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The Paternò–Büchi reaction: importance of triplet states in the excited-state reaction pathway[†]‡

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The Paternò–Büchi (PB) reaction between an excited carbonyl compound and an alkene has been widely studied, but so far little is known about the excited-state dynamics of the reaction. In this investigation, we used a compound in which a formyl and a vinyl group are attached to a [2.2]paracyclophane in order to obtain a model system in pre-reactive conformation for the PB reaction. We studied the excited-state dynamics of the isolated molecule in a molecular beam using femtosecond time-resolved photoelectron spectroscopy and *ab initio* calculations. The results show that inter-system crossing within two picoseconds competes efficiently with the reaction in the singlet manifold. Thus, the PB reaction in this model system takes place in the triplet state on a time scale of nanoseconds. This result stresses the importance of triplet states in the excited-state pathway of the PB reaction involving aromatic carbonyl compounds, even in situations in which the reacting moieties are in immediate vicinity.

1 Introduction

The cycloaddition between a photoexcited carbonyl group and an alkene to form a four-membered cyclic ether (oxetane), named the Paternò–Büchi (PB) reaction,^{1,2} has been extensively used in preparative chemistry^{3–6} and widely studied from a mechanistic perspective.^{2,7–14} The reaction is induced by exciting the (n,π^*) state of the carbonyl group containing molecule, and has a high regio- and stereoselectivity. Zimmerman suggested that the selectivity is governed by a non-concerted mechanism in which a 1,4-biradical intermediate is formed upon attack of the C=O group on the alkene moiety.⁸ As shown in Fig. 1 there are two types of 1,4-biradicals, resulting from either C (1) or O attack (2). The regioselectivity of the reaction was inferred from the stability of these 1,4-biradicals, *i.e.* that the major product is





Fig. 1 Scheme illustrating the Paternò–Büchi reaction between photoexcited formaldehyde and ground state ethylene to form oxetane. The reaction can proceed through either of two biradical intermediates, one resulting from C–C (1) and one from C–O attack (2).

formed from the most stable biradical.⁸ This step-wise mechanism was supported by results from experiments on the PB reaction between benzophenone and dioxene in which a triplet C–C 1,4-biradical intermediate was observed and its lifetime determined to be on the order of nanoseconds (ns).^{9,10} The reason for the long lifetime of the triplet biradical is that ring closure to form the oxetane has to be preceded by the forbidden process of a spin flip, as opposed to a reaction in the singlet state. A more detailed understanding of the excited-state dynamics of the reaction was achieved by computational work on the prototype system formaldehyde–ethylene by Palmer *et al.*¹¹ They revealed the presence of two conical intersections (CIs) between the singlet state ${}^1(n,\pi^*)$ and the ground state, corresponding to C–O and C–C bond formation, respectively.

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The CI corresponding to C–C bond formation is situated very close to the products on the potential energy surface (PES), meaning that ring closure to form the four-membered oxetane ring on the ground state can occur without involving any intermediates. By contrast, the CI corresponding to C–O bond formation is situated close to the reactants on the PES, and passage through this CI leads to an intermediate C–C 1,4-biradical, where ring closure to form the oxetane ring in the ground state is associated with a barrier. Studies of the photodissociation of oxetane have provided some insight in the retro PB reaction; both product kinetic energy distributions¹⁵ and femtosecond (fs) time-resolved mass spectrometry¹⁶ point to an ultrafast dissociation with the singlet reaction being the dominant reaction pathway.¹⁵

In general, aliphatic ketones react via the (n,π^*) state,^{3,17} whereas the high intersystem crossing (ISC) rates of aromatic carbonyl compounds¹⁸ means that PB reactions involving these species occur almost exclusively through the triplet state.^{3,7,17} What distinguishes the singlet from triplet pathways is the excited-state dynamics of the PB reaction, *i.e.* whether there is a 'detour' via ISC from ${}^{1}(n,\pi^{*})$ to the triplet state manifold or the entire reaction occurs in the singlet state manifold. Palmer et al. calculated the geometries and energies of the triplet biradicals in the formaldehyde-ethylene model system to be quite similar to their singlet counterparts.¹¹ They concluded that whether the ground state is populated from the triplet excited state via ISC, or from the singlet excited state via internal conversion (IC), does not significantly affect the final part of the reaction taking place in the ground state. Recent experimental work indicates that this is not the case if the reactants are substituted, however, since the conformations mediating efficient ISC in the long-lived triplet biradicals result in a different regio- and stereoselectivity than that obtained in the singlet state pathway in which the lifetime of the biradicals is much shorter.¹⁴

