)>0$), the $|V(r)|/G(r)$ ratios are close to 1, and the total energy density $H(r)$ is negative with small values.

As we advance in the reaction from C_1 to TS2, the halogen-metal distance shortens and the value of electron density and its Laplacian rise, suggesting a greater degree of covalence in the TS2 structure than in the encounter complex C_1 .

In the C_1 structures, the carbon-halogen BCPs show moderate values of the electronic charge density, $\rho(r)$, and negative values of the Laplacian, $\nabla^2\rho(r)$. Moreover, the $|V(r)|/G(r)$ ratios are greater than 2 and the total energy densities $H(r)$ have negative values. Consequently, the carbon-halogen interactions can be classified as polar covalent interactions. It is interesting to note that in the transition state structures the C-X BCPs present low values of $\rho(r)$ and positive values of its Laplacian in consonance with closed-shell interactions. However, the $|V(r)|/G(r)$ ratios and $H(r)$ values are indicative of a certain degree of covalence in this bond. These features can be visualized in Figure 5. In the C_1 intermediates, the carbon-halogen BCPs lie in a zone of

concentration of charge, that corresponds to the region where $\nabla^2\rho(r)<0$, thus indicating the presence of a shared interaction. In contrast, the C-X BCPs in TS2 are located in regions of depletion of electronic charge density ($\nabla^2\rho(r)>0$) or closed-shell interactions.

On the other hand, it can be also observed that as advancing from magnesium to barium in the group of the Periodic Table, the degree of covalence slightly increases in the C-X interactions. By comparing the Carbon-Halogen local topological properties of the electronic charge density distribution corresponding to C_1 structures and isolated CH_3X , we find a lesser degree of covalence in the C_1 intermediates than in CH_3X reactants.

In the C_2 structures the carbon-metal BCPs show low values of $\rho(r)$ and slightly positive values of its Laplacian. The $|V(r)/G(r)|$ ratios are between 1 and 2 and $H(r)$ is negative with a low value. Thus these interactions can be classified as closed shell interactions with a small degree of covalence.

4. Conclusions

In this paper, we have carried out a computational thermodynamic and kinetics study of the reactions between alkaline-earth metal monocations (Mg^+ , Ca^+ , Sr^+ and Ba^+) and halogen methanes (CH_3X ; $X=Cl, Br$). A search of the stationary points involved in these reactions has been performed, at the Density Functional Theory (DFT) level, using the mPW1K¹⁹ functional in conjunction with the QZVPP Ahlrichs's basis sets.²¹ In addition, kinetics calculations have been accomplished on the framework of the conventional/variational microcanonical transition state theory.¹³

The reactions of Mg^+ with either CH_3Cl or CH_3Br are clearly endothermic ($\Delta U_0=8.13/5.80$ kcal/mol) and have significant energetic barriers ($\Delta U_0=11.77/9.53$ kcal/mol). Thus for these reactions, under adequate experimental conditions, it should be expected the formation of a $[CH_3XMg]^+$ adduct complex.

The reactions involving Ca^+ , Sr^+ and Ba^+ are exothermic and barrierless processes. The most exothermic reactions are those initiated by barium monocation ($\Delta U_0=-34.68/-34.43$ kcal/mol).

Taken together the two halomethanes considered in our study, it can be concluded that no qualitative significant differences were observed in the energetics of the

stationary points on the PESs when bromine substitutes to chlorine in the halomethane molecule.

According to our kinetics results, in the reactions of magnesium monocation, the rate constant is controlled by the “inner” bottleneck as a direct consequence of the existence of important activation barriers in these reactions. The rate coefficients, at 295 K, for the reactions of Mg^+ with $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ are: $k_{\text{global}}=4.89 \cdot 10^{-20}/4.89 \cdot 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The global rate constant for the reactions of $\text{Ca}^+ + \text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ is mainly controlled by the “outer” component, especially at low temperatures. As the temperature increases both the “inner” and “outer” components make similar contributions to the global process. At 295, our computed rate coefficients for these reactions are respectively $k_{\text{global}}=1.72 \cdot 10^{-9}/2.74 \cdot 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The kinetics of the reactions between Sr^+/Ba^+ and $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ is controlled by the “outer” bottleneck in the whole range of temperatures considered in our study. In the reactions of Sr^+ and $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$, the rate coefficients evaluated at 295 K are $k_{\text{global}}=1.13 \cdot 10^{-9}/1.14 \cdot 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Whereas, for the reactions of Ba^+ and $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$, the rate constants at 295 K are $k_{\text{global}}=1.54 \cdot 10^{-9}/8.87 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. According to our previous experience,¹³⁻¹⁶ the above kinetics predictions should represent a reasonable approach to the corresponding experimental measurements, not yet available.

The Mulliken population analysis for the stationary points on the PESs supports a mechanistic picture in which an electron transfer from the alkaline-earth metal monocation to the CH_3X moiety in the TS2 transition structure takes place. Thus according to our results the reactions studied in this paper seem to proceed through a “harpoon”-like mechanism for the halogen-atom abstraction.

An analysis of the bonding situation for the stationary points on the PESs for these reactions has been performed in the framework of the QTAIM formalism. It is shown that when advancing in the reaction from C_1 to TS2 the halogen-metal bond, which has a closed-shell character in the C_1 structures, acquires a certain degree of covalency in the transition state structure TS2. Meanwhile, the carbon-halogen interaction, which shows a covalent character in the C_1 structures, acquires an important degree of closed-shell character in the TS2 structures.

Finally, our thermodynamic and kinetics study shows that carbon-halogen bonds in halomethanes can easily be activated by calcium, strontium and barium monocations forming the metal halogen cation.

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Table 1: Geometrical parameters (angstroms and degrees) for the stationary points involved in the reaction $M^+ + CH_3X$ ($M=Mg, Ca, Sr, Ba; X=Cl, Br$) at the MPW1K/QZVPP level of theory. For the reaction with CH_3Br , values are given in parentheses.

		CH_3X	C_1	TS2	C_2	CH_3	MX^+
[MgCH ₃ X] ⁺	C-H	1.084 (1.079)	1.078 (1.079)	1.078 (1.073)	1.082 (1.082)	1.073	-
	C-X	1.365 (1.921)	1.803 (1.953)	2.413 (2.527)	-	-	-
	C-Mg	-	-	2.671 (2.622)	2.356 (2.356)	-	-
	Mg-X	-	2.509 (2.666)	2.188 (2.341)	2.110 (2.256)	-	1.702 (2.240)
	X-C-H	109.1 (108.0)	-	108.2 (135.6)	-	-	-
	Mg-X-C	-	113.7 (108.3)	70.8 (65.1)	-	-	-
	X-Mg-C	-	-	58.55 (60.9)	180.0 (180.0)	-	-
	Mg-C-H	-	-	83.65 (135.6)	96.8 (96.9)	-	-
	H-C-Mg-X	-	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	-	-
[CaCH ₃ X] ⁺	C-H	1.084 (1.079)	1.078 (1.078)	1.074 (1.075)	1.081 (1.081)	1.073	-
	C-X	1.365 (1.921)	1.799 (1.950)	2.229 (2.344)	4.045 (4.209)	-	-
	C-Ca	-	-	4.552()	2.727 (2.725)	-	-
	Ca-X	-	2.763 (2.926)	2.462 (2.612)	2.333 (2.487)	-	2.311 (2.464)
	X-C-H	109.1 (108.0)	107.9 (107.6)	99.9 (100.4)	-	-	-
	Ca-X-C	-	117.0 (111.4)	152.0 (149.6)	40.4 (38.1)	-	-
	X-Ca-C	-	-	-	105.9 (107.6)	-	-
	Ca-C-H	-	-	-	84.4 (84.8)	-	-
	H-C-Ca-X	-	0.0 (0.0)	180.0 (60.30)	180.0 (0.0)	-	-
[SrCH ₃ X] ⁺	C-H	1.084 (1.079)	1.078 (1.078)	1.074 (1.075)	1.081 (1.081)	1.073	-
	C-X	1.365 (1.921)	1.795 (1.947)	2.221 (2.329)	4.006 (4.169)	-	-
	C-Sr	-	-	-	2.897 (2.895)	-	-
	Sr-X	-	2.961 (3.126)	2.630 (2.781)	2.476 (2.632)	-	2.456 (2.612)
	X-C-H	109.1 (108.0)	105.7 (105.1)	98.3 (98.9)	-	-	-
	Sr-X-C	-	119.6 (113.6)	160.7 (156.6)	46.0 (43.5)	-	-
	X-Sr-C	-	-	-	96.1 (97.8)	-	-
	Sr-C-H	-	-	-	83.2 (83.7)	-	-
	H-C-Sr-X	-	0.0 (0.0)	0.03 (-0.1)	0.0 (0.0)	-	-
[BaCH ₃ X] ⁺	C-H	1.084 (1.079)	1.079 (1.078)	1.076 (1.076)	1.079 (1.080)	1.073	-
	C-X	1.365 (1.921)	1.793 (1.945)	2.084 (2.184)	3.993 (4.144)	-	-
	C-Ba	-	-	-	3.096 (3.091)	-	-
	Ba-X	-	3.101 (3.256)	2.755 (2.911)	2.607 (2.769)	-	2.587 (2.748)
	X-C-H	109.1 (108.0)	105.8 (105.2)	101.0 (101.9)	-	-	-
	Ba-X-C	-	119.8 (113.5)	133.0 (130.9)	50.8 (48.2)	-	-
	X-Ba-C	-	-	-	96.7 (89.8)	-	-
	Ba-C-H	-	-	-	83.0 (83.3)	-	-
	H-C-Ba-X	-	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	-	-

Table 2. mPW1K relative (taking the reactants as a reference) adiabatic potential energies ($\Delta U_0 = \Delta U + \text{ZPE}$) and Gibbs free energies (ΔG) in kcal/mol as computed at 298 K and 1 atm for the different species involved in the reaction $M^+ + \text{CH}_3\text{X}$ ($M = \text{Mg, Ca, Sr, Ba}$, $X = \text{Cl, Br}$) in conjunction with Ahlrichs' QZVPP basis sets.

