

Computational Design of Gallium Imides for Methane Activation

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Abstract

Activation of the strong, non-polar C-H bond in methane is very difficult, especially in solution. Modifiying the electronic properties of the NacNacGa gallium imide reduced the overall reaction barrier from 123 kJ/mol to 93 kJ/mol.Structural pre-straining reduced the reaction barrier even more to just 62 kJ/mol. Dimerization can be prevented with bulky groups that do not affect the reactionbarrier. Modified NacNacGa is a viable methane reagent in solution

Motivation and background

Can Gallium Imides be a reagent for methane activation?

Methane conversion is expensive, difficult, and overwhelmingly done using a bulk catalyst under high pressures and temperatures (zeolites, steam reformation, or partial oxidation). Cheap and reliable one-step solution-pgase processes are desired, but due to the high thermodynamic stability and low chemical reactivity of methane, few reliable methods exist. [1]

Reaction Mechanism and its Electronic and Steric factors

Density functional theory at the ω B97X-D/6-311++G(d,p) level of theory was used for all models. Nine combinations of R groups were considered as shown in **(1)**. Transition states were found by the Nudged Elastic Band method (NEB). Reactant and product states were identified by following the intrinsic reaction coordinate and optimizing the endpoints of the IRC. The R₂ nitrogen and the gallium atoms are allowed to react. All reactions are concerted.



The relationship between ΔE_{rxn} and ΔE^{TS} are plotted. Compared to what was previously known, (red star), one can reduce the ΔE^{TS} by up to 10 kJ/mol, or make the ΔE_{rxn} up to 30

Homogenous catalysts however allow for the possibility of rational design, tuning to improve the rate of the methane activation and to achieve greater control of the overall reaction mechanism. In addition, the stabilization of products through solvation effects and/or hydrogen acceptors can make the thermodynamics of the process more favorable. In turn, favorable thermodynamics can result in lower reaction temperature, reduced energy consumption, and improved yields. Lower temperatures can eliminate or reduce the formation of undesirable by-products, such as coke, and allow a variety of effective heat management strategies.

Homogenous catalysts for alkane activation are known on Iridium and other expensive transition-metal complexes, exploiting the high reactivity of transition metal complexes in general. However, they tend to be expensive, difficult to use and potentially unstable. Main group elements however, tend to be cheap and are less toxic. Frustrated Lewis Pairs, and radicals been shown to activate C-H bonds, with much work done in the FLP space.

Gallium Nitride has recently been shown to activate methane. In addition, a gallium imide "NacNacGa"(1)[2] has been shown to activate C-H bonds on activated molecules. What if we could extend this to activate methane itself, and tune it to reduce the activation barrier and overall reaction exothermicity?



kJ/mol less exothermic. No single molecule both reduces ΔE^{TS} and ΔE_{rxn} .



Energy decomposition analysis was performed to examine the transition state from the reactant state by considering alchemically the processes that are implicated. ΔE_{SEP} , mostly Van-der-Waals forces between the reactant and the methane, ΔE_{GD} , the energy barrier to distort the molecules to the transition state, and ΔE_{INT} , the interaction between the methane and the catalyst at the transition geometry. ΔE_{INT} is further decomposed using ALMO[3] to examine the frozen repulsion ΔE_{FRZ} , charge transfer ΔE_{CT} and ΔE_{POL} . In all cases, the factors that were contributing to raise ΔE^{TS} in a chemically-accessible way were ΔE_{GD} and ΔE_{CT} . Four systems (**A**, **B**, **C**, **D**) were investigated to further explore this.



Optimizing ΔE_{rxn} , ΔE^{TS} and minimizing Dimerization

Deplanarizing the reactant state reduces the barrier needed to reach the transition state reliably. Unfortunately trying to tune the charge transfer is more difficult because the transition state does not lie reliably at the same place on the reaction coordinate - it can be "late" or "early", and there is no good way of predicting which it is. Reducing ΔE^{TS} however also tends to increase ΔE_{rxn} .

	ΔE^{\ddagger}	$\Delta E_{\rm rxn}$	$\Delta E_{ m dim}$	$\Delta G_{ m dim}^0$	a)
	${\rm kJmol^{-1}}$	${ m kJmol^{-1}}$	${ m kJmol^{-1}}$	${\rm kJmol^{-1}}$	
Ref.	100	-197	-224	-186	
Α	93	-210	-272	-234	
в	115	-183	-148	-110	c)
С	73	-260	-588	-550	
D	62	-251	-105	-65	CHR 3

Unmodified **C** however is very prone to dimerization. Adding bulky groups to it in **D** reliably prevents dimerization while preserving the same favourable ΔE^{TS} . Reactions on **D** are also slightly less exothermic than in **C** but the reaction energy still precludes use of either as a catalyst.





Conclusions

In this computational work, electronic and steric effects are exploited to modify the structure of an experimentally reported gallium imide to activate strong non-polar C-H bonds in methane. DFT calculations show that changing and adding to gallium imide substituents can lower the energy barrier for the cleavage of methane bonds from 123 kJ/mol to 93 kJ/mol. For example, swapping positions of TMS and aryl substituents in the original imide reduces the barrier to 103 kJ/mol while preserving a similar reaction energy ΔE_{rxn} . Distorting the imide molecule allows to reduce the energy barrier even further to 62 kJ/mol. Dimerization can be prevented by bulky substituents, allowing imides to retain their ability to cleave C – H bonds in solution.

References

1. Nkinahamira, F.; Yang, R.; Zhu, R.; Zhang, J.; Ren, Z.; Sun, S.; Xiong, H.; Zeng, Z. Current Progress on Methods and Technologies for Catalytic Methane Activation at Low Temperatures. *Advanced Science* **2022**, *10*, *2204566*.

2.] Kassymbek, A.; Spasyuk, D.; Dmitrienko, A.; Pilkington, M.; Nikonov, G. I. Facile C-H bond activation on a transient gallium imide. *Chem. Commun.* **2022**, *58*, *6946–6949*.

3. Khaliullin, R. Z.; Cobar, E. A.; Lochan, R. C.; Bell, A. T.; Head-Gordon, M. Unravelling theOrigin of Intermolecular Interactions Using Absolutely Localized Molecular Orbitals. *J. Phys.Chem. A* **2007**, *111, 8753–8765.*

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