

# Quantum Tunnelling in Triplet Carbenes Explained by Instanton Theory

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**Abstract:** The temperature-dependent reactivity of three triplet carbenes (denoted as **C1**, **C2** and **C3**) were investigated using instanton theory. Experiments showed that **C1** undergoes an intramolecular reaction at very low temperatures, while **C2** requires heating, and **C3** remains stable despite heating. The reactions studied involved both hydrogen transfer and intersystem crossing, and therefore we considered sequential and concerted processes as possible candidates for the reaction mechanism. Calculations of instanton tunnelling pathways in conjunction with double-hybrid density functional theory showed that the sequential mechanism dominates the reaction at high temperatures while the concerted mechanism is the predominant channel at low temperatures. The observed temperature-dependent reactivity can thus be explained in terms of a crossover temperature where the mechanism switches. This study suggests a powerful way to control the reactivity of triplet carbenes solely by tuning temperature.

**Keywords:** Carbenes · Instanton theory · Quantum chemistry · Quantum tunnelling



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## 1. Introduction

Carbene chemistry has captured the interest of both experimentalists and theorists due to strong quantum tunnelling effects at low temperatures. The two unshared valence electrons in a carbene can either be paired (singlet carbene) or unpaired (triplet carbene) in its ground state. While several theoretical and experimental studies have largely focused on tunnelling in singlet carbenes,<sup>[1–6]</sup> here we review our recent investigation of triplet carbenes.<sup>[7]</sup>

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We focused on a set of three triplet carbene reactions (Fig. 1) which undergo intramolecular hydrogen transfer (HT) to form a product in the singlet state. In the first reaction, (*E*)-1-(3-thienyl) ethylidene (**C1**) transforms to (*E*)-3-vinylthiophene (**P1**) at a low temperature of 10 K and the half-life of this reaction was measured to be 68 hours.<sup>[8]</sup> In the second reaction, 1-phenylethylidene (**C2**) forms styrene (**P2**), but only when heated to 65 K, with a half-life of 40 minutes.<sup>[9]</sup> On the other hand, the third carbene, 1-(2-naphthyl)ethylidene (**C3**), did not show any reactivity, despite heating up to 40 K.<sup>[10]</sup> Note that the temperature of the experiments is limited to about 40 K in an Argon matrix or 70 K in Xenon.<sup>[11]</sup> In all three carbenes, no discernable reaction was observed after deuteration of the methyl group, even upon heating.

Considering the cryogenic temperatures at which the experiments were performed, and the lack of reactivity upon deuteration, quantum tunnelling is the likely driver in these reactions. In our recent work,<sup>[7]</sup> we studied the mechanism of these reactions, to

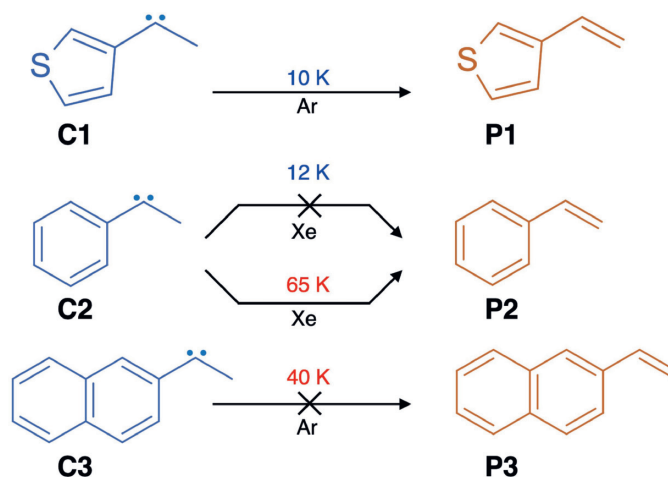


Fig. 1. Intramolecular hydrogen transfer and intersystem crossing reactions of the three carbenes studied in this work. Figure adapted from ref. [7].

rationalize the difference in reactivities of C1, C2 and C3, despite their apparent structural similarity.