In this work we present a fs time-resolved study of the PB reaction with the aim of providing new insights into the excited-state dynamics of the reaction, focusing on the interplay between the singlet and triplet manifolds. To obtain the clearest picture of the reaction, free from solvent effects, we conducted experiments on isolated molecules in the gas phase. In the present study, we use pseudo-*gem*-vinylformyl[2.2]paracyclophane (GEM, Fig. 2) as a model system for investigating the dynamics of the PB reaction. The validity of using this compound as a model



Fig. 2 The pseudo-*gem*-vinylformyl[2.2]paracyclophane (GEM) and pseudo-*para*-vinylformyl[2.2]paracyclophane (PARA) compounds used in the experiments. GEM is shown in two conformers, the *anti–anti* (aa) and the *anti–syn* (as), that will be mentioned later.

system is experimentally confirmed, since the PB reaction product was isolated posterior to irradiation of GEM in solution.¹⁹ The pseudo-*para*-isomer of GEM (PARA, Fig. 2), in which the functional groups cannot react, was used as a reference compound to account for effects of the paracyclophane scaffold. Being an aromatic carbonyl compound, ISC should be very efficient in GEM, making it suitable for studying the interplay between the singlet and triplet state dynamics in the PB reaction. The excited-state dynamics of the isolated molecules in a molecular beam was studied using fs time-resolved photoelectron spectroscopy^{20–31} (TRPES) and the experimental results supplemented by *ab initio* calculations.

2 Experimental

2.1 Compounds

Pseudo-*gem*-vinylformyl[2.2]paracyclophane (GEM) was synthesized as described by Hopf and co-workers.¹⁹ The synthesis of the pseudo-*para*-isomer (PARA) is described in the ESI.[‡]

2.2 X-ray single crystal diffraction

Crystal data: The pseudo-gem-vinylformyl[2,2]paracyclophane, $C_{19}H_{18}O, M_r = 262.33$, monoclinic, $P2_1/n, a = 7.5369(7), b =$ 10.9410(9), c = 16.6813(16) Å, $\beta = 102.521(4)$, V = 1342.8 Å³, Z = 4, λ (Mo K α) = 0.71073 Å. Data collection: A colourless plate ca. $0.45 \times 0.35 \times 0.20$ mm was mounted on Bruker Kappa APEXII diffractometer. A total of 28853 data were recorded to 2θ 66°, of which 5244 were independent (R_{int} 0.023). Structure refinement: The structure was refined using SHELXL-97.³² The terminal C=O group was modeled as being disordered (60 : 40) over two sites (related by $\sim 180^{\circ}$ rotation about the attached C-C bond). For the disordered carbon atoms the bond distances, bond angles and thermal parameters were restrained. The hydrogen atoms were placed in calculated positions and refined using a riding model. The final R2 (all reflections) was 0.177 for all intensities and 194 parameters (4 restraints) with $R1 (I > 2\sigma(I)) 0.060; S 1.06.$

2.3 Spectroscopic methods

The UV-Vis gas phase absorption spectra were recorded with a Varian 5e (GEM) and a PerkinElmer Lambda 1050 spectrophotometer (PARA) by subliming the solid at 120 $^{\circ}$ C in homemade cells with an optical path length of 10 cm.

TRPES experiments were performed by combining a femtosecond laser system with a supersonic molecular beam magnetic bottle time-of-flight photoelectron spectrometer. The molecular beam magnetic bottle apparatus has been described in detail elsewhere.³³