M	X	$M^+ + \text{CH}_3\text{X}$		C_1		TS2		C_2		$\text{MCl}^+ + \text{CH}_3$	
		ΔU_0	ΔG	ΔU_0	ΔG	ΔU_0	ΔG	ΔU_0	ΔG	ΔU_0	ΔG
Mg	Cl	0.0	0.0	-21.66	-16.69	11.77	17.23	-18.68	-13.59	8.13	6.59
	Br	0.0	0.0	-22.73	-17.74	9.53	15.20	-20.32	-15.17	5.80	4.28
Ca	Cl	0.0	0.0	-17.41	-12.69	-4.14	-0.02	-36.57	-32.69	-23.04	-24.64
	Br	0.0	0.0	-17.64	-12.91	-7.35	-8.55	-36.24	-32.24	-22.63	-24.21
Sr	Cl	0.0	0.0	-14.13	-9.67	-1.26	2.22	-33.02	-29.04	-21.85	-23.48
	Br	0.0	0.0	-14.26	-9.72	-4.73	-1.17	-33.01	-29.00	-21.72	-23.30
Ba	Cl	0.0	0.0	-14.16	-9.70	-6.11	-1.63	-41.66	-37.77	-33.01	-34.68
	Br	0.0	0.0	-14.29	-9.79	-10.30	-5.61	-41.61	-37.64	-32.80	-34.43

Table 3: Kinetic rate coefficients in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the $\text{M}^+ + \text{CH}_3\text{Cl}$ reactions (M=Mg, Ca, Sr, Ba)

T/K	$\text{Mg}^+ + \text{CH}_3\text{Cl}$				$\text{Ca}^+ + \text{CH}_3\text{Cl}$			$\text{Sr}^+ + \text{CH}_3\text{Cl}$			$\text{Ba}^+ + \text{CH}_3\text{Cl}$		
	k_{inner}	k_{outer}	k_{exit}	k_{global}	k_{inner}	k_{outer}	k_{global}	k_{inner}	k_{outer}	k_{global}	k_{inner}	k_{outer}	k_{global}
135	1.08E-30	1.50E-08	5.90E-22	1.08E-30	1.74E-07	1.45E-08	3.23E-09	7.55E-09	2.23E-09	1.50E-09	3.28E-07	2.61E-09	2.57E-09
175	2.92E-26	1.38E-08	6.52E-19	2.92E-26	1.15E-07	1.30E-08	2.51E-09	5.98E-09	1.92E-09	1.30E-09	2.09E-07	2.12E-09	2.09E-09
215	1.91E-23	1.32E-08	5.65E-17	1.91E-23	8.52E-08	1.23E-08	2.12E-09	5.27E-09	1.77E-09	1.20E-09	1.48E-07	1.86E-09	1.82E-09
255	1.74E-21	1.29E-08	1.26E-15	1.74E-21	6.77E-08	1.19E-08	1.89E-09	4.96E-09	1.67E-09	1.15E-09	1.12E-07	1.70E-09	1.66E-09
295	4.90E-20	1.28E-08	1.25E-14	4.89E-20	5.65E-08	1.18E-08	1.72E-09	4.87E-09	1.62E-09	1.13E-09	8.92E-08	1.59E-09	1.54E-09
335	6.46E-19	1.28E-08	7.30E-14	6.44E-19	4.89E-08	1.17E-08	1.60E-09	4.91E-09	1.58E-09	1.13E-09	7.31E-08	1.51E-09	1.46E-09
375	5.07E-18	1.29E-08	2.98E-13	5.05E-18	4.35E-08	1.18E-08	1.50E-09	5.03E-09	1.56E-09	1.13E-09	6.13E-08	1.45E-09	1.40E-09
415	2.74E-17	1.30E-08	9.38E-13	2.72E-17	3.94E-08	1.18E-08	1.41E-09	5.21E-09	1.54E-09	1.13E-09	5.24E-08	1.40E-09	1.34E-09
455	1.12E-16	1.31E-08	2.44E-12	1.12E-16	3.64E-08	1.19E-08	1.34E-09	5.43E-09	1.53E-09	1.14E-09	4.54E-08	1.36E-09	1.30E-09
495	3.74E-16	1.32E-08	5.45E-12	3.69E-16	3.40E-08	1.20E-08	1.28E-09	5.68E-09	1.53E-09	1.15E-09	3.98E-08	1.33E-09	1.26E-09
535	1.05E-15	1.33E-08	1.09E-11	1.04E-15	3.22E-08	1.21E-08	1.21E-09	5.95E-09	1.52E-09	1.17E-09	3.53E-08	1.30E-09	1.23E-09
575	2.60E-15	1.34E-08	1.98E-11	2.55E-15	3.07E-08	1.22E-08	1.16E-09	6.24E-09	1.52E-09	1.18E-09	3.15E-08	1.28E-09	1.21E-09
615	5.76E-15	1.35E-08	3.33E-11	5.62E-15	2.96E-08	1.23E-08	1.11E-09	6.55E-09	1.52E-09	1.19E-09	2.83E-08	1.26E-09	1.18E-09
655	1.17E-14	1.36E-08	5.28E-11	1.13E-14	2.88E-08	1.24E-08	1.06E-09	6.86E-09	1.52E-09	1.21E-09	2.57E-08	1.24E-09	1.16E-09
695	2.21E-14	1.37E-08	7.94E-11	2.12E-14	2.81E-08	1.25E-08	1.01E-09	7.18E-09	1.52E-09	1.22E-09	2.34E-08	1.22E-09	1.14E-09
735	3.91E-14	1.38E-08	1.14E-10	3.72E-14	2.76E-08	1.26E-08	9.65E-10	7.51E-09	1.52E-09	1.23E-09	2.15E-08	1.21E-09	1.13E-09
775	6.56E-14	1.39E-08	1.59E-10	6.19E-14	2.73E-08	1.27E-08	9.23E-10	7.84E-09	1.52E-09	1.24E-09	1.98E-08	1.20E-09	1.11E-09
815	1.05E-13	1.40E-08	2.13E-10	9.83E-14	2.71E-08	1.28E-08	8.84E-10	8.18E-09	1.52E-09	1.25E-09	1.84E-08	1.19E-09	1.10E-09
855	1.62E-13	1.40E-08	2.79E-10	1.50E-13	2.69E-08	1.29E-08	8.46E-10	8.51E-09	1.52E-09	1.27E-09	1.72E-08	1.19E-09	1.09E-09
895	2.42E-13	1.41E-08	3.56E-10	2.20E-13	2.69E-08	1.30E-08	8.11E-10	8.85E-09	1.53E-09	1.28E-09	1.61E-08	1.18E-09	1.08E-09
935	3.50E-13	1.42E-08	4.46E-10	3.14E-13	2.70E-08	1.31E-08	7.77E-10	9.18E-09	1.53E-09	1.29E-09	1.51E-08	1.18E-09	1.07E-09
975	4.93E-13	1.42E-08	5.47E-10	4.34E-13	2.71E-08	1.31E-08	7.45E-10	9.52E-09	1.53E-09	1.30E-09	1.42E-08	1.17E-09	1.06E-09
1015	6.77E-13	1.43E-08	6.59E-10	5.87E-13	2.72E-08	1.32E-08	7.14E-10	9.85E-09	1.54E-09	1.31E-09	1.35E-08	1.17E-09	1.06E-09
1055	9.10E-13	1.43E-08	7.84E-10	7.75E-13	2.75E-08	1.32E-08	6.85E-10	1.02E-08	1.54E-09	1.32E-09	1.28E-08	1.17E-09	1.05E-09
1095	1.20E-12	1.43E-08	9.18E-10	1.00E-12	2.77E-08	1.33E-08	6.57E-10	1.05E-08	1.54E-09	1.32E-09	1.22E-08	1.17E-09	1.05E-09
1135	1.56E-12	1.43E-08	1.06E-09	1.27E-12	2.80E-08	1.33E-08	6.31E-10	1.08E-08	1.54E-09	1.33E-09	1.17E-08	1.17E-09	1.04E-09

Table 4: Kinetic rate coefficients in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the $\text{M}^+ + \text{CH}_3\text{Br}$ reactions (M=Mg, Ca, Sr, Ba)

