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COMMUNICATION

On the Tunneling Instability of a Hypercoordinated Carbocation

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$C(CH_3)_5^+$, a pentacoordinate carbocation, was recently described as a "fleeting" molecule, that is, stable only at low temperatures. Herein it is shown with theoretical methods that, owing to carbon tunneling, the molecule is not persistent even at 0 K. One possible way to lengthen its lifespan is by deuterium substitution, in spite of the fact that no bond to hydrogen is broken.

A recent communication exploring the limits of carbon bonding by McKee, Schleyer and coworkers[1] described the theoretical existence of $C(CH_3)_5^+$ near absolute zero as "fleeting".[2] This term was coined by Hoffmann, Schleyer and Schaeffer in their essay: "Predicting Molecules—More Realism, Please!", indicating a molecule where the sole energetic criterion of its stability is a vibrational analysis (thus being a real minimum in the potential energy surface).

$C(CH_3)_5^+$, a C_{3h} pentacoordinate carbocation, is more a proof of concept for the feasible bonding possibilities of carbon rather than a molecule with real perspectives to be synthesized. Although the "classical" thermal barriers suggest that this carbocation might be detectable at extremely low temperatures, herein it is shown that due to quantum mechanical tunneling (**QMT**) the existence of $C(CH_3)_5^+$ is much more ephemeral than was considered, even at absolute zero.[3,4]

The two decomposition pathways for $C(CH_3)_5^+$ (described in detail in the original communication[1]) are shown in Fig. 1. The first pathway, going through a C_3 symmetry transition state (**TS1**), involves a CH_3^+ loss by elongation of an axial methyl C-C bond, followed by a hydrogen abstraction and CH_3 migration, generating a relatively stable tertiary carbocation. This process has a $\Delta(E+ZPE)^{\ddagger}$ of 1.65 and a $\Delta E^{\ddagger}$ of 4.35 kcal/mol (calculated at the CCSD(T)/CBS level, as reported in the original communication[1]). The second decomposition pathway, via a

transition state of C_s symmetry (**TS2**), involves a bending mode joining an axial and an equatorial carbon to give ethane and *tert*-butyl carbocation, with $\Delta(E+ZPE)^{\ddagger}$ = 1.37 and $\Delta E^{\ddagger}$ = 2.32 kcal/mol. Thus, despite these extremely low degradation barriers, transition state theory in its simplest form predicts that the cation should have a fleeting,[2] possibly observable existence near absolute zero.

However, due to the low and (more critical) narrow[3–6] barriers in the decomposition patterns of $C(CH_3)_5^+$, the tunneling effect may be a crucial factor to take into account, even if QMT of "heavy" atoms is involved. Carbon tunneling is an unusual but well documented effect, which has been observed or calculated in reactions such as the automerization of cyclobutadiene and other antiaromatic molecules (starting with the pioneering work of Carpenter),[5,7–13] or in different carbene insertion reactions and other reactive systems.[6,14–17] All these systems had something in common: low and considerably narrow barriers. In the decomposition of $C(CH_3)_5^+$ the carbon atoms travel over great distances, but the effective barrier for tunneling is tight (that is, from the reactant stage to the point of same energy in the product side of the reaction coordinate), and therefore may be prone to react by a QMT mechanism.

It must be pointed out that QMT on the related CH_5^+ carbocation has been thoroughly studied (see for instance Ref. [18]). However, the differences between both systems are significant. For CH_5^+, the tunneling concerns only the hydrogens ("light atom" QMT) mostly in its fluxionality;[19] for $C(CH_3)_5^+$, tunneling will primarily affect the carbon structure ("heavy atom" QMT) in its chemical degradation.

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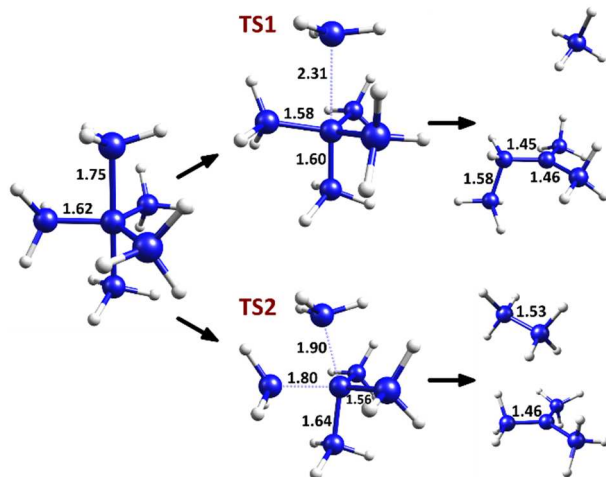
Figure 1. Decomposition pathways for $C(CH_3)_5^+$, with selected C-C bond distances at the M06-2X/6-31G(d) level.