The femtosecond laser system consisted of a Ti:Sapphire oscillator (Spectra Physics, Tsunami, 80 MHz, 800 nm, 80 fs) pumped by a Nd:YLF diode laser (Spectra Physics, Millenia). The output of the oscillator was amplified by a Ti:Sapphire regenerative amplifier (Coherent, Legend, 1 kHz, 100 fs) pumped by two Nd:YLF lasers (Positive Light, Evolution). Femtosecond laser pulses of wavelengths $\lambda_p = 256$ nm or $\lambda_p = 320$ nm were used in the pump step of the experiment. Pulses of $\lambda_p = 256$ nm were generated by non-collinear sum frequency mixing of the fundamental with the output of an optical parametric

amplifier (TOPAS, Light Conversion), followed by frequency doubling. Pulses of $\lambda_{\rm p} = 320$ nm were generated by the fourth harmonic of the output of the TOPAS. For the probe step we used the second harmonic ($\lambda_{\rm e} = 400$ nm) of the fundamental. Pulse energies for $\lambda_{\rm p} = 256$ nm, $\lambda_{\rm p} = 320$ nm and $\lambda_{\rm e} = 400$ nm were 2.0 µJ, 1.2–2.2 µJ and 17–20 µJ, respectively. The pulses were focused mildly into the interaction region by a f/100 concave Al mirror.

The temporal cross correlation between the pump and probe pulses was determined using [1,2'] ionization of NO to be 150 ± 10 fs. The time delay between the pump and the probe pulse was computer controlled by a motorized linear translation stage. At each time delay, the pump-probe signal was determined from the total signal by subtracting the background signal due to electrons generated by the pump and probe pulses alone.

In the interaction region, a high intensity, supersonic molecular beam propagated perpendicular to the incoming laser pulses. The beam was generated by a 1 kHz Even–Lavie valve³⁴ with a 250 μ m diameter conical nozzle.³⁵ Helium was used as carrier gas with a backing pressure of 3 kTorr. The solid sample was introduced into the body of the valve and sublimed by heating the valve to 120–130 °C. To prevent condensation of solid sample in the valve opening, the nozzle was heated by a separate heater to keep its temperature approximately 20 °C higher than the temperature of the body, but still below the decomposition temperature of the compounds. The photoelectron kinetic energies were calibrated using the well known photoelectron spectrum of NO.³⁶

2.4 Computational

Ground state optimized geometries and frequencies were determined at the B3LYP/6-31G(d) level of theory using Gaussian 03.37 TURBOMOLE V5.8 was used to calculate RI-CC2/cc-pVDZ vertical singlet^{38,39} and triplet⁴⁰ excitation energies at these geometries. State-averaged complete active space self consistent field (SA-CASSCF) calculations were performed using MOLPRO 2010.1.41 A conical intersection (CI) between S_1 and S_0 corresponding to C–O attack was located using SA-CASSCF(6,5)/6-31G(d). The active space in the CAS calculations consisted of six electrons distributed among the oxygen lone pair and the π orbitals as well as the two lowest unoccupied π^* orbitals. Near the CI, these orbitals are primarily localized on the formyl and vinyl groups, justifying the use of the limited active space. The excited-state part of a PB reaction path corresponding to C-O attack was defined by a linear interpolation in internal coordinates between the FC structure and the structure at the CI. Potential energy curves along this path were constructed from vertical excitation energies calculated using RI-CC2/cc-pVDZ.

3 Results

3.1 Gas phase absorption spectra

The UV absorption spectra of GEM and PARA are shown in Fig. 3. Importantly, the spectra are quite similar, indicating a corresponding similarity of the electronic structures of the two molecules. This justifies using PARA as a non-reactive counterpart to GEM, making the former an important reference



Fig. 3 Gas phase UV absorption spectra of GEM and PARA, arbitrarily normalized to the maximum around 260 nm.

when interpreting the time-resolved experimental results. The absorption maxima corresponding to the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions are not clearly distinguishable, but maxima have been tentatively assigned to 310–315 nm and 340 nm, which fit well with the spectrum of GEM recorded in ethanol solution.¹⁹ Further to the blue part of the spectrum, there are more well-defined maxima at 256 and 259 nm for GEM and PARA, respectively.

3.2 Crystal structure determination

Only data from crystals of GEM has been recorded. Two conformers are present in the crystal in the ratio 40 : 60; the *anti–anti* and *anti–syn* conformers shown as overlayed structures in Fig. 4. Based on previous experience⁴² and crystal data obtained on pseudo-*gem*-diformyl[2.2]paracyclophane⁴³ it is anticipated that the two conformers of GEM can interconvert at the low temperatures of the diffraction experiment, indicating that the barrier for rotation of the formyl group is exceedingly small.