T/K	$\text{Mg}^+ + \text{CH}_3\text{Br}$				$\text{Ca}^+ + \text{CH}_3\text{Br}$			$\text{Sr}^+ + \text{CH}_3\text{Br}$			$\text{Ba}^+ + \text{CH}_3\text{Br}$		
	k_{inner}	k_{outer}	k_{exit}	k_{global}	k_{inner}	k_{outer}	k_{global}	k_{inner}	k_{outer}	k_{global}	k_{inner}	k_{outer}	k_{global}
135	3.27E-27	2.47E-08	2.49E-18	3.26E-27	2.09E-06	2.90E-08	5.96E-09	5.72E-07	1.74E-09	1.73E-09	2.33E-06	1.30E-09	1.30E-09
175	1.29E-23	2.32E-08	3.80E-16	1.29E-23	1.33E-06	2.54E-08	4.44E-09	3.70E-07	1.45E-09	1.44E-09	1.45E-06	1.09E-09	1.09E-09
215	2.54E-21	2.27E-08	9.51E-15	2.53E-21	9.37E-07	2.39E-08	3.61E-09	2.67E-07	1.29E-09	1.28E-09	9.96E-07	9.86E-10	9.84E-10
255	1.01E-19	2.27E-08	9.05E-14	1.01E-19	7.06E-07	2.32E-08	3.10E-09	2.05E-07	1.21E-09	1.19E-09	7.31E-07	9.26E-10	9.23E-10
295	1.55E-18	2.31E-08	4.82E-13	1.55E-18	5.56E-07	2.30E-08	2.74E-09	1.65E-07	1.15E-09	1.14E-09	5.59E-07	8.91E-10	8.87E-10
335	1.29E-17	2.35E-08	1.76E-12	1.28E-17	4.53E-07	2.31E-08	2.48E-09	1.37E-07	1.12E-09	1.11E-09	4.41E-07	8.69E-10	8.65E-10
375	7.02E-17	2.41E-08	4.95E-12	6.99E-17	3.77E-07	2.34E-08	2.26E-09	1.17E-07	1.10E-09	1.08E-09	3.55E-07	8.56E-10	8.50E-10
415	2.83E-16	2.47E-08	1.15E-11	2.81E-16	3.20E-07	2.37E-08	2.09E-09	1.02E-07	1.08E-09	1.07E-09	2.91E-07	8.48E-10	8.41E-10
455	9.08E-16	2.52E-08	2.33E-11	9.01E-16	2.75E-07	2.41E-08	1.93E-09	8.97E-08	1.08E-09	1.06E-09	2.41E-07	8.43E-10	8.35E-10
495	2.46E-15	2.58E-08	4.24E-11	2.43E-15	2.40E-07	2.45E-08	1.80E-09	8.00E-08	1.07E-09	1.05E-09	2.02E-07	8.40E-10	8.30E-10
535	5.81E-15	2.63E-08	7.07E-11	5.73E-15	2.12E-07	2.49E-08	1.68E-09	7.22E-08	1.07E-09	1.05E-09	1.71E-07	8.38E-10	8.27E-10
575	1.23E-14	2.69E-08	1.10E-10	1.21E-14	1.88E-07	2.53E-08	1.57E-09	6.58E-08	1.07E-09	1.05E-09	1.46E-07	8.37E-10	8.25E-10
615	2.39E-14	2.73E-08	1.62E-10	2.34E-14	1.69E-07	2.56E-08	1.47E-09	6.04E-08	1.07E-09	1.05E-09	1.26E-07	8.37E-10	8.23E-10
655	4.32E-14	2.78E-08	2.28E-10	4.21E-14	1.53E-07	2.60E-08	1.38E-09	5.59E-08	1.07E-09	1.04E-09	1.09E-07	8.37E-10	8.21E-10
695	7.35E-14	2.82E-08	3.09E-10	7.11E-14	1.40E-07	2.64E-08	1.29E-09	5.21E-08	1.07E-09	1.05E-09	9.45E-08	8.38E-10	8.20E-10
735	1.19E-13	2.85E-08	4.06E-10	1.14E-13	1.28E-07	2.67E-08	1.21E-09	4.89E-08	1.07E-09	1.05E-09	8.27E-08	8.39E-10	8.19E-10
775	1.83E-13	2.88E-08	5.18E-10	1.75E-13	1.19E-07	2.70E-08	1.14E-09	4.61E-08	1.08E-09	1.05E-09	7.28E-08	8.40E-10	8.17E-10
815	2.73E-13	2.91E-08	6.45E-10	2.58E-13	1.11E-07	2.73E-08	1.07E-09	4.37E-08	1.08E-09	1.05E-09	6.44E-08	8.40E-10	8.16E-10
855	3.93E-13	2.94E-08	7.88E-10	3.68E-13	1.04E-07	2.75E-08	1.01E-09	4.16E-08	1.08E-09	1.05E-09	5.72E-08	8.41E-10	8.14E-10
895	5.50E-13	2.96E-08	9.45E-10	5.09E-13	9.75E-08	2.77E-08	9.55E-10	3.97E-08	1.08E-09	1.05E-09	5.11E-08	8.41E-10	8.12E-10
935	7.51E-13	2.97E-08	1.12E-09	6.86E-13	9.22E-08	2.79E-08	9.01E-10	3.81E-08	1.08E-09	1.05E-09	4.59E-08	8.41E-10	8.10E-10
975	1.00E-12	2.99E-08	1.30E-09	9.04E-13	8.77E-08	2.81E-08	8.51E-10	3.67E-08	1.09E-09	1.05E-09	4.13E-08	8.40E-10	8.07E-10
1015	1.31E-12	3.00E-08	1.50E-09	1.17E-12	8.37E-08	2.82E-08	8.05E-10	3.54E-08	1.09E-09	1.05E-09	3.74E-08	8.39E-10	8.04E-10
1055	1.69E-12	3.00E-08	1.70E-09	1.48E-12	8.02E-08	2.84E-08	7.61E-10	3.43E-08	1.08E-09	1.05E-09	3.40E-08	8.38E-10	8.00E-10
1095	2.13E-12	3.01E-08	1.91E-09	1.84E-12	7.72E-08	2.85E-08	7.21E-10	3.33E-08	1.08E-09	1.05E-09	3.10E-08	8.35E-10	7.96E-10
1135	2.66E-12	3.01E-08	2.13E-09	2.25E-12	7.46E-08	2.85E-08	6.83E-10	3.24E-08	1.08E-09	1.04E-09	2.84E-08	8.32E-10	7.91E-10

Table 5. MPW1K/QZVPP alkaline earth metal, halogen (parentheses), and CH₃ [brackets] partial charges (au) and spin densities according to Mulliken Population Analysis (MPA).**M(Cl)[CH₃]**

	Partial Charge			
	Mg ⁺	Ca ⁺	Sr ⁺	Ba ⁺
C ₁	0.778(-0.094)[0.316]	0.825(-0.125)[0.300]	0.851(-0.140)[0.289]	0.861(-0.146)[0.285]
TS2	0.985(-0.296)[0.311]	1.143(-0.367)[0.224]	1.158(-0.370)[0.212]	1.179(-0.335)[0.156]
C ₂	1.197(-0.414)[0.217]	1.362(-0.500)[0.138]	1.399(-0.526)[0.127]	1.438(-0.551)[0.113]

^a MPA values for CH₃Cl are: -0.188 (Cl) and -0.137 (C).

	Spin Density			
	Mg ⁺	Ca ⁺	Sr ⁺	Ba ⁺
C ₁	0.972(0.023)[0.005]	0.997(-0.003)[0.006]	0.998(-0.005)[0.007]	1.003(-0.006)[0.003]
TS2	0.548(0.070)[0.382]	0.554(-0.069)[0.515]	0.561(-0.067)[0.506]	0.582(-0.014)[0.432]
C ₂	0.128(0.033)[0.839]	0.093(0.0006)[0.906]	0.083(-0.001)[0.918]	0.079(-0.001)[0.922]

M(Br)[CH₃]

	Partial Charge			
	Mg ⁺	Ca ⁺	Sr ⁺	Ba ⁺
C ₁	0.722(0.012)[0.266]	0.778(-0.030)[0.252]	0.806(-0.051)[0.245]	0.829(-0.068)[0.239]
TS2	0.888(-0.146)[0.258]	1.088(-0.277)[0.189]	1.099(-0.279)[0.180]	1.118(-0.241)[0.123]
C ₂	1.075(-0.289)[0.214]	1.257(-0.396)[0.139]	1.301(-0.430)[0.129]	1.349(-0.464)[0.115]

^a MPA values for CH₃Br are: -0.139 (Br) and -0.191 (C).

