Mechanistic Aspects of Ketene Formation Deduced from Femtosecond Photolysis of Diazocyclohexadienone, o-Phenylene Thioxocarbonate, and 2-Chlorophenol

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ⓢ Supporting Information

ABSTRACT: The photochemistry of diazocyclohexadienone (**1**), o-phenylene thioxocarbonate (**2**), and 2-chlorophenol (**3**) in solution was studied using time-resolved UV−vis and IR transient absorption spectroscopies. In these three cases, the same product cyclopentadienyl ketene (**5**) is formed, and two different mechanistic pathways leading to this product are discussed: (a) rearrangement in the excited state (RIES) and (b) a stepwise route involving the intermediacy of vibrationally excited or relaxed carbene. Femtosecond UV−vis detection allows observation of an absorption band assigned to singlet 2-oxocyclohexa-3,5-dienylidene (**4**), and this absorption feature decays with an ∼30 ps time constant in hexane and acetonitrile. The excess vibrational energy present in nascent carbenes results in the ultrafast Wolff rearrangement of the hot species. IR detection shows that photoexcited o-phenylene thioxocarbonate (**2**) and 2-chlorophenol (**3**) efficiently form the carbene species while diazocyclohexadienone (**1**) photochemistry proceeds mainly by a concerted process.
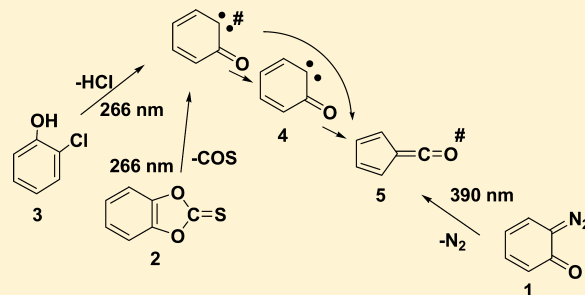
1. INTRODUCTION

Professor Zimmerman is one of the fathers of modern photochemistry and was one of the giants of twentieth century organic chemistry. Although none of the authors of this paper formally studied under Professor Zimmerman, we gratefully acknowledge his intellectual influence on our research and are proud to help honor his legacy in this memorial issue.

The rich photochemistry of diazo carbonyl compounds has been extensively studied and is highly diverse: Wolff rearrangement (WR) and several other intra- and intermolecular chemical processes are all known.[1,2] Intramolecular processes may proceed in the diazo excited state in a concerted process known as RIES (rearrangement in the excited state) and/or by a stepwise (carbene-mediated) process. Historically, the dual mechanisms were deduced from studies of the persistent products formed upon photolysis. Support for the RIES mechanism has been provided by the observation of a "nontrappable carbene" route to rearranged products.[3] The previous failure to directly observe certain carbenes in ultrafast time-resolved experiments and the absence of carbene-specific photoproducts found by steady-state spectroscopy and analysis (UV−vis, IR, NMR, GC−MS) may indicate the occurrence of an

RIES process. As the typical lifetime of a diazo singlet excited state is less than 0.4 ps, the concerted process can be confirmed by a fast product rise (<0.4 ps).

Occasionally, theory supports a concerted mechanism in which case the carbene collapses to the product (ketene, alkene) in a barrierless fashion (below 1 kcal/mol) during optimization.[4,5] In an acyclic singlet carbene, the carbonyl group prefers to be orthogonal to the plane defined by the carbene carbon atom and the two atoms directly bonded to the carbene carbon.[2,4] Incorporating a carbonyl carbene within a small ring enforces planarity (or near planarity). This destabilizes the singlet carbene and thereby accelerates WR; thus, the rigid enforcement of planarity (or near planarity) of the molecule can be a major factor in ketene formation.[4,5]

The stepwise process has been confirmed by detection of carbene species, as well as by the correlation of carbene decay and ketene rise, in time-resolved studies.[6,7] Initially formed carbene species are produced in a vibrationally hot state and undergo

subsequent cooling by collisions with surrounding solvent molecules. Vibrational cooling proceeds with a time constant of a few picoseconds and is manifested by band narrowing of the carbene absorption peak (in both UV–Vis and IR transient absorption experiments) and a blue shift of the absorption maximum.[2] It seems intuitive that nascent, hot carbenes will have greater reactivity than thermalized species.[6,7] In our previous studies of a *p*-biphenylketocarbene, a fast reaction pathway from hot carbene species to ketene was deemed unlikely on the basis of the constant carbene population (as measured by band area) over a 0.8−30 ps time window. This is despite a relatively small energy barrier required for isomerization (calculated to be 4.4 kcal mol^{-1}).[8]