3.3 Computational results

3.3.1 Pseudo-gem-vinylformyl[2.2]paracyclophane. As presented above, both the *anti–anti* and *anti–syn* conformers of GEM are present in the crystal. Hence, both conformers will be present in the molecular beam after sublimation of the solid sample. Thus, we have optimized the geometries of both conformers and calculated vertical excitations to singlet states in order to obtain insights into their electronic structure in the Franck–Condon (FC) region. In Table 1, the calculated excitation energies are listed together with the experimental values obtained from the gas phase absorption spectra.



Fig. 4 Crystal structures of the *anti–anti* and *anti–syn* conformers (see Fig. 2) of GEM, shown overlayed.

 Table 1
 RI-CC2/cc-pVDZ singlet excitation energies (oscillator strengths) of GEM (anti-anti and anti-syn conformer) and PARA compared to experimental values obtained from the gas phase absorption spectra. Energies are in eV

GEM				PARA	
	Calc. anti-anti	Calc. anti-syn	Exp.	Calc.	Exp.
$S_1(n,\pi^*)$ $S_2(\pi,\pi^*)$ $S_2(\pi,\pi^*)$	$3.80 (7.7 \times 10^{-5}) 4.09 (2.7 \times 10^{-3}) 4.30 (1.6 \times 10^{-2})$	$\begin{array}{c} 3.79 \ (3.1 \times 10^{-4}) \\ 4.10 \ (3.1 \times 10^{-3}) \\ 4.25 \ (1.5 \times 10^{-2}) \end{array}$	3.8 4.1 4.8	$\begin{array}{c} 3.80 \ (1.3 \times 10^{-4}) \\ 4.07 \ (1.4 \times 10^{-3}) \\ 4.33 \ (2.2 \times 10^{-2}) \end{array}$	3.8 4.0 4.8



Fig. 5 RI-CC2/cc-pVDZ orbitals involved in the most important configurations describing the lowest excited states of GEM.

The orbitals involved in the lowest lying electronic states of the *anti–anti* conformer are shown in Fig. 5 (those of the *anti–syn* conformer are practically identical – see ESI[‡]).

The most important configuration in the description of the S₁ state is an $(n(O),\pi^*)$ excitation. The S₂ state is mainly a (π_a,π^*) excitation, whereas the most important configuration in the S₃ state is (π_b,π^*) . The S₁ state is expected to be the reactive state in a PB reaction, analogously to the (n,π^*) state in the formaldehyde–ethylene model system. The S₃ state is interesting because of its pronounced similarity to the reactive (π,π^*) state in the [2+2]cycloaddition in the pseudo-gem-divinyl[2.2]paracyclophane studied recently.⁴⁴

Since the focus of this work is on the interplay between the excited-state singlet and triplet manifolds in the PB reaction, the triplet states of interest are the ones located below the reactive S₁ state and therefore available for ISC. Table 2 shows the RI-CC2/cc-pVDZ calculated excitation energies of the first four triplet states, three of which lie energetically below S₁. Note that at the FC geometry, the order of the (n,π) and (π,π^*) states is reversed in the triplet as compared to the singlet state.

To investigate how the PB reaction in GEM compares to the prototype reaction between formaldehyde and ethylene, we conducted a search for S_1/S_0 CIs which might be similar to those found by Palmer *et al.*¹¹ As it is generally accepted that C–O attack is favored for electron rich alkenes³ such as GEM,

 Table 2
 RI-CC2/cc-pVDZ excitation energies of the first four triplet states of GEM (anti-anti and anti-syn conformer) and PARA. Values are in eV

	GEM		
	anti–anti	anti-syn	PARA
$T_1(\pi,\pi^*)$	3.23	3.27	3.20
$T_{2}(n,\pi^{*})$	3.42	3.43	3.42
$T_{3}(\pi,\pi^{*})$	3.56	3.54	3.56
$T_4(\pi, \pi^*)$	3.91	3.95	3.90



Fig. 6 The geometry, gradient difference (g) and derivative coupling (h) vectors at the S₁/S₀ CI corresponding to C–O attack in the PB reaction in GEM. Distances are in Å.

we focused on the CI corresponding to C–O attack. The structure, the gradient difference (g) and derivative coupling (h) vectors at the CI are shown in Fig. 6 and are very similar to the parameters obtained by Palmer *et al.*¹¹ This indicates that the PB reaction commencing through C–O attack in GEM proceeds along a pathway that is very similar to the PB reaction between ethylene and formaldehyde. An RI-CC2/cc-pVDZ calculation shows that the CI is situated 3.4 eV above the ground state minimum which is 0.4 eV below the S₁-energy in the FC region, indicating that the CI is energetically accessible.