	Spin Density			
	Mg ⁺	Ca ⁺	Sr ⁺	Ba ⁺
C ₁	0.955(0.043)[0.002]	0.994(0.0002)[0.004]	0.994(-0.001)[0.007]	1.001(-0.006)[0.005]
TS2	0.544(0.114)[0.312]	0.545(-0.086)[0.541]	0.565(-0.091)[0.526]	0.602(-0.011)[0.409]
C ₂	0.116(0.051)[0.833]	0.092(0.003)[0.905]	0.000(0.083)[0.917]	0.081(-0.002)[0.921]

Table 6. Local Topological Properties (in au.) of the Electronic Charge Density Distribution Calculated at the Position of the Bond Critical Points for the different CH₃CIM species.^a

Species		Bond	$\rho(\mathbf{r})$	$\nabla^2 \rho(\mathbf{r})$	$ V(\mathbf{r}) /G(\mathbf{r})$	$H(\mathbf{r})$
CH ₃ CIMg	C ₁	C-Cl	0.170	-0.231	2.868	-0.124
		Cl-Mg	0.027	0.114	0.926	0.00196
		C-H	0.299	-1.174	10.299	-0.329
	TS	C-Cl	0.0502	0.0703	1.318	-0.008
		Cl-Mg	0.052	0.316	0.963	0.003
		C-H	0.304	-1.233	11.291	-0.341
	C ₂	C-Mg	0.0269	0.088	1.065	-0.002
		Cl-Mg	0.065	0.379	1.014	-0.001
		C-H	0.291	-1.118	9.571	-0.316
CH ₃ ClCa	C ₁	C-Cl	0.172	-0.239	2.902	-0.127
		Cl-Ca	0.024	0.099	0.872	0.003
		C-H	0.294	-1.172	10.166	-0.329
	TS	C-Cl	0.064	0.073	1.455	-0.015
		Cl-Ca	0.050	0.183	1.071	-0.004
		C-H	0.300	-1.181	10.040	-0.332
	C ₂	C-Ca	0.020	0.062	0.984	0.00025
		Ca-Cl	0.071	0.258	1.138	-0.010
		C-H	0.291	-1.100	8.953	-0.315
CH ₃ ClSr	C ₁	C-Cl	0.174	-0.247	2.927	-0.128
		Cl-Sr	0.021	0.081	0.851	0.0026
		C-H	0.299	-1.163	9.743	-0.328
	TS	C-Cl	0.0502	0.0703	1.539	-0.0189
		Cl-Sr	0.044	0.147	1.068	-0.003
		C-H	0.300	-1.178	9.850	-0.332
	C ₂	C-Sr	0.018	0.053	0.954	0.0006
		Cl-Sr	0.066	0.199	1.177	-0.011
		C-H	0.293	-1.114	8.814	-0.319
CH ₃ ClBa	C ₁	C-Cl	0.175	-0.251	2.944	-0.129
		Cl-Ba	0.022	0.081	0.859	0.0023
		C-H	0.299	-1.162	9.702	-0.328
	TS	C-Cl	0.098	0.023	1.866	-0.037
		Cl-Ba	0.046	0.150	1.074	-0.003
		C-H	0.298	-1.150	9.233	-0.327
	C ₂	C-Ba	0.017	0.047	0.945	0.0006
		Cl-Ba	0.067	0.169	1.238	-0.012
		C-H	0.293	-1.112	8.866	-0.320
CH ₃ Cl		C-Cl	0.192	-0.304	3.134	-0.143
		C-H	0.296	-1.127	8.913	-0.323

^a The electronic charge density [$\rho(\mathbf{r})$], the Laplacian [$\nabla^2 \rho(\mathbf{r})$], the relationship between the potential energy density $V(\mathbf{r})$ and the lagrangian form of kinetic energy density $G(\mathbf{r})$, and the total energy density, [$H(\mathbf{r})$].

Table 7. Local Topological Properties (in au.) of the Electronic Charge Density Distribution Calculated at the Position of the Bond Critical Points for the different CH3BrM species.^a

Species		Bond	$\rho(\mathbf{r})$	$\nabla^2 \rho(\mathbf{r})$	$ V(\mathbf{r}) /G(\mathbf{r})$	$H(\mathbf{r})$
CH3BrMg	C ₁	C-Br	0.146	-0.159	2.836	-0.087
		Br-Mg	0.026	0.085	1.011	-0.00024
		C-Hplano	0.299	-1.166	10.013	-0.328
	TS	C-Br	0.049	0.055	1.355	-0.008
		Br-Mg	0.045	0.231	0.984	0.0009
		C-Hplano	0.304	-1.220	10.809	-0.340
	C ₂	C-Mg	0.027	0.086	1.067	0.0015
		Mg-Br	0.057	0.275	1.036	-0.003
		C-H	0.292	-1.120	9.536	-0.317
CH3BrCa	C ₁	Br-C	0.147	-0.162	2.850	-0.088
		Br-Ca	0.024	0.0784	0.936	0.001
		C-Hplano	0.299	-1.164	9.900	-0.328
	TS	C-Br	0.065	0.052	1.544	-0.016
		Br-Ca	0.045	0.147	1.085	-0.003
		C-Hplano	0.299	-1.171	9.809	-0.330
	C ₂	Br-Ca	0.062	0.194	1.151	-0.009
		C-Ca	0.020	0.062	0.984	0.0002
		C-Hplano	0.291	-1.101	8.930	-0.315
CH3BrSr	C ₁	C-Br	0.148	-0.166	2.863	-0.090
		Br-Sr	0.020	0.062	0.904	0.0014
		C-H	0.299	-1.157	9.561	-0.327
	TS	C-Br	0.067	0.054	1.548	-0.0165
		Br-Sr	0.040	0.109	1.103	-0.003
		C-H	0.299	-1.162	9.527	-0.329
	C ₂	C-Sr	0.018	0.053	0.956	0.0006
		Br-Sr	0.056	0.149	1.179	-0.008
		C-H	0.293	-1.114	8.814	-0.319
CH3BrBa	C ₁	C-Br	0.149	-0.167	2.869	-0.090
		Br-Ba	0.021	0.063	0.920	0.0011
		C-H	0.299	-1.156	9.524	-0.327
	TS	C-Br	0.093	0.015	1.897	-0.033
		Br-Ba	0.040	0.117	1.087	-0.003
		C-H	0.296	-1.135	8.922	-0.325
	C ₂	C-Ba	0.017	0.048	0.947	0.0005
		Br-Ba	0.057	0.132	1.221	-0.008
		C-H	0.293	-1.111	8.870	-0.319
CH3Br		C-Br	0.158	-0.192	2.932	-0.0992
		C-H	0.296	-1.125	8.812	-0.322

^a The electronic charge density [$\rho(\mathbf{r})$], the Laplacian [$\nabla^2 \rho(\mathbf{r})$], the relationship between the potential energy density $V(\mathbf{r})$ and the lagrangian form of kinetic energy density $G(\mathbf{r})$, and the total energy density, [$H(\mathbf{r})$].