In this paper, we will present studies on a cyclic keto carbene intermediate, 2-oxocyclohexa-3,5-dienylidene (**4**), with a small energy barrier expected for the carbene−ketene isomerization process, as a result of the rigid ring architecture destabilizing the hypothetical carbene species.[4] Excess vibrational energy in a destabilized carbene should have an effect on its chemical reactivity and accelerate the isomerization process, as reported for other classes of molecules.[9,10]

The intermediacy of singlet keto carbene, 2-oxocyclohexa-3,5-dienylidene (**4**), has been proposed in the aqueous phase environmental photochemistry of 2-chlorophenol.[11,12] It is generally accepted that keto carbene isomerizes to cyclopentadiene ketene (**5**), which in water gives cyclopentadiene-carboxylic acid. This photoproduct has been observed for neutral and anionic forms of 2-chlorophenol.[13] All past attempts to detect the keto carbene failed (IR in low-temperature argon matrix, IR spectroscopy, nanosecond time-resolved photolysis).[14−16] In addition to the generation of ketene from the singlet carbene, one can expect the triplet carbene to be produced by intersystem crossing (ISC). In the case of the 2-chlorophenol photochemical precursor, ISC seems to be a minor process (quantum yield of $\Phi_T \sim 0.003$). However, the triplet carbene was clearly observed in laser flash photolysis studies of 2-bromophenol ($\Phi_T \sim 0.04$), identified by a transient absorbing at λ_{max} = 360, 375, and 388 nm in aqueous solution.[15,16] In this paper, we will report the first direct experimental singlet keto carbene detection of, specifically, 2-oxocyclohexa-3,5-dienylidene (**4**).

The mechanism of cyclopentadienyl ketene (**5**) formation will be studied for three different precursors: diazocyclohexadienone (**1**), *o*-phenylene thioxocarbonate (**2**), and 2-chlorophenol (**3**, Chart 1). Based on previous studies,[4,5,17] we expect that the

Chart 1
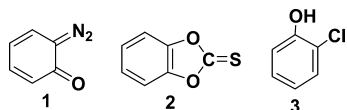
photochemistry of the small cyclic diazocarbonyl compound will mainly proceed by the concerted mechanism (competing carbene path is minor). But for the other two precursors, we predict a stepwise process, with carbene intermediacy, since mechanistic complexity makes RIES less probable.[18] Product formation will be directly studied using ultrafast time-resolved IR spectroscopy, since the ketene possesses a convenient strong and characteristic IR signal (located at ~2140 cm^{-1}).

2. RESULTS AND DISCUSSION

6-Diazo-2,4-cyclohexadienone. Diazoquinone photochemistry has been studied in an argon matrix using light with wavelengths above 350 nm. Cyclopentadienyl ketene (**5**) was detected by its strong absorption IR band at 2138 cm^{-1}.[19,20] The position of this band is in excellent agreement with our calculations (Table S1, Supporting Information). In solution, an equilibrium between 6-diazo-2,4-cyclohexadienone (**1**) and 1,2,3-benzoxadiazole has been reported.[19] In our studies, we chose chloroform or methanol, since in these solvents the dominant form is the diazoquinone (Chart 2).[19] The stationary

