

Reactivity of first-row transition metal monocations with methyl fluoride: a computational kinetic study

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The study of gas-phase reactions between metal cations and organic substrates has been the focus of a great deal of attention in the last few years. Its importance is mainly attributable to gas-phase reactions relevance in synthetic chemistry and their applications in several fields including catalysis, biological activity, atmospheric chemistry, and in the study of potential semiconductor materials. Among the organic substrates methyl fluoride deserves a special interest, since it constitutes a simple molecule to analyze the Carbon-Fluorine bond activation as well as the competition between C-F and C-H activation. In this context, reactions of first-row transition-metal single-charged cations with methyl fluoride become fundamental processes. Previous theoretical works within this field [1,2] proved very useful to fully understand this type of reactions.

In the present communication the gas-phase reactivity of methyl fluoride with selected first-row transition metal monocations has been investigated. Our thermochemical and kinetics study shows that early transition-metal cations exhibit a much more active chemistry than the latest transition metal monocation Zn^+ . In the present computational study we combine the characterization of the PESs for the $\text{M}^+ + \text{CH}_3\text{F}$ reactions and kinetics calculations, allowing us to compute rate constants to be compared with available experimental data [3]. The present systematic study does provide valuable mechanistic information about a number of reaction paths leading to different products, thus complementing the experimental information available.

[1] Varela-Álvarez, A., Rayón, V. M., Redondo, P., Barrientos, C., Sordo, J. A., *J. Chem. Phys.*, 131: 144309 (1–11), 2009.

[2] Varela-Álvarez, A.; Sordo, J. A.; Redondo, P.; Largo, A.; Barrientos, C.; Rayón, V. M., *Theor. Chem. Acc.*, 128: 609–618, 2011.

[3] Zhao, X., Koyanagi, G. K., Bohme, D. K., *J. Phys. Chem. A*, 110: 10607–10618, 2006.