## 2. Results and Discussion

We started by studying the topology of the lowest singlet and triplet states using double-hybrid density functional theory (DFT). Our calculations (which are summarized in Fig. 2) show that on the reactant side, the minimum on the triplet state,  $R_T$ , is slightly lower in energy than the minimum on the singlet state,  $R_S$ . However, as one would expect from a consideration of the molecular orbitals, on the product side, the singlet minimum,  $P_S$ , is significantly more stable than the minimum on the triplet state,  $P_T$ . Additionally, the barrier to the transition state was much higher on the triplet state as compared to the singlet.

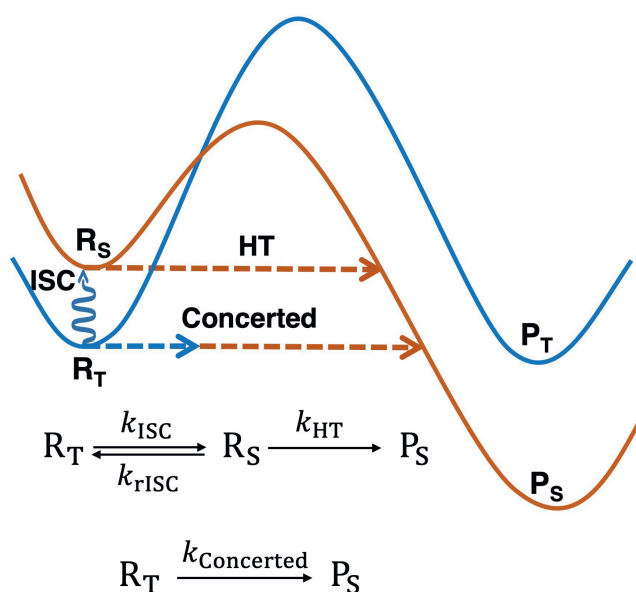


Fig. 2. Sequential and concerted reaction mechanisms. ISC and HT indicate intersystem crossing and hydrogen transfer. Blue and red colours represent the triplet and singlet potential energy surfaces. The rate constants for individual steps are indicated below. Figure adapted from ref. [7].

Since the reactions involve both HT and intersystem crossing (ISC), they can either proceed through a sequential (ISC followed by HT)<sup>[12]</sup> or a concerted mechanism (Fig. 2). The overall rate constant of the sequential mechanism,  $k_{seq}$ , has contributions from the individual steps: ISC, reverse ISC, and HT, with associated rate constants  $k_{ISC}$ ,  $k_{rISC}$ , and  $k_{HT}$ , respectively:

$$k_{seq} = \frac{k_{HT}k_{ISC}}{k_{rISC} + k_{HT}} \quad (1)$$

The rate constant for the concerted mechanism is simply  $k_{concerted}$ , since it is a one-step process.

Rate constants for adiabatic reactions are typically calculated using transition state theory (TST) and those for nonadiabatic reactions using nonadiabatic transition state theory (NA-TST).<sup>[13]</sup> However, these methods cannot account for quantum tunnelling effects, which are expected to be an important factor in these reactions. Therefore, we used instanton theory, which is a generalization of these classical rate theories. Instanton theory is a semiclassical approach based on the path-integral formulation of quantum mechanics.<sup>[14,15]</sup> It uses classical-like tunnelling paths instead of wavefunctions, making it computationally efficient. Moreover, since an optimal tunnelling pathway is obtained, along with rate

constants that can be compared to experiments, it also provides mechanistic insights.

For the adiabatic rate constant,  $k_{HT}$ , adiabatic instanton theory<sup>[16]</sup> was used, and the rate is given by

$$k_{inst}^A = \frac{2}{\beta\hbar} \frac{Z_{inst}^A}{Z_R} e^{-S_A/\hbar} \quad (2)$$

where  $\beta = 1/k_B T$  is the reciprocal temperature,  $S_A$  is the action of the path on the singlet state,  $Z_R$  is the reactant partition function and  $Z_{inst}^A$  accounts for the fluctuations around the instanton. At high temperatures, this instanton path collapses to the transition state, thus recovering classical TST results.