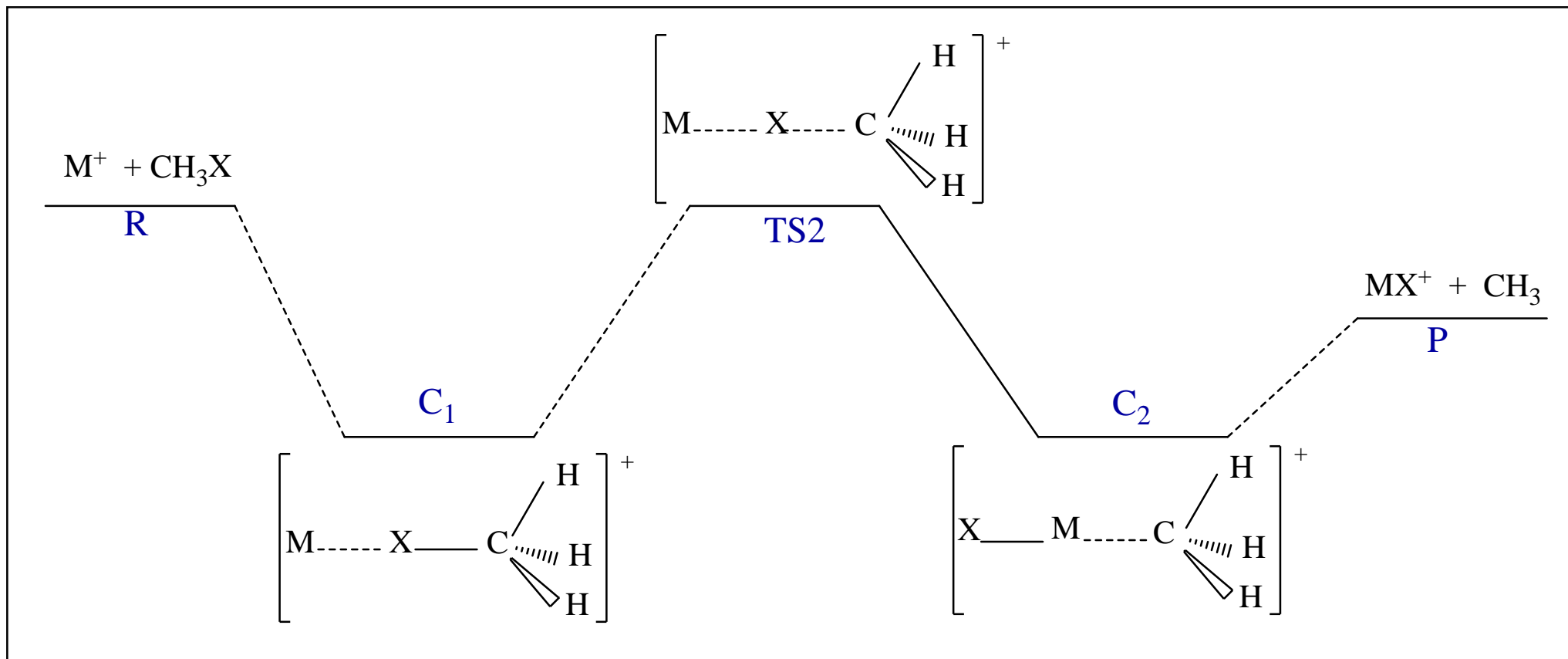


Figure 1

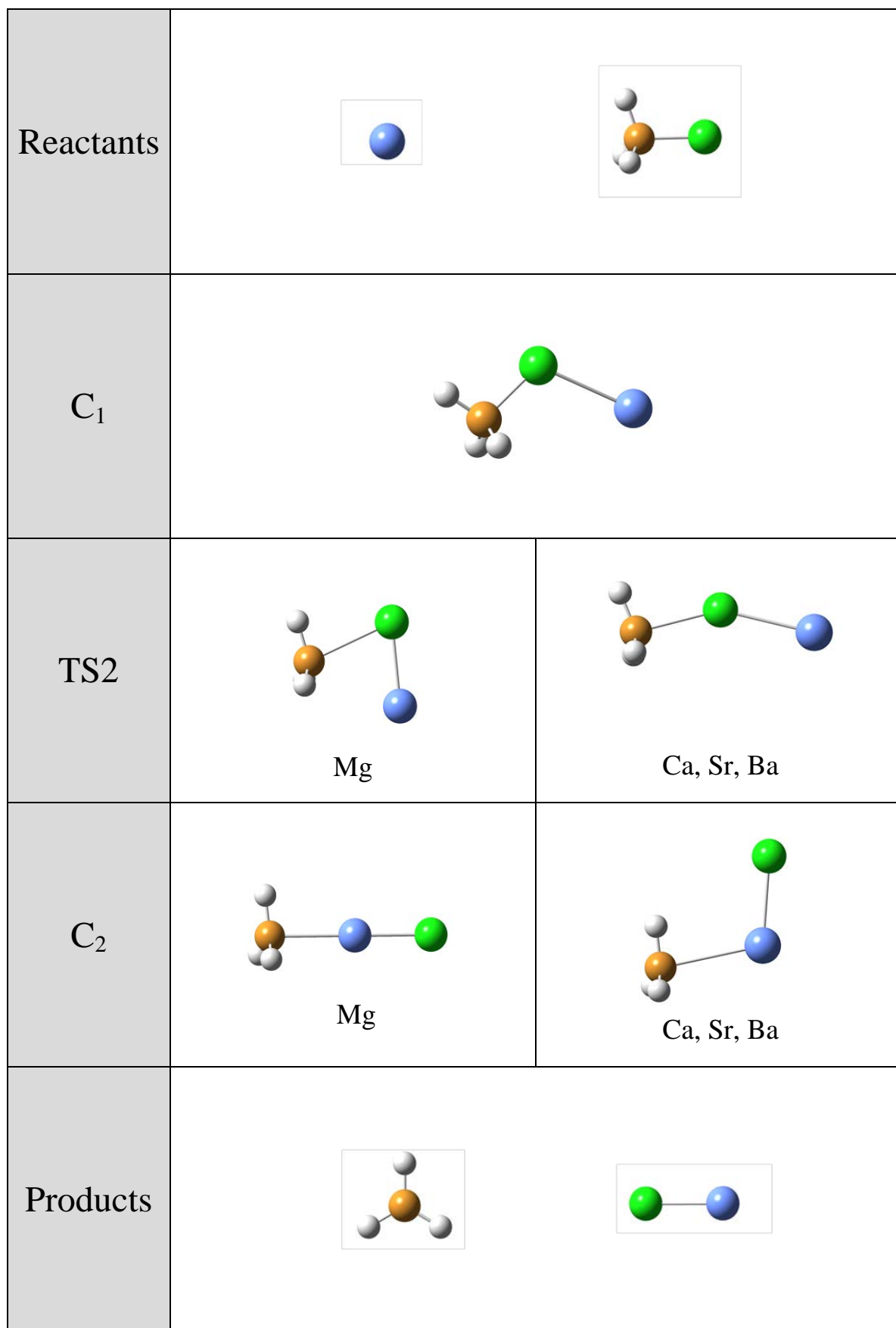


Figure 2

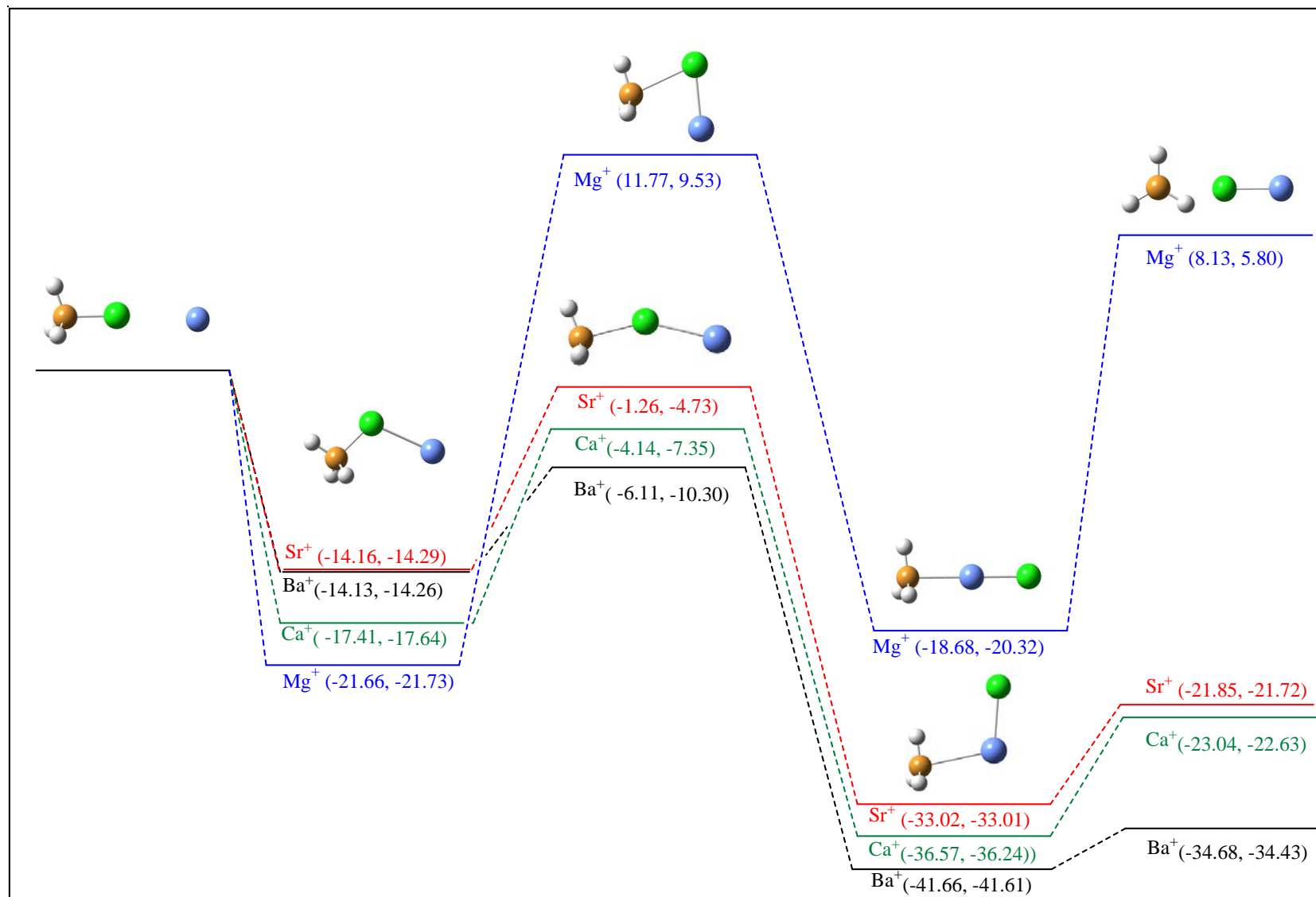


Figure 3

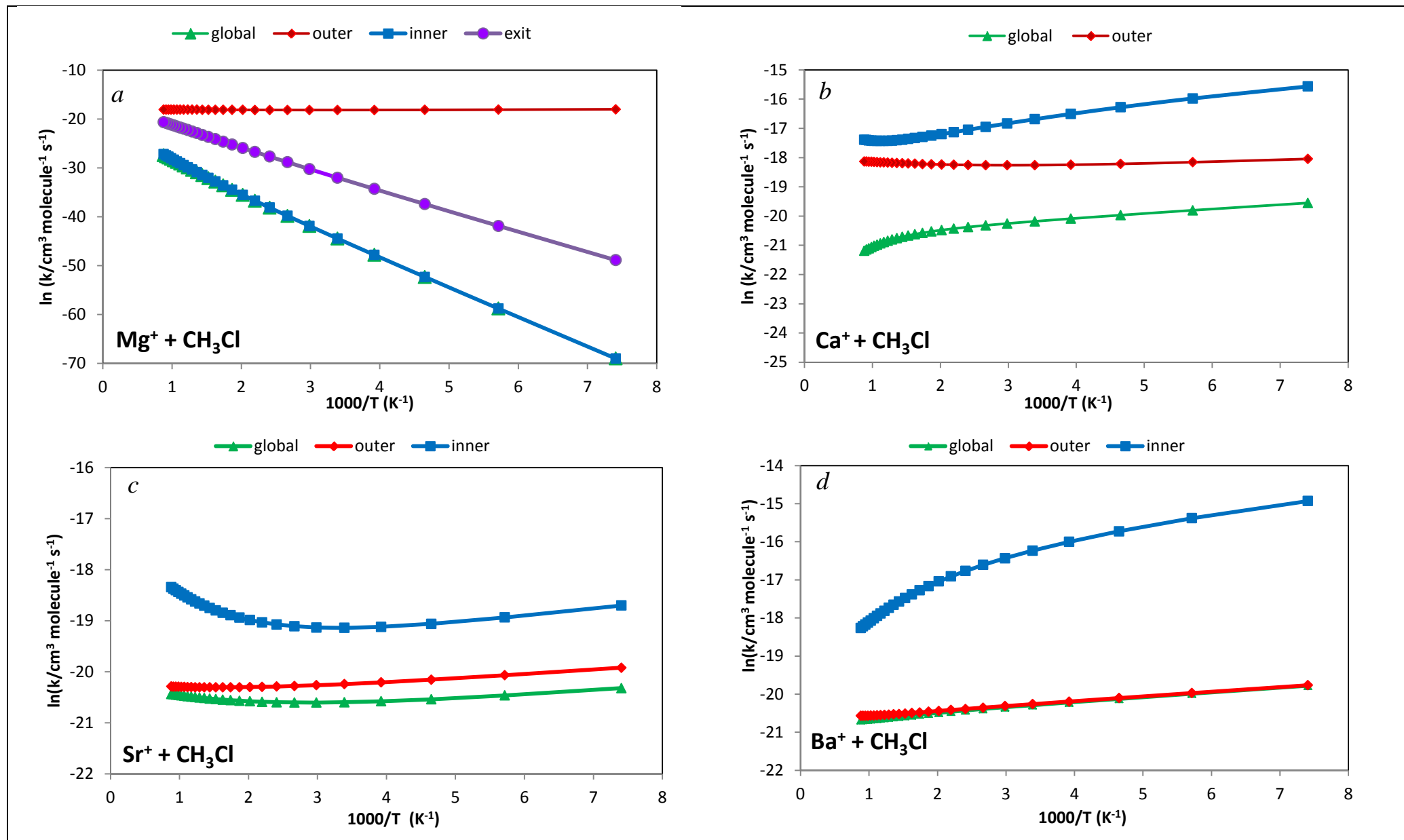


Figure 4

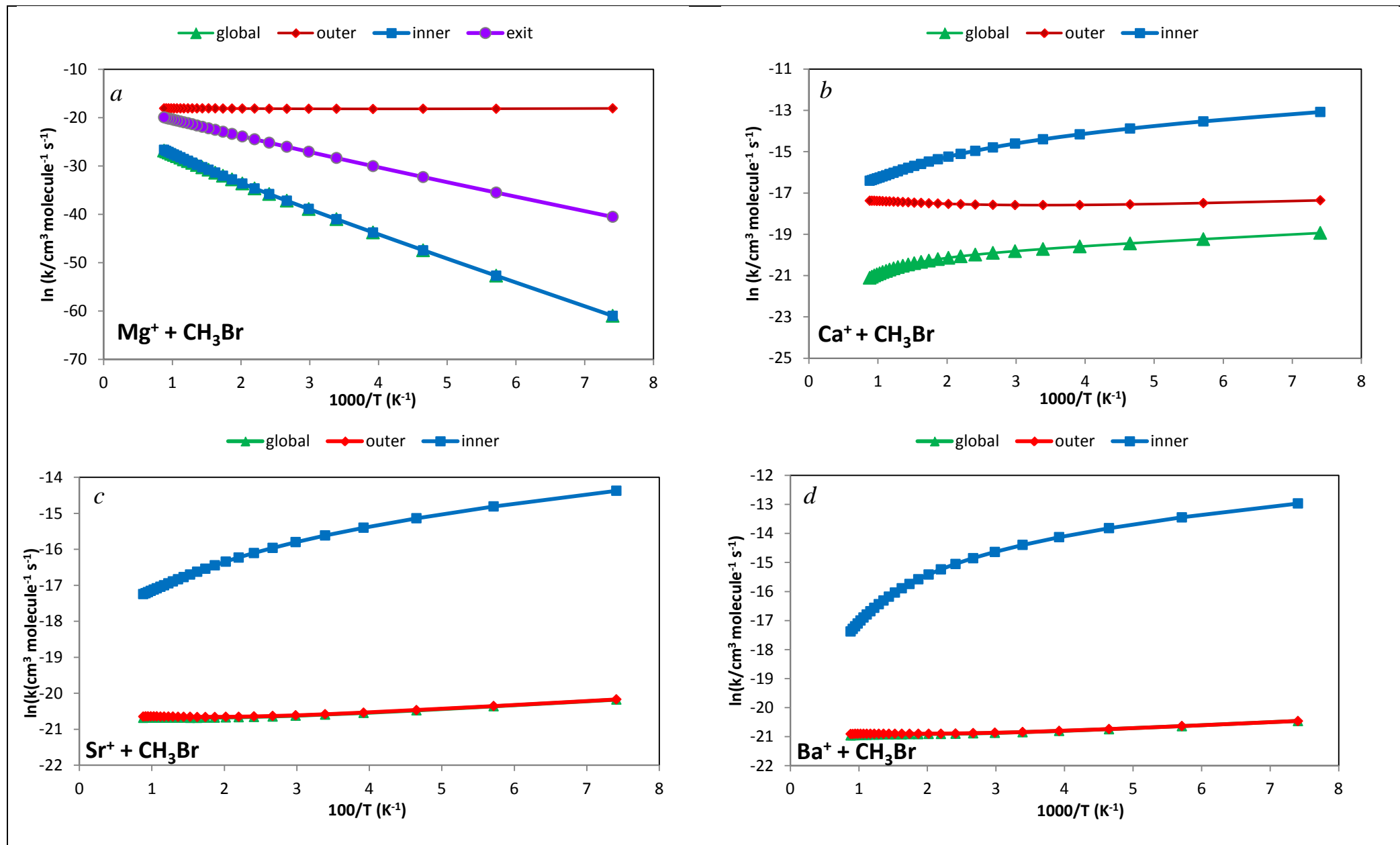


Figure 5

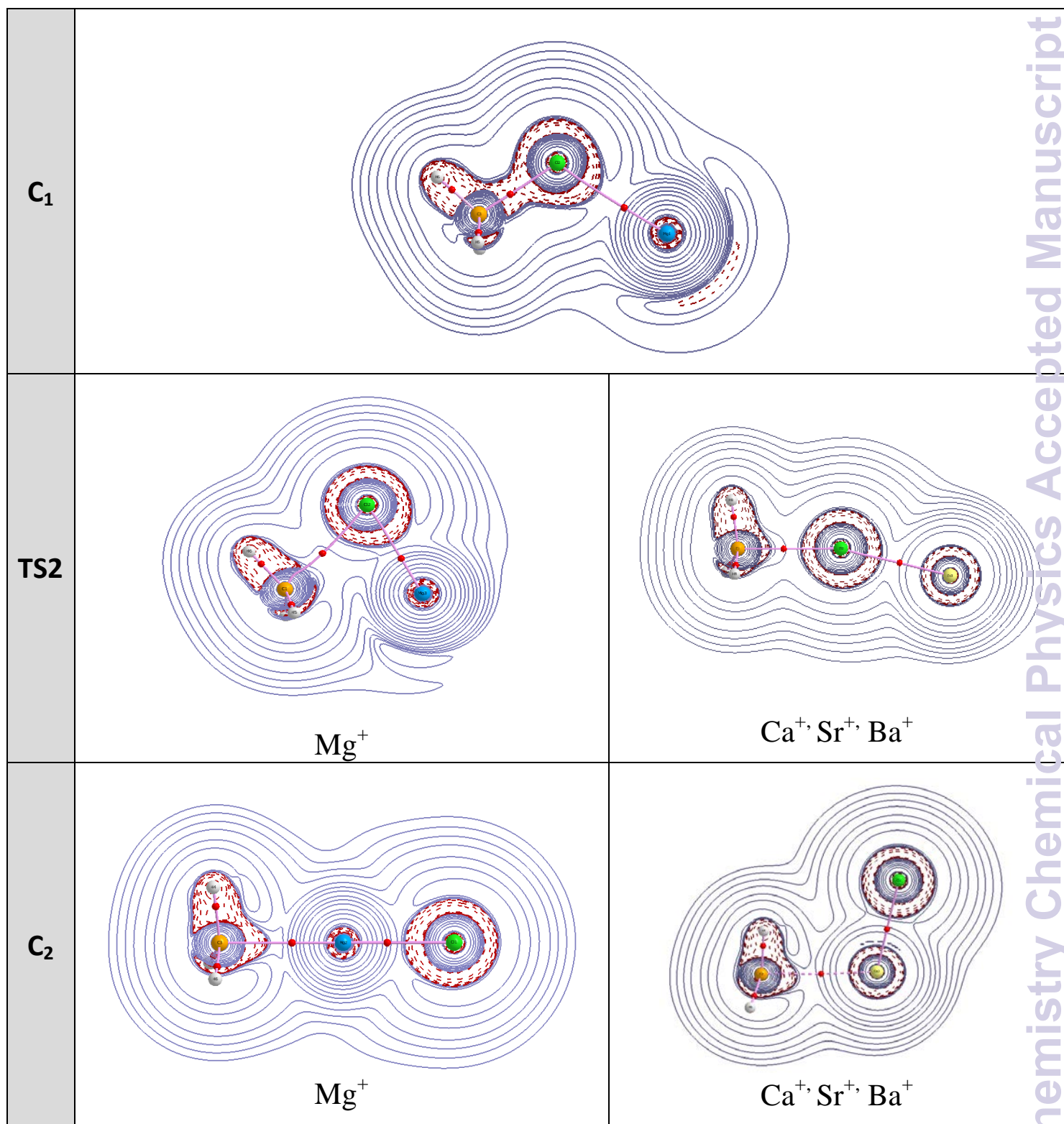


Figure 6

Figure Captions

Figure 1. General representation of the energetic profile of the $M^+ + CH_3X$ reactions ($M=Mg, Ca, Sr, Ba$; $X=Cl, Br$).

Figure 2. Structures of the reactants (M^+ and CH_3X), intermediates (C_1 and C_2), transition structures (TS_2) and products (MX^+ and CH_3) of the $M^+ + CH_3X$ reactions ($M=Mg, Ca, Sr, Ba$; $X=Cl, Br$).

Figure 3. Potential Energy Surface for the $M^+ + CH_3X$ reactions ($M=Mg, Ca, Sr, Ba$; $X=Cl, Br$). Values, in kcal/mol, correspond to the relative adiabatic potential energies (taking reactants as a reference) obtained at the mPW1K/QZVPP level including ZPE corrections. First value refers to the reaction with CH_3Cl and the second one to the reactions with CH_3Br one.