Chart 2
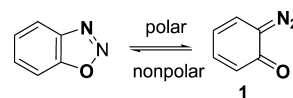
UV−vis spectrum is shown in Figure S1 (Supporting Information) and compared with the results of TD-B3LYP/6-31+G(d) calculations (Table S4, Supporting Information). On the basis of these calculations, we can assume that laser excitation at 390 nm will populate the S_2 state of diazo-2,4-cyclohexadienone, while 266 nm generates higher singlet excited states S_n ($n \geq 4$). We can also expect that the shorter excitation wavelength may result in more efficient RIES as a result of the greater excitation energy.[17] The results of ultrafast time-resolved experiments using 266 and 390 nm excitations with IR detection are shown in Figure 1.
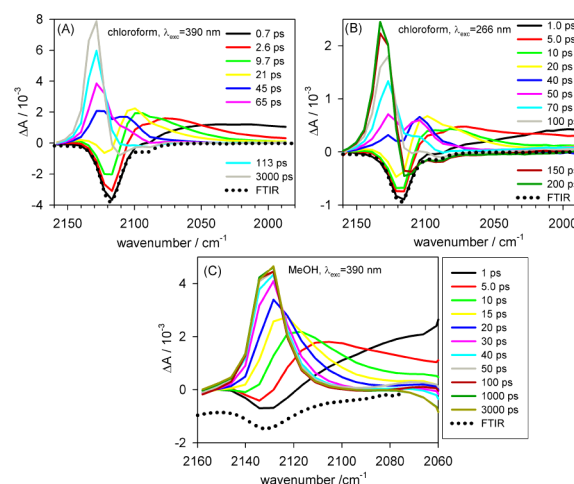
Figure 1. Time-resolved infrared transient absorption spectra obtained after photoexcitation of diazocyclohexadienone (2×10^{-3} M) at 390 nm (A) and 266 nm (B) in chloroform and at 390 nm in methanol (C). The dotted line shows the stationary IR spectrum of diazocyclohexadienone in given solvent.

At initial delays, a positive band is present in chloroform at about 2000 cm^{-1} and a negative band is seen at 2120 cm^{-1}. The initial positive band can be assigned to the vibrationally hot ketene species. There is a possible contribution from a hot diazo species produced by internal conversion. The ketene species undergoes vibrational relaxation as confirmed by band-narrowing and the spectral frequency upshift of the initial positive IR band over a 100 ps time window (Figure 1A). Additional experiments performed at about 1630 cm^{-1} demonstrate that ground-state diazoquinone undergoes a

recovery ($\Phi_{IC} = 30\%$) in chloroform after 390 nm excitation. Thus, we can assume the same decay of amplitude of the $\nu_{N=N}$ bleach takes place at about 2120 cm^{-1} (Figure 1A) as for $\nu_{C=O}$ at 1630 cm^{-1}. Excitation at 266 nm (Figure 1B), compared to 390 nm (Figure 1A), produces a similar amount of ketene deduced by comparison of the IR band amplitude ratio of thermalized ketene to initial $\nu_{N=N}$ bleach.

The occurrence of a RIES process as the major ketene formation route might be confirmed by unchanged yield of ketene formation in methanol, a carbene-trapping solvent, compared to the relatively inert solvent as chloroform. Measurements performed using the same experimental conditions show that the intensity of the thermalized ketene band in both solvents is similar (λ_{exc} = 390 nm). Thus only a small amount of methanol-trappable carbene can be formed from diazoquinone, implying that the major path of ketene formation is RIES. An alternative scenario excludes RIES, if methanol is unable to compete efficiently with carbene isomerization.

To investigate the mechanism of the ketene formation in the ground and the excited state of the precursor, we carried out further calculations using the Turbomole program. This mechanism has been investigated computationally in the past, however, with semiempirical calculations.[21] We carried out relaxed scans on the ground state to estimate the barrier of (1) nitrogen extrusion and carbene formation (stepwise mechanism) and (2) ketene formation without forming the carbene intermediate (concerted mechanism). As shown in Figure S2 (Supporting Information), when the ground state is optimized with constrained C–N bond lengths, carbene formation begins around 1.8–1.9 Å. Further elongation of the C–N bond does not change the energy significantly; however, when the C–N bond length reaches about 2.6 Å, the carbene rearranges to form the ketene. This is consistent with previous studies,[4,5] which suggested that carbonyl carbenes lie in a shallow well that can almost barrierlessly rearrange to form the corresponding ketene product. Figure S2 (Supporting Information) also suggests that the carbene formation has a barrier of about 32–35 kcal/mol on the ground state along the C–N bond length.

To investigate the concerted mechanism, the potential energy surface along C–C bond length was scanned as shown in Figure S2 (Supporting Information). As the C–C distance shortens the C–N bond length increases and the energy rapidly rises. When the C–C bond length is about 2.0 Å, the energy rises to about 36 kcal/mol above the ground state's energy, and compression of the C–C bond any further rapidly drops the energy of the system to immediately yield the ketene product without the formation of any carbene intermediate.

In order to characterize the excited states of the diazocyclohexadienone, we obtained the difference density plots for the first four excited states using a procedure described elsewhere.[22] Figure 2 depicts the computed difference density plots of the four S_1–S_4 excited states. The red and green color contours indicate depletion and accumulation of electronic density upon electronic excitation, respectively. It is clear that the S_1 state is a $\pi \rightarrow \pi^*$ (out-of-plane) excited state while S_2–S_4 states have significant n $\rightarrow \pi^*$ character with a notable contribution from the carbonyl unit. The electronic density is significantly depleted at C–N$_2$ bond in the S_1 state, which suggests that the C–N bond cleavage may proceed in the S_1 excited state and can lead to carbene formation.