For the ISC rate constants,  $k_{ISC}$  and  $k_{rISC}$ , nonadiabatic instanton theory<sup>[17]</sup> was used. This is a semiclassical approximation to Fermi's golden-rule with the rate constant

$$k_{inst}^{NA} = \sqrt{2\pi} \frac{\beta\Delta^2}{\hbar} \frac{Z_{inst}^{NA}}{Z_R} e^{-S_{NA}/\hbar} \quad (3)$$

where  $\Delta$  is the spin-orbit coupling, and  $S_{NA}$  is the nonadiabatic action which has contributions from both the singlet and the triplet states. At high temperatures, the nonadiabatic instanton collapses to the minimum-energy crossing point between the singlet and triplet surfaces and reduces to NA-TST. Unlike the adiabatic instanton which describes a tunnelling pathway connecting the reactant side to the product side on the same surface, a nonadiabatic instanton spans both surfaces and is connected by a hopping point (where the instanton switches from one surface to another).

In the sequential mechanism, HT is adiabatic while ISC is a nonadiabatic step, such that both variants of instanton theory were used separately. The concerted mechanism is also classified as a nonadiabatic process and is defined as a saddle point of  $S_{NA}$ . Interestingly, this instanton has some unique features which distinguish it from ordinary nonadiabatic instantons used in our previous work.<sup>[18–21]</sup> First, the hopping point is not the highest energy point along the instanton, and second, there is no high-temperature equivalent for this instanton. Therefore, this pathway only exists at low temperatures and disappears as the temperature increases. In addition to the nonadiabatic ISC from triplet to singlet, the instanton must also tunnel under the singlet potential energy barrier, as in an adiabatic reaction. Therefore, it combines aspects of adiabatic and nonadiabatic instantons. Nonetheless a careful derivation from first principles shows that it can be evaluated by applying Eqn. (3) to the concerted pathway.<sup>[22]</sup>

Practically, instantons can be optimized by a code developed in-house which requires potentials, gradients and Hessians calculated by standard electronic-structure packages. In this instance, we used ORCA 6.0<sup>[23]</sup> with the B2-PLYP functional and a triple- $\zeta$  basis set (def2-TZVPD). An empirical shift was included to correct the singlet–triplet gap, which can be poorly described by DFT.

We found that HT was the rate-determining step in the sequential mechanism, implying that we can employ a pre-equilibrium approximation,

$$k_{seq} \approx \frac{k_{ISC}}{k_{rISC}} k_{HT} = K_{eq} k_{HT} \quad (4)$$

Here,  $K_{eq}$  is the equilibrium constant between the singlet and triplet states of the reactant, which can be approximated as  $K_{eq} \approx \frac{1}{3} \exp(-\beta\Delta E_R)$ , where  $\Delta E_R$  is the difference in potential energy between the triplet and singlet states of the reactant.

The half-lives calculated using instanton theory were compared with experimental measurements (Table 1). Note that perfect agreement between experiment and theory cannot be expected due to the intrinsic errors of DFT, the instanton approximation and the neglect of environmental effects. However,

Table 1. Experimental half-lives compared with those calculated from instanton theory.

Carbene	Expt.	Sequential	Concerted
<b>C1</b> (10 K)	68 h	$6.4 \times 10^{21}$ y	105 h
<b>C2</b> (12 K)	> 24 h	$4.7 \times 10^{33}$ y	257 h
<b>C3</b> (14 K)	> 28 h	$6.3 \times 10^{29}$ y	491 h
<b>C1</b> (65 K)	NA <sup>[a]</sup>	11 min	105 h
<b>C2</b> (65 K)	40 min	116 min	252 h
<b>C3</b> (40 K)	> 28 h	$7.8 \times 10^2$ y	491 h

<sup>[a]</sup>No experiment performed.

we do expect qualitative agreement allowing us to determine the mechanism. The experimental half-life of **C1** at 10 K has the same order of magnitude as that calculated for the concerted pathway. On the other hand, for **C2**, the experimental half-life at 65 K is consistent with that calculated for the sequential pathway. In the case of **C3**, the calculated half-lives are very long at both temperatures and for both mechanisms, which is again consistent with the experiment.