It is desirable to calculate a minimum-energy path in the S_1 state from the FC region to the CI, since that would give an idea about the path the wave packet follows in the excited-state part of the PB reaction. At the CASSCF level, this would require a balanced description of the electronic structure of the S_1 state along the entire path, a requirement that the CAS(6,5) does not fulfill and that would only be satisfied by including all the π electrons in the paracyclophane scaffold in the active space – a prohibitively expensive computational task. Instead, potential



Fig. 7 RI-CC2/cc-pVDZ potential energy curves of the ground state and first three singlet (solid) and triplet (dashed) adiabatic excited states along an approximated excited-state PB reaction path, corresponding to C–O attack in GEM. The curves were constructed from vertical excitation energies calculated at geometries defined through a linear interpolation in internal coordinates from the FC (0) to the S_1/S_0 CI structure (21).

energy curves of the first three singlet and triplet adiabatic excited states were calculated at the RI-CC2 level along an approximated path of the excited-state part of the PB reaction corresponding to C–O attack. The path was constructed by linear interpolation in internal coordinates from the FC to the CI structure and the resulting potential energy curves are shown in Fig. 7.

We note the presence of a small barrier along the curve of the reactive S₁ state. This is not a definite proof of an excitedstate barrier in the PB reaction in GEM, though, since a barrier-free path could exist. Interestingly, the adiabatic T₁ state is indeed reactive in the PB reaction, although it has (π,π^*) character in the FC region. This is due to strong mixing between the (n,π^*) and (π,π^*) states along the pathway, which is present in both the singlet and triplet state manifold. This mixing is important for the interpretation of the time-resolved photoelectron spectra, since it means that the states are likely to show corresponding ionization correlations,⁴⁵ *i.e.* they all ionize to the electronic ground state of the cation.

Finally it is important to note that quite near the FC region there is a crossing between the $S_1(n,\pi^*)$ and the $T_3(\pi,\pi^*)$ state. According to El-Sayed's rules^{46–48} ISC between S_1 and T_3 will be allowed, since in this case the change in spin is accompanied by a change in orbital angular momentum. Furthermore, according to the energy gap law^{17,18} ISC is most efficient for isoenergetic states and the S_1/T_3 crossing is therefore important, since it means that it is likely that ISC will compete efficiently with the singlet state reaction pathway of the PB reaction.

3.3.2 Pseudo-*para*-vinylformyl[2.2]paracyclophane. Since we use PARA as a reference compound in this study, it is important to confirm that the electronic structures of the excited states are quite similar to those of GEM. We therefore optimized the ground state geometry of PARA and calculated singlet excited states from this structure. The vertical excitation energies are shown in Table 1. The values are, within the accuracy of the method, identical to those of GEM, agreeing with the similarity of the corresponding absorption spectra. Also the orbitals involved in the most important configurations of the excited states are almost identical to those of GEM (see the ESI[‡]).

The similarity between PARA and GEM carries over to the triplet states and vertical excitation energies at the FC structure shown in Table 2. This means that PARA can work as a reference system for the ISC rate in a case where the PB reaction channel is not present.

3.4 Time-resolved photoelectron spectra

TRPES data was recorded using two different pump wavelengths, $\lambda_p = 320$ nm and $\lambda_p = 256$ nm. In both cases the probe wavelength was $\lambda_{\rm e} = 400$ nm. Although the exact ionization potentials (IPs) for GEM and PARA are not known experimentally, they can be estimated from photoelectron spectroscopy data on a series of vinyl-substituted [2.2]paracyclophanes reported by Yang et al.⁴⁹ As previously mentioned, all excited states are likely to ionize to the D_0 state of the cation. As can be seen from Fig. 5 the HOMO (π_b) has almost no density at the formyl group. Thus, we approximate the IP of GEM to be similar to the IP of the molecule without the formyl group, determined to be 8.0 eV.⁴⁹ Since the HOMO of PARA (not shown) exhibits the same properties as the HOMO of GEM, the IP of PARA is likewise approximated to the same value. For comparison, the IPs of pseudo-gem and pseudo-para-divinyl[2.2]paracyclophane are 7.8 and 7.9 eV, respectively,⁴⁹ supporting this approximation.