Table 1. Rate constants with and without tunneling correction (SCT and CVT, respectively) in s^{-1}, and half-life in seconds for both decomposition pathways of $C(CH_3)_5^+$.[a]

	TS1			TS2		
T(K)	CVT	SCT	$t_{1/2}$	CVT	SCT	$t_{1/2}$
10	1.2×10^{-39}	1.2×10^5	6×10^{-6}	6.8×10^{-36}	1.5×10^4	4×10^{-5}
20	3.2×10^{-14}	1.2×10^5	6×10^{-6}	4.2×10^{-12}	1.6×10^4	4×10^{-5}
50	1.0×10^2	2.2×10^5	3×10^{-6}	1.5×10^3	5.6×10^5	1×10^{-6}
100	2.8×10^7	8.7×10^7	8×10^{-9}	2.2×10^8	7.0×10^8	1×10^{-9}
150	2.5×10^9	4.2×10^9	2×10^{-10}	1.5×10^{10}	2.2×10^{10}	3×10^{-11}
200	2.6×10^{10}	3.6×10^{10}	2×10^{-11}	1.5×10^{11}	1.6×10^{11}	4×10^{-12}
300	3.1×10^{11}	3.6×10^{11}	2×10^{-12}	1.6×10^{12}	1.6×10^{12}	5×10^{-13}

[a] Due to the change in the symmetry number of TS2 (going from a C_{3h} reactant to a C_s transition state), the rate constants for this pathway were tripled and the $t_{1/2}$ were divided by 3.[27]

To study the effect of quantum mechanical tunneling on the degradation of $C(CH_3)_5^+$, we used canonical variational theory (CVT) to compute the semi-classical rate constant (without the tunneling component),[20] and the small curvature tunneling approximation (SCT)[21] including the quantized reactant state tunnelling (QRST) approximation[22] to compute the rate constant including tunneling. Polyrate[23] program was used to this effect, and Gaussian09[24] was employed for the DFT calculations (with Gaussrate[25] as the interface between Polyrate and Gaussian). Since high-quality, wave-function-based calculations are not practical for the demanding SCT calculations, all rate constants calculations were carried out with the M06-2X functional[26] and the 6-31G(d) basis set. The combination of this functional and basis set has shown good accuracy for tunneling calculations of organic reactions,[12,26] and reasonably agrees with the CCSD(T)/CBS methodology, generating values of 2.27 and 2.16 kcal/mol for the $\Delta(E+ZPE)^{\ddagger}$ of **TS1** and **TS2**, respectively.

Table 1 shows the calculated rate constants for both decomposition pathways with (SCT) and without (CVT) tunneling effect included, and the SCT half-life at different temperatures (see the SI for the complete tables).

It is clear that the stability of $C(CH_3)_5^+$ is strongly influenced by carbon tunneling, with extremely high SCT rate constants, even at cryogenic temperatures. Half-lives ($t_{1/2} = \ln 2 / k$) of only 6 and 40 µs for the decomposition of $C(CH_3)_5^+$ were computed for pathways 1 and 2, respectively, below 20 K. Without the inclusion of QMT, the reaction is predicted to take several millennia to occur even at 20 K, thus confirming the fleeting characteristics of the system based in transition state theory alone (i.e. without considering QMT).

Although the whole QMT picture is more complex than the analysis of the motion of individual particles (since the reduced mass of the whole system in the least action pathway must be considered[28,29]), the influence of each atom can still be analyzed by studying the carbon ($^{12}C/^{13}C$) and hydrogen (H/D) kinetic isotope effects (KIE) on the SCT rate constant.

Figure 2 shows the KIE of each inequivalent atom on the **TS1** pathway at cryogenic temperatures. The carbon of the departing methyl group is the most crucial carbon atom for the QMT process with a KIE of 1.72, but the central carbon also exerts a significant effect (KIE of 1.20). Surprisingly, the lower axial carbon provides a negative secondary KIE of 0.94. The KIE after substituting all the carbons by ^{13}C is 2.03, virtually identical to the product of all the individual substitutions ($1.72 \times 1.20 \times 0.94 \times 1.02^3 = 2.05$). Thus, there is a largely independent contribution of each carbon to the tunneling probability.
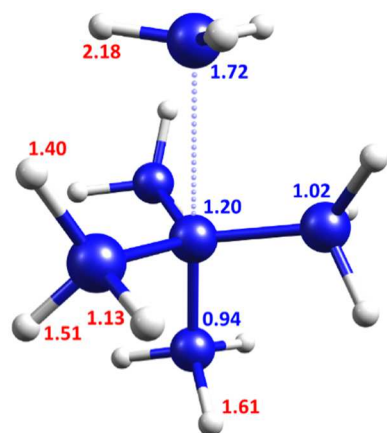
Figure 2. **TS1** geometry, with the KIE values for inequivalent atoms in C_3 symmetry. Blue values are for $^{12}C/^{13}C$ KIE, red for H/D KIE.