Obtaining the same information for the S_1 state as discussed above required the optimized geometry of the precursor on the S_1 surface. We used the ground-state-optimized geometry to
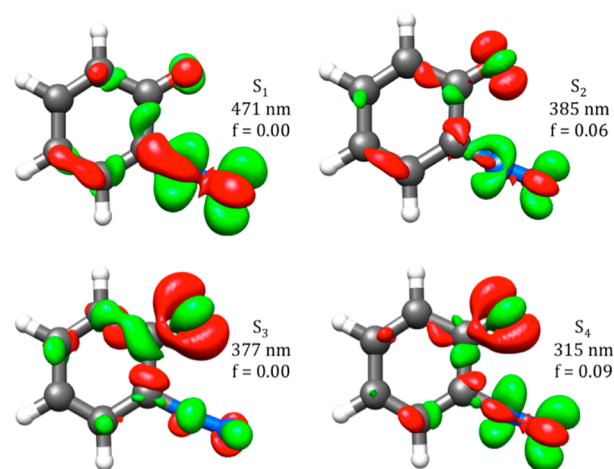

Figure 2. Difference density plots for the S_1–S_4 excited states of diazocyclohexadienone as computed at the B3LYP/TZVP level of theory. The red contours depict depletion and green contours depict accumulation of electron density in the excited state upon electronic excitation from the S_0 ground state, respectively. S_1–S_4 plots are plotted with isocontour values of ± 0.005 a.u.

optimize the S_1 state geometry. As observed earlier for phenyldiazomethane,[22] the diazo unit attains an angular geometry in the S_1 excited state and the C–N$_2$ bond length elongates significantly when compared to the ground state geometry (Figure 3).
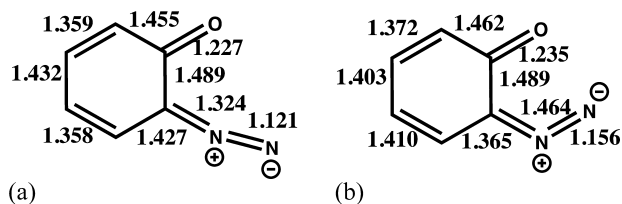

Figure 3. Optimized (a) ground state and (b) S_1 excited-state geometry of diazocyclohexadienone calculated at the B3LYP/TZVP and TD-B3LYP/TZVP levels of theory, respectively. The bond lengths are shown in angstroms.

We carried out the relaxed scans on the S_1 surface using this optimized geometry along C–N and C–C bond lengths to investigate the stepwise and concerted mechanisms, respectively. As shown in Figure 4a, the stepwise extrusion of molecular nitrogen from the diazo precursor has an energy barrier of only 6 kcal/mol compared to 35 kcal/mol on the ground state, which suggests that the nitrogen extrusion to form carbene is more facile on the S_1 state. On the other hand, the scan for the concerted mechanism is shown in Figure 4b, where the energy barrier to nitrogen extrusion and simultaneous ketene formation is almost the same on the S_1 state and S_0 state surfaces. Consequently, we conclude that the diazo precursor extrudes molecular nitrogen first and then rearranges to form the ketene. However, it is possible that the C–N bond cleavage generates a carbene with excess vibrational energy and as a result, ketene formation proceeds immediately (<1 ps) after the departure of molecular nitrogen.

