Communication

A Theoretical Study of Alkane Protonation in HF/SbF$_5$ Superacid System

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Foram realizados cálculos ab initio para a protonação de ligações C-H e C-C do metano, etano, propano e isobutano com um agregado representando a estrutura de um superácido. Para a protonação na ligação C-H (troca H/H) o estado de transição se parece com um íon H-carbônio coordenado com o superácido. A energia de ativação para a troca H/H foi cerca de 16 kcal.mol^{-1} em nível B3LYP/6-31++G** + RECP (Sb), independentemente do tipo de ligação C-H sendo protonada. Para a protonação de ligações C-C a energia de ativação depende da estrutura do hidrocarboneto e foi sempre maior que a energia de ativação para a protonação na ligação C-H, indicando uma maior repulsão estérica.

Ab initio calculations for the protonation of the C-H and C-C bonds of methane, ethane, propane and isobutane by a superacid moiety was carried out. For the C-H protonation (H/H exchange) the transition state resembles an H-carbonium ion coordinated with the superacid. The activation energy for the H/H exchange was about 16 kcal.mol^{-1}, at B3LYP/6-31++G** + RECP (Sb) level, regardless the type of C-H bond being protonated. For the C-C protonation the activation energy depends on the structure of the hydrocarbon and was always higher than the activation energy for C-H protonation, indicating a higher steric demand.

Keywords: superacid, carbonium ions, alkane, DFT

The protonation of alkanes in superacids was independently studied by Olah[1] and Hogeveen[2] during the late 60's. The proton transfer to a σ bond forms a pentacoordinated carbonium ion[3], which contains a two electron three center bond. Based on product distribution analysis Olah proposed[4] the following order of σ bond reactivity in superacids: tert-C-H > C-C > sec-C-H > prim-C-H > CH$_4$. Nevertheless, this order is roughly qualitative, and dependent on the steric hindrance of the hydrocarbon and the superacid system. In a recent theoretical study on the energetics of the butonium[5] cations, we have found that the C-butonium ions, hypothetically formed through the protonation of the C-C bonds of isobutane and n-butane, are significantly lower in energy than the H-butonium ions, formed upon protonation of the C-H bonds of isobutane and n-butane. The calculations are in agreement with gas phase results[6], where protonation of the C-C bond of isobutane prevails over protonation in the tert-C-H bond. Previous calculations also indicated[7] that some higher carbonium ions cannot be considered discrete intermediates,

as they spontaneously decompose into a carbenium ion and methane or hydrogen. An interesting reaction accompanying alkane ionization in superacid is the H/D exchange[8]. The exchange[9] of propane and isobutane with superacids occurs faster than ionization to carbenium ions and is generally used as an evidence for the intermediation of pentacoordinated carbonium ions in alkane reactions in superacids. In this communication we wish to report preliminary theoretical results of σ bond protonation in a series of alkanes by a cluster representing the superacid moiety.
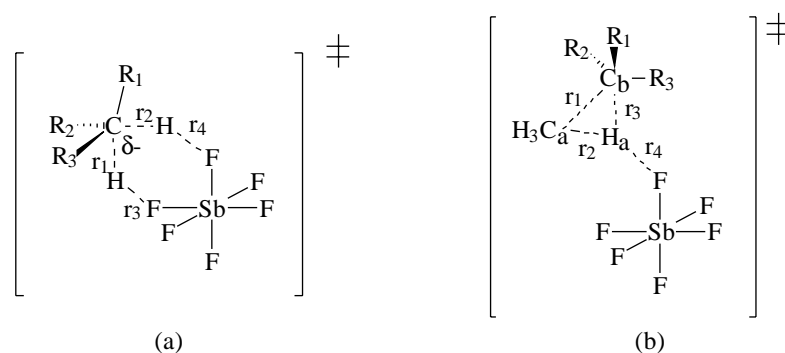
A cluster comprising an HF molecule and SbF$_5$ was used to represent the superacid moiety. The transition states (TS) for the H/H exchange and C-C protonation (Scheme 1) were fully optimized using the Berny algorithm and characterized, by vibrational analysis, as having only one imaginary frequency, which corresponds to the reaction mode. A relativistic effective core potential (RECP) was used to describe the antimony atom[10] in the SbF$_5$ molecule. All the calculations involving the H/H exchange and the C-C protonation were performed at B3LYP/6-31++G** + RECP(Sb) level using the GAUSSIAN 94 package[11]. All energies corresponding to the optimized structures were corrected for thermal (298.15 K) and zero-point

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energy. Unless otherwise stated all reported energies refer to enthalpy[12] differences between the transition states and the separate alkane and $HSbF_6$ moiety at 298.15 K and 1 atm.

Table 1 shows the activation parameters at 298.15 K and the main geometric data for the transition states of H/H exchange and C-C protonation of several alkanes by the superacid cluster model. It can be observed that the enthalpy of activation for the H/H exchange is around 16 kcal.mol^{-1} for all C-H bonds investigated. All the transition states have an approximate symmetric structure (C_s). While one hydrogen atom is being transferred to the hydrocarbon, the other is being transferred back to the superacid. Hence, no discrete

pentacoordinated carbonium ion seems to be formed as intermediate, but the TS closely resembles the calculated structure of the isolated methonium[13], ethonium[14], proponium[15] and isobutonium[7] cations. The C-H distance in the three center bond does not differ significantly within the series, ranging from 1.23 Å, for exchange with methane, to approximately 1.28 Å for exchange of the tertiary C-H of isobutane. On the other hand the F-H distance shows a significant variation, ranging from 1.477 Å, for exchange with methane, to 1.587 Å, for exchange of the methine hydrogen of isobutane. These results suggest that steric repulsion, associated with the hydrocarbon substituent groups, plays an important role.