**C2** presents an interesting case where the reaction was observed only upon heating. Our calculations (Table 1) show that the dominant mechanism switches from the concerted to the sequential process as the temperature is raised. An Arrhenius plot (Fig. 3) of the two rates shows that there is a crossover at about 52 K. This is consistent with the experiment, which reported a steady increase in the reaction on heating above 55 K.<sup>[9]</sup>

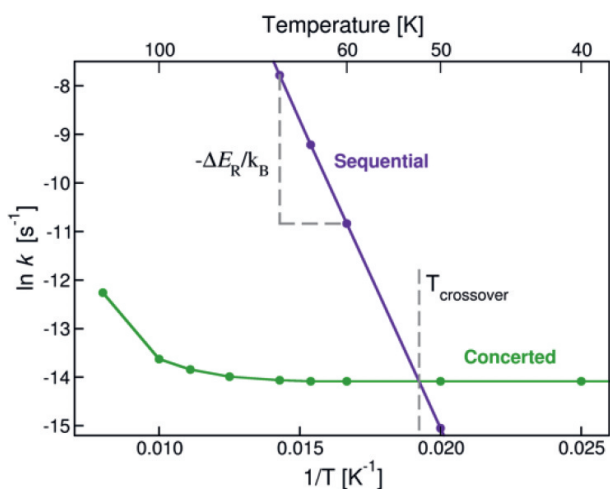


Fig. 3. Arrhenius plot showing how  $k_{\text{seq}}$  and  $k_{\text{concerted}}$  depend on temperature for **C2**. The slope of the sequential pathway,  $-\Delta E_{\text{R}}/k_{\text{B}}$ , gives the singlet–triplet energy gap. The plot is qualitatively similar for **C1** and **C3**. Figure adapted from ref. 7.

This motivated us to calculate rates of the sequential mechanism at higher temperatures for **C1** and **C3** as well. In a similar way, we saw the dominant mechanism switch to the sequential pathway at crossover temperatures of 45 K and 55 K, respectively. The existence of the crossover temperature can be rationalized by the fact that the first step in the sequential pathway, ISC, is energetically uphill and is thus a thermally-activated step. This compulsory energy cost to reach the  $R_{\text{S}}$  intermediate is only affordable at higher temperatures. However, following ISC, HT proceeds relatively quickly since the barrier is low and hydrogen is light enough to tunnel. The Arrhenius plot of  $k_{\text{seq}}$  is thus linear with a slope that corresponds to the energy gap between  $R_{\text{T}}$  and  $R_{\text{S}}$ . The concerted pathway does not have to visit the  $R_{\text{S}}$  state,

and therefore is approximately independent of temperature in the deep-tunnelling regime. We believe this crossover temperature will be a common feature for many triplet carbenes.

### 3. Conclusions

This article summarized the work of ref. [7], in which we used instanton theory to discover the reaction mechanisms and calculate rate constants in three triplet carbenes. Two pathways – one sequential and one concerted – were tested as possible reaction mechanisms. The sequential mechanism was modelled using both adiabatic and nonadiabatic instanton theory. The concerted mechanism required a new type of instanton. The fact that it was possible to generalize instanton theory in this way underlines its versatility to uncover previously unknown mechanisms.

The aim of this work was to explain the observed differences in the reactions of the three carbenes. However, we found that the three carbenes are quite similar in that both mechanisms exist as available channels for the reaction. The difference arises in the temperature ranges in which the individual mechanisms dominate, leading to a crossover temperature. While experiments have not been performed for **C1** at high temperatures, and experiments for **C3** were restricted to 40 K due to the Argon matrix used, we predict that if heated above their respective crossover temperatures, the sequential pathway will become the dominant reaction mechanism. Due to its Arrhenius-like behavior, the rate will then accelerate rapidly even for small increases in temperature.

We believe the concerted mechanism may also exist in many other molecules involving HT and ISC. Most excitingly, it may be possible to use temperature to modify the reactivity of triplet carbenes by switching between the two mechanisms, which if designed carefully may give control over product yields.

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