Time constants and decay-associated photoelectron spectra were determined by fitting the TRPES data set $S(\Delta t, E)$ to the following expression, using a Levenberg–Marquardt global fitting routine

$$S(\Delta t, E) = \sum_{i} A_i(E) P_i(\Delta t) \otimes g(\Delta t)$$

where the decay-associated spectrum (DAS) $A_i(E)$ represents the fitted amplitudes across the kinetic energy spectrum of the time-dependent population $P_i(\Delta t)$ of the *i*th channel, convolved with the experimentally determined Gaussian cross-correlation $g(\Delta t)$. For further details, see ref. 50.

3.4.1 Pseudo-para-vinylformyl[2.2]paracyclophane. For PARA, only data with $\lambda_p = 315$ nm were recorded. The resulting TRPES spectrum is shown in Fig. 8(c). From the IP and the total photon energy of one pump and two probe photons, the maximum kinetic energy of the photoelectrons in the [1,2'] ionization scheme is 2.2 eV. The data analysis will focus on the [1,2'] region of the spectrum. The PE spectrum is broad and has no obvious structure. We made the same observation in TRPES experiments on divinyl[2.2]paracyclophanes⁴⁴ and discussed it in terms of inhomogeneous broadening caused by an ensemble of conformations having different twist angles of the vinyl groups with respect to the benzene rings. Accordingly, this should apply to the formyl group as well. Furthermore, in a series of REMPI experiments on substituted [2.2]paracyclophanes, Schon et al. observed extended progressions of largeamplitude vibrations involving the paracyclophane scaffold.51,52 Those progressions are likely to be present in our PE spectra as well, however insufficient energy resolution makes them appear as a broadening of the spectra. The spectrum was fitted to a biexponential decay with time constants of 130 \pm 20 fs and 1.7 ± 0.2 ps as well as a constant offset component, which represents a signal that lives indefinitely on the time scale of our experiment. The DAS are shown in Fig. 9(c).



Fig. 8 TRPES spectra of GEM and PARA. In all experiments a probing wavelength of $\lambda_e = 400$ nm was used. (a) GEM excited at $\lambda_p = 320$ nm. (b) GEM excited at $\lambda_p = 256$ nm. (c) PARA excited at $\lambda_p = 315$ nm.

3.4.2 Pseudo-gem-vinylformyl[2.2]paracyclophane. For GEM, data with pump wavelengths of $\lambda_p = 320$ nm and $\lambda_p = 256$ nm, respectively, were recorded. In both experiments a probe wavelength of $\lambda_e = 400$ nm was used. The corresponding TRPES spectra are shown in Fig. 8(a) and (b), respectively. In a [1,2'] ionization scheme, the maximum kinetic energy of the photoelectrons is 2.1 eV and 3.1 eV in the $\lambda_p = 320$ nm and $\lambda_p = 256$ nm experiment, respectively. The data analysis will focus on the [1,2'] region of the spectra. The spectrum in the $\lambda_p = 320$ nm experiment is very similar to that of PARA discussed above.

The data recorded at $\lambda_p = 320$ nm was fitted to a biexponential decay with time constants of 110 ± 15 fs and 1.8 ± 0.2 ps as well as a constant offset component. The corresponding DAS are shown in Fig. 9(a). The similarity of the fits to the PARA and GEM data at this pump wavelength is striking.

For the data recorded with $\lambda_p = 256$ nm, we observe the low kinetic energy part of the spectrum to be delayed in time as compared to the high kinetic energy part (not visible to the eye in Fig. 8(b)). This is the signature of a lower lying state being populated by IC from the initial state excited at the FC geometry.



Fig. 9 Decay-associated spectra obtained from global fits of the corresponding TRPES spectra in Fig. 8.