Scheme 1. Schematic representation of the TS for H/H exchange (a) and C-C protonation (b) of alkanes in superacid.

Table 1. Activation enthalpy, main geometric parameters and charge variation at the exchanging carbon atom for the H/H exchange and C-C protonation of alkanes calculated at the B3LYP/6-31++G** + RECP (Sb) level.

Transition State	$\Delta H_0^{\neq}$ (kcal.mol^{-1})[a]	ν (cm^{-1})	δq[b]	Bond Distances (Å)			
				r_1	r_2	r_3	r_4
H/H Exchange[c]							
CH_4	16.8	470i	-0.151	1.233	1.234	1.480	1.477
C_2H_6	15.8	326i	-0.045	1.233	1.234	1.523	1.514
⋀★	16.0	311i	-0.125	1.232	1.234	1.528	1.518
★⋀	15.6	223i	-0.069	1.255	1.233	1.502	1.597
⋎★	16.1	275i	-0.115	1.231	1.234	1.527	1.546
⋎★	16.4	154i	-0.069	1.258	1.258	1.587	1.587
C-C Protonation							
C_2H_6	28.6	168i		1.826	1.243	1.272	2.035
C_3H_8	25.1	259i		1.789	1.315	1.281	1.638
i-C_4H_{10}	22.7	510i		1.743	1.345	1.351	1.510

[a] 1 cal = 4.18 J; [b] δq = (absolute charge of the carbon atom in the TS) - (absolute charge of the carbon atom in the reactant). The charges were calculated using the ChelpG scheme[19]; [c] The ★ indicates the hydrogen atom being exchanged.

The calculated activation enthalpy for H/H exchange of methane (16.8 kcal.mol^{-1}) and ethane (15.8 kcal.mol^{-1}) correlates well with the reported experimental $\Delta H^{\ddagger}$ for H/D exchange in DF/SbF$_5$ solutions. The exchange with methane and ethane involves activation enthalpies of 18 and 16.6 kcal.mol^{-1}, respectively[16]. For propane and isobutane the exchange is always accompanied by ionization. Hence, precise measurements of activation enthalpy are not available. Nevertheless, a reported[17] activation enthalpy of 18.3 kcal.mol^{-1} for isobutane ionization is in fairly good agreement with the calculated $\Delta H^{\ddagger}$ for exchange of the methine hydrogen, indicating that H/D exchange and ionization to tertiary carbenium ions are related reactions. We are investigating the use of larger superacid cluster in the $\Delta H^{\ddagger}$ of H/H exchange and ionization of alkanes.

The calculated TS geometries for the H/H exchange of alkanes in the superacid cluster model used in this study are similar to the calculated[18] TS for the H/H exchange in zeolites. However, the calculated activation energy for exchange in zeolites is about 30 kcal.mol^{-1}, regardless of the type of C-H bond being exchanged.

Table 1 also shows that the exchanging carbon atom bears a small negative charge variation, when going from the ground to the transition state. This reflects the almost constant activation enthalpy for the H/H exchange, as the substitution of alkyl groups in the exchanging carbon atom would barely stabilize the TS. The same trend was observed for the calculated H/H exchange in zeolites.

For the C-C protonation the calculations showed a different picture. The calculated activation enthalpy is significantly higher for C-C protonation than for H/H exchange, ranging from 22.6 kcal/mol, for isobutane, to 29 kcal.mol^{-1} for ethane. This is in agreement with the experimental results of alkane protonation in superacid, where H/D exchange occurs much faster than ionization[8,9]. The reason for the higher activation energy for the C-C protonation in superacids is associated to the steric hindrance in protonating the inner, and less accessible, C-C bonds. The C-H distance in the TS for C-C protonation of isobutane is about 1.34 Å. This value is about 0.1 Å longer than the C-H distance for H/H exchange of the tertiary hydrogen atom of isobutane. The same trend is observed for propane and ethane.

The low imaginary frequencies observed for the C-H and C-C protonation indicates that the carbonium ions and the anion moiety are loosely bounded in the TS. Hence, explaining the experimental results in terms of carbonium ion formation is a good approximation, although free carbonium ions do not seem to be formed in these reactions.

As we have recently shown[5], the experimental order of σ bond reactivity in superacid, observed by Olah, reflects the kinetics of σ bond protonation in these media, rather than the intrinsic basicity of the σ bonds. Hence, the barrier for attacking the outer, and more accessible C-H bonds, is lower than the activation energy for protonating the C-C bonds, which are more difficult to be reached by bulky electrophiles. It should be noticed however that, rearrangement of carbonium ions is an easy process. Calculations indicated[7] that protonation at the primary C-H bond of isobutane would, straightforwardly, give methane plus isopropyl cation, the products arising from C-C protonation. The fact that discrete carbonium ion intermediates are not involved in H/H exchange and C-C protonation reactions might give a clue to understand the σ bond protonation in zeolites[20] and enzymes[21]. We are presently investigating the effect of using larger superacid cluster models in acid strength and the energetics of σ bond protonation for various alkane molecules.

Acknowledgements

Electronic supplementary information

Main geometric parameters for the HSbF$_6$ and the TS for H/H exchange and C-C protonation. Available at: http://www.sbq.org.br/jbcs/2000/vol11_n4/indice.

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12. Enthalpy is calculated according to: H(T) = [U + ZPE] + E_{vib}(T) + E_{rot}(T) + E_{trans}(T) + RT.

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