***o*-Phenylene Thioxocarbonate.** Vinylene thioxocarbonates have been proposed as sources for the synthesis of ketenes and for mechanistic study of the Wolff rearrangement (WR).[18,23] Photolysis of *o*-phenylene thioxocarbonate (**2**) in an argon
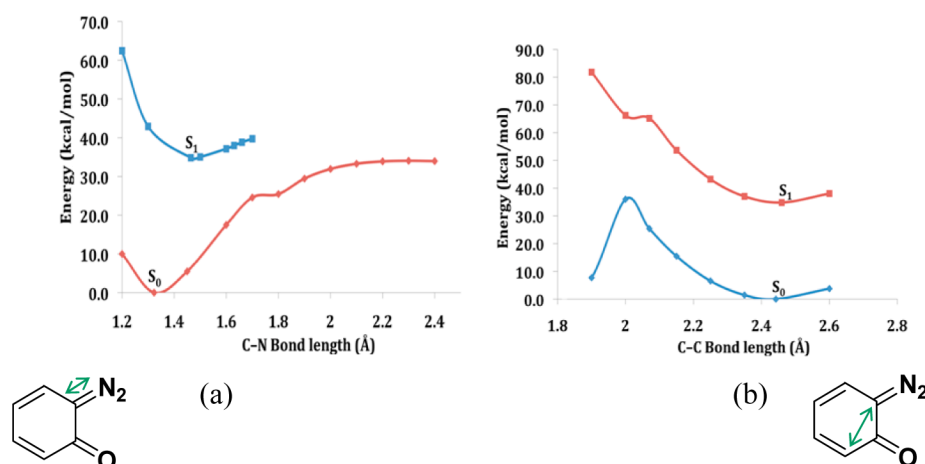
Figure 4. Relaxed scan of diazocyclohexadienone along the (a) C−N and (b) C−C bond lengths to investigate stepwise and concerted mechanism, respectively, as computed at the B3LYP/TZVP and TD-B3LYP/TZVP level of theory for ground and excited states, respectively.
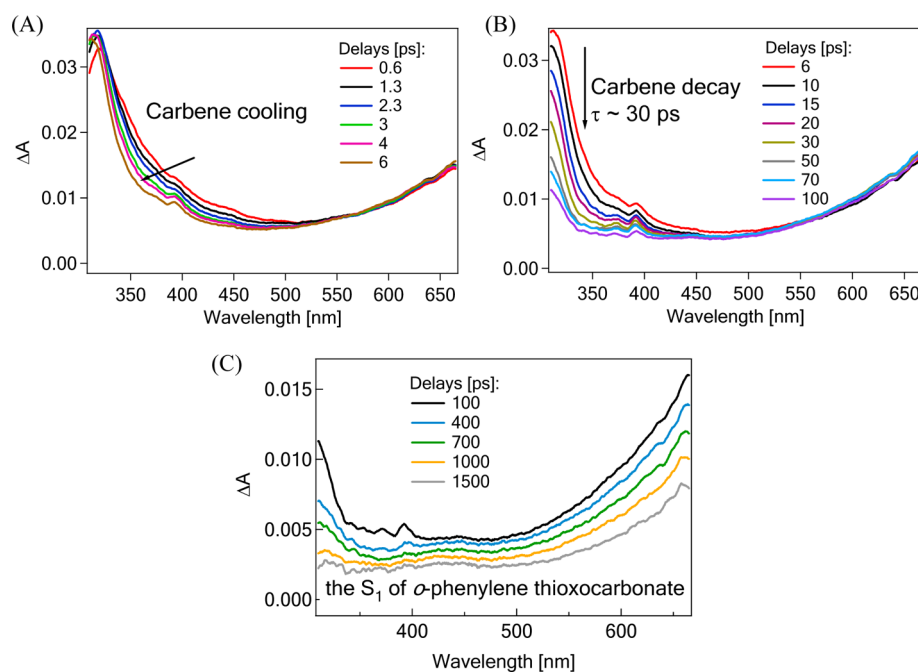

Figure 5. Transient absorption spectra recorded over a 0.6−6 ps (A), 6−100 ps (B), and 100−1500 ps time window following photoexcitation of *o*-phenylene thioxocarbonate (2×10^{-3} M) at 266 nm in acetonitrile.

matrix with 270 nm light was studied by Torres et al.[23] This group reported the formation of cyclopentadienylketene with strong absorptions at 2133 and 2130 cm^{-1} upon excitation of this precursor. WR was assumed to proceed from the ketocarbene, but this species was not observed in the argon matrix studies.

The stationary UV−vis spectrum of *o*-phenylene thioxocarbonate (**2**) has a maximum at 285 nm in acetonitrile (Figure S3, Supporting Information). Based on TD-DFT calculations, we can assume that 266 nm excitation will generate the S_2 state (Table S6, Supporting Information). The transient UV−vis spectrum produced with 266 nm excitation (Figure 5A) clearly shows a band peaking at 320 nm. This band can be attributed to the singlet carbene, 2-oxocyclohexa-3,5-dienylidene (**4**) on the basis of our theoretical calculations at several different levels of theory (Table S7, Supporting Information). The carbene band is formed instantaneously (<0.4 ps), implying that its precursor, *o*-phenylene thioxocarbonate in the S_2 state, is very short-lived. In a

6 ps time window, a band-narrowing effect is observed for the carbene, due to vibrational cooling. An additional possibility, however, is that a fast decrease of carbene population takes place due to hot carbene-ketene isomerization, and at this time, this possibility can not be excluded. The decay of the carbene band over 6−100 ps can be observed clearly.