That process converts electronic to vibrational energy, thereby shifting the signal to lower kinetic energies. Thus, the best fit was obtained by using three exponential decays as well as a constant offset component. The DAS are shown in Fig. 9(b). The temporal shift in the TRPES data is modeled by the fit in the spectrum associated with a 50 ± 10 fs time-constant; the negative amplitude in the low-energy region shows that this part of the spectrum rises on the same ultrashort time-scale as the high energy part decays. The temporal shift is illustrated in Fig. 10 that displays energy-integrated slices of the TRPES



Fig. 10 Energy-integrated and normalized slices (dots) of the TRPES spectrum shown in Fig. 8(b), as well the corresponding slices of the global fit function (solid lines). The slices are obtained from a low and a high kinetic energy region, respectively, illustrating the initial ultrafast shift of the signal.

spectrum and the global fit function in two different energy regions. The ultrafast temporal shift is followed by a biexponential decay (to a constant offset) which is described by time constants of 110 ± 15 fs and 1.7 ± 0.2 ps, values which are virtually identical to those obtained from GEM in the experiments with $\lambda_p = 320$ nm, as well as the data obtained from PARA.

4 Discussion

4.1 Pseudo-para-vinylformyl[2.2]paracyclophane

Upon excitation with $\lambda_p = 315$ nm the S₂ state is reached. Thus, the two time constants of 130 fs and 1.7 ps represent the decay of the S_2 and the S_1 state, respectively. The offset component is thereby assigned to a state in the triplet manifold. This assignment is supported by the fact that the DAS of the offset component is shifted towards lower kinetic energies as compared to the DAS assigned to the S_1 state, indicating that the former represents ionization of a state that lies energetically below S_1 . The most interesting finding from the reference experiment is that ISC from S₁ proceeds in less than two ps. The high ISC rate indicates that the population in the (n,π^*) state is transferred to a (π,π^*) state (likely T₃) according to El-Sayed's rules. Since the time scale of ISC is an order of magnitude shorter than the reaction time for [2+2]cycloaddition in pseudo-gem-divinyl[2.2]paracyclophane that we investigated recently,⁴⁴ we claim that ISC can compete with any reactive dynamics in the S_1 state of GEM.

4.2 Pseudo-gem-vinylformyl[2.2]paracyclophane

As in PARA, excitation of GEM at $\lambda_p = 320$ nm populates the S₂ state. This allows for a similar assignment of the decay times: the lifetime of the S₂ state in GEM is 110 ± 15 fs, whereas the S₁ state is depopulated in 1.8 ± 0.2 ps. Importantly, the offset component assigned to the triplet state is also present in the GEM data. The finding that the S₁ lifetime is not reduced as compared to PARA, leads to the conclusion that ISC competes very efficiently with the singlet PB reaction, making the latter a minor decay pathway in GEM.

As mentioned in the introduction, the PB reaction was established as a major decay pathway following photoexcitation.¹⁹ As the TRPES results do not provide explicit evidence of the product of the PB reaction, we assume this to be situation in the gas phase as well. Based on this assumption and the fact that there is no notable difference in the lifetimes of the singlet states in GEM and PARA, we claim that the reaction predominantly takes place on the triplet state manifold. As mentioned in the introduction this is also the case in PB reactions involving aromatic ketones in solution.^{3,7,17} Most likely ISC in GEM occurs to $T_3(\pi,\pi^*)$ which can decay by IC to the reactive $T_2(n,\pi^*)$ state. The presence of this reactive pathway in GEM seems to disagree with the fact that the lifetime of the triplet state is more than one ns (the value cannot be extracted from the fit, since data was not recorded for time delays longer than 700 ps) in both PARA and GEM. However, it should be remembered that the PB reaction in the triplet state will lead to a triplet biradical that has to undergo ISC to decay to S_0 , which is an inherently slow process that takes place on the order of ns or even longer (see introduction). Thus, the reaction channel available in GEM does not shorten the lifetime of the triplet state as compared to PARA to an extent that a difference between the molecules could be observed in our experiment.

In the experiment with $\lambda_p = 256$ nm, the pump pulse excites the $S_3(\pi,\pi^*)$ state which, as mentioned in the computational section, could lead to a cycloaddition reaction that resembles the concerted [2+2]cycloaddition leading to the dimerization of ethylene. Such a concerted reaction is interesting because the mechanism is conceptually different to the step-wise PB cycloaddition reaction involving a biradical ground state intermediate. The lifetime of the S₃ state is reflected in the first time constant of the fit, $\tau_1 = 50$ fs. From the fit, it is not possible to conclude whether S₃ decays to S₂ and S₁ *via* a sequential or a parallel process. The last two time constants of 110 fs and 1.7 ps are assigned to the lifetimes of the S₂ and the S₁ state, respectively. These values are listed in Table 3 together with the values obtained from the experiments presented above.