Figure 4. Arrhenius plots for the rate constants of the $M^+ + CH_3Cl$ reactions ($M=Mg, Ca, Sr, Ba$); k_{global} (green), k_{inner} (blue), k_{outer} (red), and k_{exit} (gray).

Figure 5. Arrhenius plots for the rate constants of the $M^+ + CH_3Br$ reactions ($M=Mg, Ca, Sr, Ba$); k_{global} (green), k_{inner} (blue), k_{outer} (red), and k_{exit} (gray).

Figure 6. Contour maps of the Laplacian distribution of the electron density for the different critical points. Red dashed lines indicate regions of electronic charge concentration ($\nabla^2\rho(r) < 0$), and blue continuous lines denote regions of electronic charge depletion ($\nabla^2\rho(r) > 0$). Also molecular graphs of electron density are shown, small red spheres represent bond critical points (BCPs)

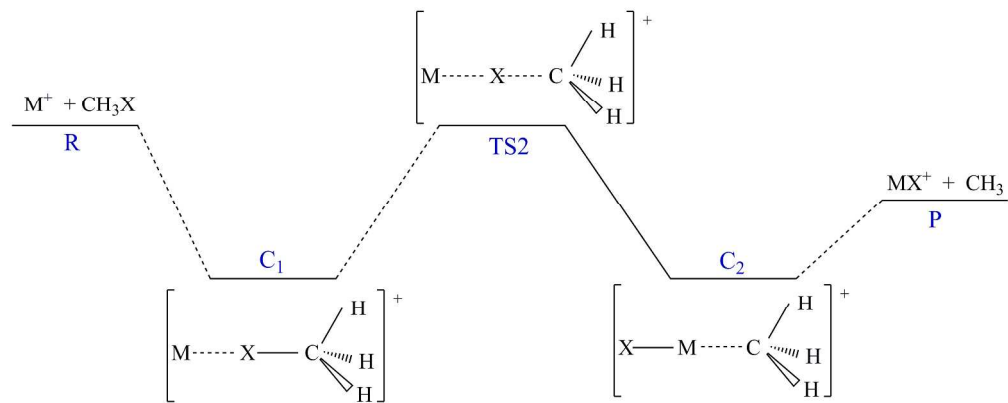


Figure 1. General representation of the energetic profile of the $M^+ + CH_3X$ reactions ($M=Mg, Ca, Sr, Ba$; $X=Cl, Br$).
259x106mm (300 x 300 DPI)

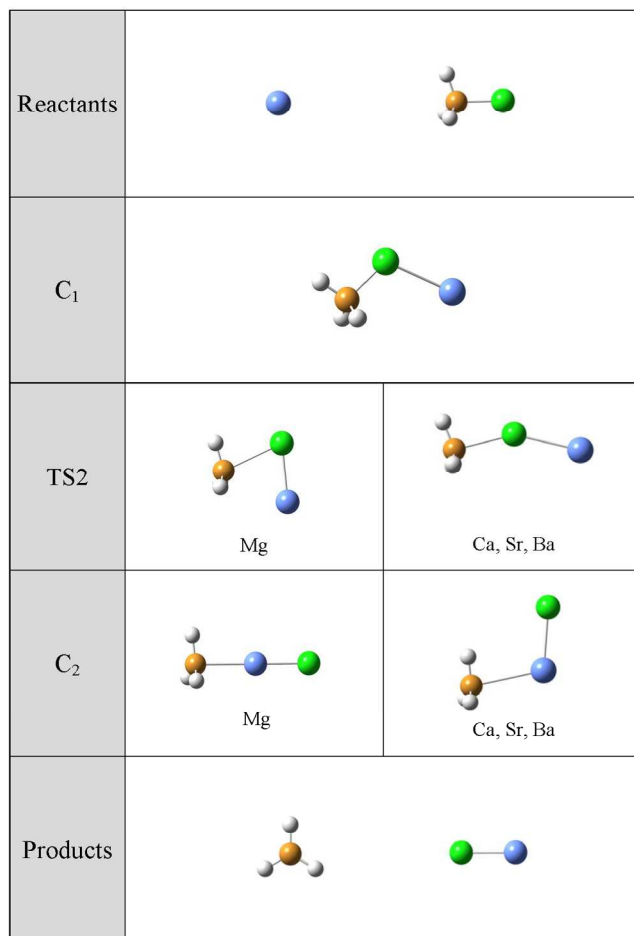


Figure 2

Figure 2. Structures of the reactants (M^+ and CH_3X), intermediates (C_1 and C_2), transition structures (TS2) and products (MX^+ and CH_3) of the $M^+ + CH_3X$ reactions ($M=Mg, Ca, Sr, Ba$; $X=Cl, Br$).
210x297mm (200 x 200 DPI)

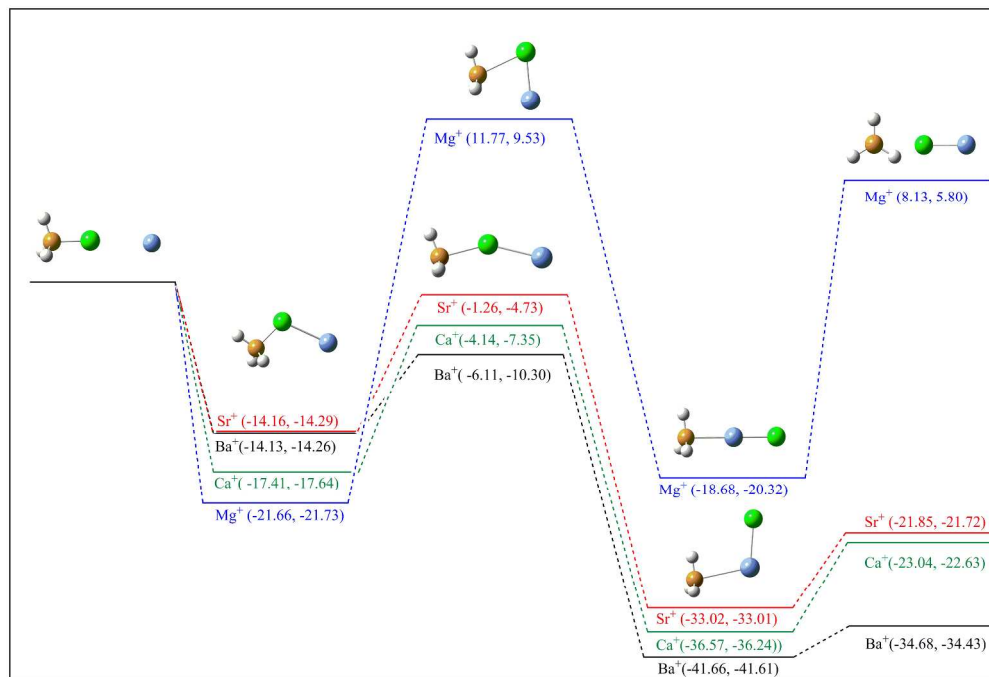


Figure 3. Potential Energy Surface for the $M^+ + CH_3X$ reactions ($M=Mg, Ca, Sr, Ba; X=Cl, Br$). Values, in kcal/mol, correspond to the relative adiabatic potential energies (taking reactants as a reference) obtained at the mPW1K/QZVPP level including ZPE corrections. First value refers to the reactions with CH_3Cl and the second one to the reactions with CH_3Br one.
275x187mm (300 x 300 DPI)