However, the contribution of each H/D substitution is not totally independent. Replacing all of the hydrogen atoms with deuterium results in a KIE of 613. Since no C-H bond is broken, this large value is remarkable. Moreover, it is higher than the product of individual contributions ($2.18^3 \times 1.61^3 \times 1.51^3 \times 1.40^3 \times 1.13^3 = 592$, see fig. 2), suggesting a small synergistic hydrogen contribution to the tunneling probability.

The high H/D KIE value goes beyond the effect of the higher mass of the particles on the tunneling probability. As pointed out by a reviewer, more than being exclusively a carbon tunneling process, the process can be considered as a methyl group tunneling, since the hydrogens connected to the dissociating carbon are moving as well. In that sense, the mass change of one H/D substitution on the departing CH_3 group should be as important for the tunnelling probability as a $^{13}C/^{12}C$ substitution on the same group. However, the H/D replacement produces a significantly higher KIE than the carbon replacement (2.18 vs. 1.72). Moreover, all the other hydrogens have a strong influence on the rate, while other carbons have not. This is despite the fact that these hydrogens are not directly "involved" in the C-C breaking process (at least not in the reaction section important to QMT). More than the direct effect of the mass, what is strongly influencing the tunneling rate is a factor that is traditionally connected to a change in the semi-classical KIE, the zero point energy. The ZPE change is also a mass effect, but the extra mass indirectly affects the QMT probability through a higher and broader barrier.

The additive lowering of the ZPE of the reactant by each H/D substitution increases the $\Delta(E+ZPE)^{\ddagger}$ value and reduces the tunneling probability. One H/D axial methyl group substitution raises the $\Delta(E+ZPE)^{\ddagger}$ from 2.27 to 2.39 kcal/mol, while the replacement of all 15 H's by D's raises the $\Delta(E+ZPE)^{\ddagger}$ to 2.99 kcal/mol for decomposition via **TS1**. Considering that this ZPE difference is a major component relative to the activation energy, the lower ZPE of the reactant in deuterated systems significantly affects the tunneling-based KIE[30] of the degradation of $C(CH_3)_5^+$ by raising and broadening the barrier, in addition to the increase of the methyl mass. Contrary to this, the $^{12}C/^{13}C$ substitution does not change the ZPE

appreciably, and therefore its KIE is a direct mass effect on the tunneling probability.

Notably, this change in the ZPE greatly extends the lifetime of $C(CD_3)_5^+$. Its computed half-life of 4 ms is three orders of magnitude longer than that of the $C(CH_3)_5^+$ isotopologue. Replacing all the hydrogen atoms with tritium would lead to a $\Delta(E+ZPE)^{\ddagger}$ of 3.31 kcal/mol and a still brief, but drastically longer, half-life of 0.2 seconds. The $\Delta(E+ZPE)^{\ddagger}$ values for decomposition through **TS2** are less sensitive to an isotopic replacement, with values of 2.16, 2.41 and 2.53 kcal/mol for $C(CH_3)_5^+$, $C(CD_3)_5^+$ and $C(CT_3)_5^+$, respectively. Nevertheless, due to the wider barriers, the half-lives of these species considering only decomposition through **TS2** are longer than those via **TS1**: 40 µs, 60 ms, and 10 s. This technique of prolonging the lifetime and stabilizing a molecule prone to degradation by QMT with H/D substitutions is, to the best of our knowledge, unheard of in reactions not based on hydrogen migration.

Conclusions

Considering the short lifetime of the hypothetical $C(CH_3)_5^+$ pentacoordinate carbocation, the definition of a "fleeting system"[2] as one that can be detected at extremely low temperatures may require revision. Molecules that have a low but definite decomposition barrier (with all positive frequencies in a vibrational analysis) might be expected to be persistent close to 0 K, but QMT calculations may show otherwise. Therefore, is $C(CH_3)_5^+$ "fleeting" or not? This semantic problem may be solved by adding a new term, "tunneling stability" (similar to the concept of "tunneling control"[31]) to the already established "kinetic persistence" and "thermodynamic stability" definitions. Indeed, other molecules predicted to be fleeting[32,33] have been computed to be unstable due to tunneling,[34] indicating that QMT should be a factor to take into account in stability analyses.

In this sense, the decomposition of $C(CH_3)_5^+$ through QMT by no means refute the hypothetical existence of the five-fold C-C bonding motif of $C(CH_3)_5^+$ as predicted by Schleyer et al.[1] However, we now know that it will probably be impossible to detect this cation experimentally due to its exceptionally short life expectancy.

Interestingly, deuterium or tritium substitution is predicted to extend the lifespan of $C(CH_3)_5^+$ much more than ^{13}C substitution, in spite of the fact that we are breaking C-C and not C-H bonds. The added mass is only one factor for this extra longevity, which is mainly caused by the effect of hydrogen isotopes on the ZPE.

One can only wonder how many other fleeting systems have been theoretically predicted but will not pass the tunneling test. Or, quoting the title of the essay of Hoffmann, Schleyer and Schaeffer,[2] we may say: "Predicting Molecules—More Realism, Please!".

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