As in the interpretation of the data obtained in those experiments, the constant offset component is assigned to a triplet state. Thus, there is no indication of a concerted photocycloaddition reaction following excitation of the S_3 state; it just decays to populate the lower lying states and eventually to a state in the triplet state manifold, as described above.

Finally, it is worth noting that the measured lifetimes of the S_2 and S_1 states in GEM are identical in the $\lambda_p = 320$ nm and $\lambda_p = 256$ nm experiments. Interestingly, this means that the transition from S_1 to S_0 is not influenced by vibrational energy content to an extent that IC can compete with ISC, even though the reactive S_1/S_0 CI is energetically accessible. Following a Landau–Zener approach,⁵³ one could expect the rate of $S_1 \rightarrow S_0$ population transfer by IC to depend on vibrational

Table 3 Excited-state life times of GEM and PARA extractedthrough global fits of the TRPES spectra shown in Fig. 8. Thecorresponding decay-associated spectra are shown in Fig. 9

	S ₃ (fs)	S ₂ (fs)	S ₁ (ps)
GEM, $\lambda_p = 256 \text{ nm}$ GEM, $\lambda_p = 320 \text{ nm}$ PARA, $\lambda_p = 315 \text{ nm}$	50 ± 10 	$\begin{array}{c} 110 \pm 15 \\ 110 \pm 15 \\ 130 \pm 20 \end{array}$	$\begin{array}{c} 1.7 \pm 0.2 \\ 1.8 \pm 0.2 \\ 1.7 \pm 0.2 \end{array}$

energy content, since then the "speed" of the nuclear trajectory through the region of non-adiabatic coupling will vary. But as recently discussed by Lee et al.54 on the basis of experimental results, it is the magnitude of the velocity along the branching space coordinates which has to vary, in order to increase the rate of the non-adiabatic transition leading to IC. Furthermore, Lee et al. suggest that in the case of sloped CIs55 an increased speed along the seam space coordinates can even decrease the rate of IC.⁵⁴ In other words, in such cases the rate of IC is governed by the relative speeds of the trajectories along the branching and seam space coordinates. Unfortunately, it cannot be assessed whether the PB reaction in GEM represents such a case, since topographical information about the PESs at the CI is not currently available. What can be concluded, however, is that the increased speed of the nuclei does not increase the rate of IC to an extent that it efficiently competes with ISC.

5 Conclusion

With the aim of studying the excited-state dynamics of the Paternò-Büchi (PB) reaction, we have performed time-resolved photoelectron spectroscopy experiments on the model system pseudo-gem-vinylformyl[2.2]paracyclophane (GEM). Reference experiments on pseudo-para-vinylformyl[2.2]paracyclophane (PARA), in which the functional groups cannot react, have been conducted in order to study the influence of the paracyclophane scaffold on the lifetimes of the excited states. The measured singlet state lifetimes in GEM and PARA are nearly identical: the $S_2(\pi,\pi^*)$ state decays in ~100 fs and the $S_1(n,\pi^*)$ state decays to the triplet state manifold in less than two ps. This leads to the conclusion that intersystem crossing competes efficiently with singlet state reaction, such that in GEM the excited-state dynamics of the PB reaction, formation of the C-O bond, takes place in the triplet state. The creation of the C-C bond leading to ring-closure and oxetane formation in the S_0 state has to be preceded by ISC, meaning that the time scale of the second part of the PB reaction in GEM exceeds the range accessible to our experiments.

The most important conclusion to be drawn from this study is that the ISC rate exceeds the rate of singlet state reaction, such that the excited-state dynamics of the PB reaction takes place in the triplet state manifold. This was already known to be the case in bimolecular PB reactions between aromatic carbonyl compounds and alkenes in solution, for which the rate of ISC exceeds the rate of bimolecular collision controlled by diffusion. Interestingly, the PB reaction still occurs *via* the triplet state even when the carbonyl and vinyl groups are in immediate proximity at the moment of excitation, indicating that ISC is an important and natural aspect of these dynamics.

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