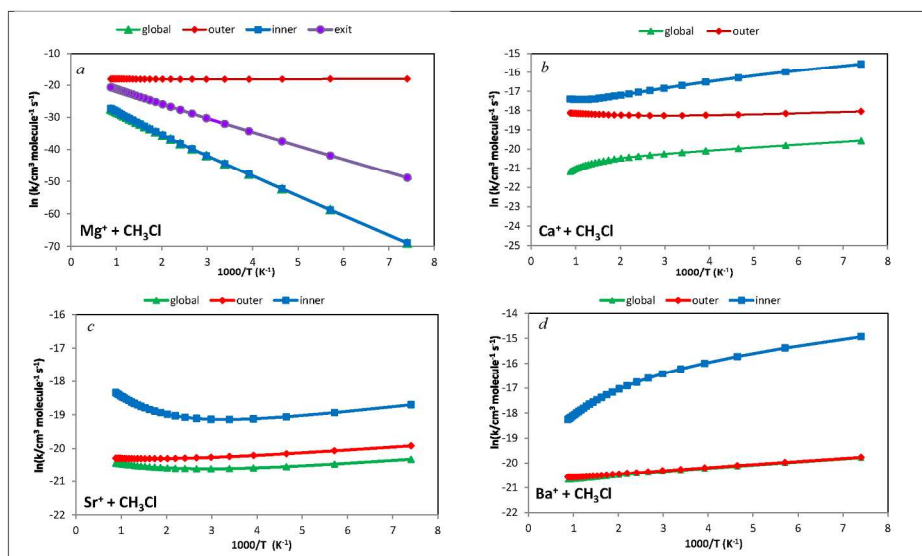


Figure 4

Figure 4. Arrhenius plots for the rate constants of the $M^+ + \text{CH}_3\text{Cl}$ reactions ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$); kglobal, (green), kinner (blue), kouter (red), and kexit (gray).
297x210mm (200 x 200 DPI)

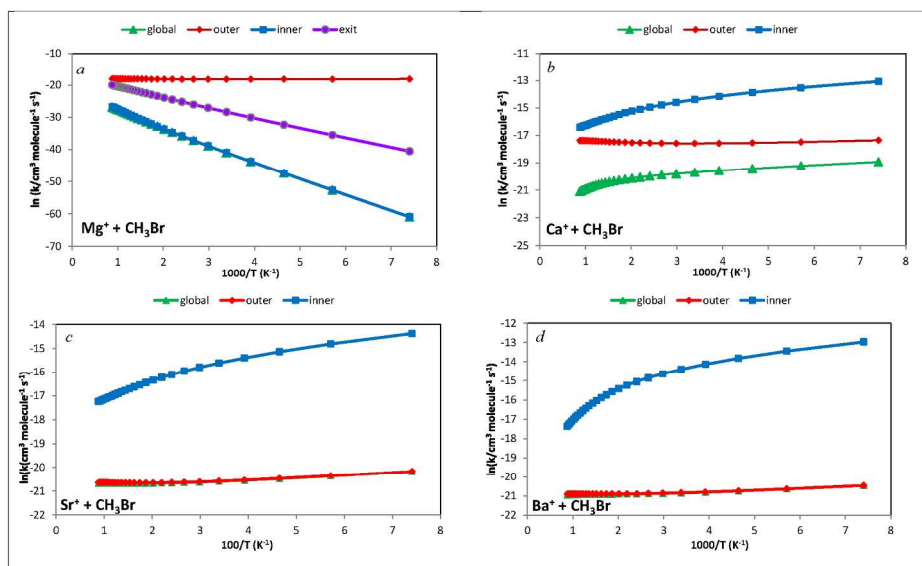


Figure 5

Figure 5. Arrhenius plots for the rate constants of the $M^+ + \text{CH}_3\text{Br}$ reactions ($M=\text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$); kglobal, (green), kinner (blue), kouter (red), and kexit (gray).
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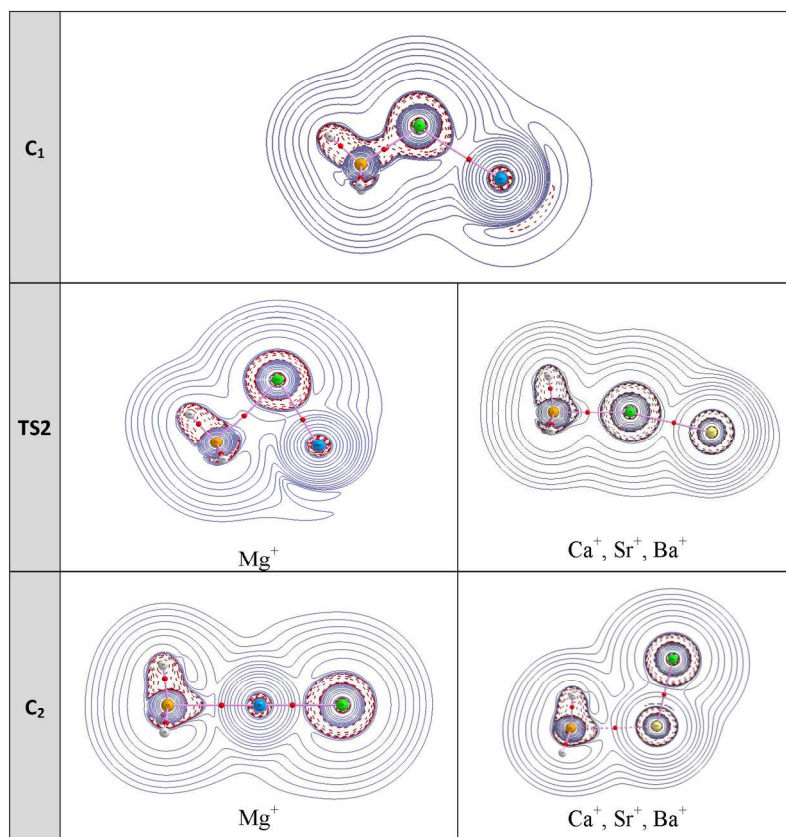
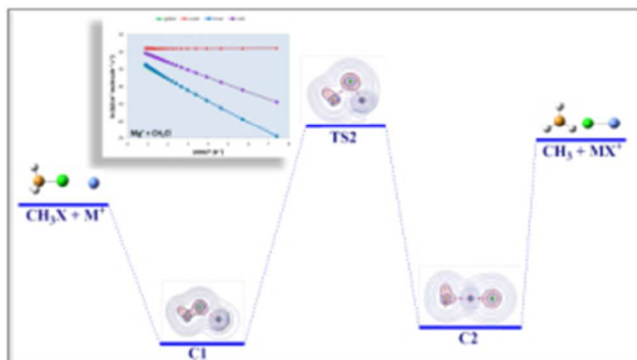


Figure 6

Figure 6. Contour maps of the Laplacian distribution of the electron density for the different critical points. Red dashed lines indicate regions of electronic charge concentration ($\nabla^2(r) < 0$), and blue continuous lines denote regions of electronic charge depletion ($\nabla^2(r) > 0$). Also molecular graphs of electron density are shown, small red spheres represent bond critical points (BCPs)

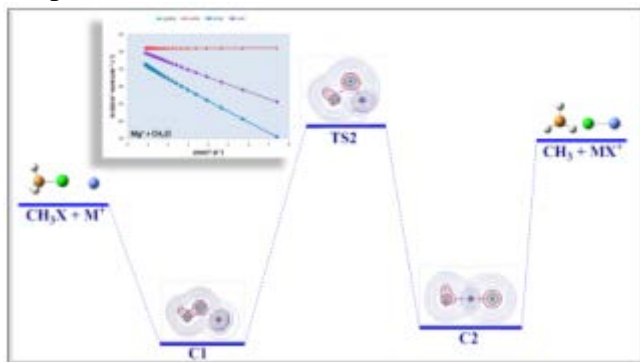
210x297mm (224 x 224 DPI)



TOC Colour Graphic
84x48mm (96 x 96 DPI)

Graphical Abstract

Graphic:



Text:

Gas-phase reactions between alkaline-earth metal monocations (Mg^+ , Ca^+ , Sr^+ , Ba^+) and halogen methanes (CH_3X ; $X=Cl, Br$) have been theoretically analyzed.