Global analysis of the transient UV−vis absorption spectra in the 315−670 nm spectral range (Figure 5A−C) using three time constants led to the following values: 3.5, 25, and 1500 ps. The fast component is related to the initially formed hot carbene species, the longer component describes the carbene lifetime, and the longest value is assigned to *o*-phenylene thioxocarbonate in the S_1 excited state. The latter assignment agrees with time-correlated single-photon counting (TCSPC) fluorescence measurements (λ_{exc} = 266 nm and λ_{em} = 320 nm) revealing the S_1 lifetime of 2.1 ± 0.1 ns. The transient absorption spectrum at 100 ps (Figure 5C) corresponds mainly to *o*-phenylene

thioxocarbonate in the S_1 excited state. Inspection of the band peaking above 650 nm at early delays (Figure 5A) indicates instantaneous S_1 formation (<0.4 ps) through internal conversion ($S_2 \rightarrow S_1$). Complementary data were recorded using ultrafast time-resolved IR studies. Figure 6 shows two
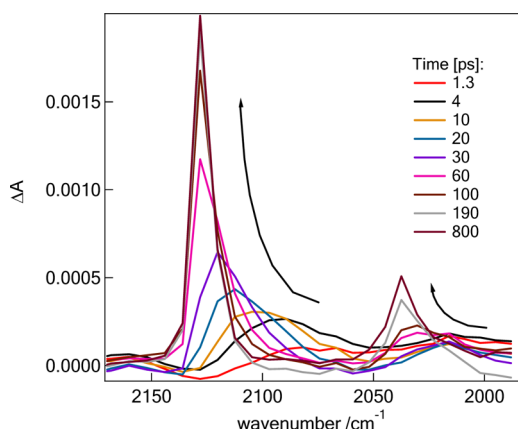

Figure 6. Time-resolved infrared transient absorption spectra obtained in hexane after photoexcitation of *o*-phenylene thioxocarbonate (2 × 10^{-3} M) at 266 nm.

absorption bands: ketene at 2130 cm^{-1} and COS at 2040 cm^{-1} (in agreement with calculations, ~2027 cm^{-1}, Table S8, Supporting Information). Both species are born in a vibrationally hot state and undergo subsequent cooling, as evidenced by the frequency upshift.

The hot ketene shows significant band area at 4 ps (Figure 6); thus, the hot carbene might be an important channel for producing ketene, in addition to the isomerization channel involving a thermalized, and thus less reactive, carbene species. Carbene intermediacy is also confirmed by a small reduction of the ketene to COS band intensity ratio in methanol, a carbene scavenging solvent, as compared to chloroform, which is less reactive. A proposed mechanism for photoexcited *o*-phenylene thioxocarbonate is shown in Scheme 1. The picosecond UV−vis and IR transient absorption data incline us to favor the stepwise WR process (with carbene intermediacy).

Scheme 1. Photochemistry of *o*-Phenylene Thioxocarbonate
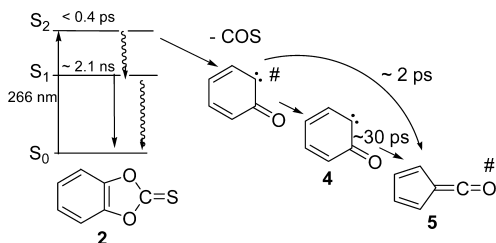
2-Chlorophenol. Cyclopentadiene derivatives have been observed as major products upon photolysis of 2-chlorophenol (**3**) in methanol and hexane;[11] thus, these solvents were chosen for time-resolved studies. On the basis of the recorded UV−vis stationary spectra and TD DFT calculations (Figure S4 and Table S10, Supporting Information), 266 nm excitation promotes the $S_0 \rightarrow S_1$ transition. Kinetic traces recorded at 320 nm depict the shortening of the carbene lifetime from 23 ± 5 ps in hexane to 5 ± 1 ps in methanol, a carbene-trapping solvent (Figure 7).
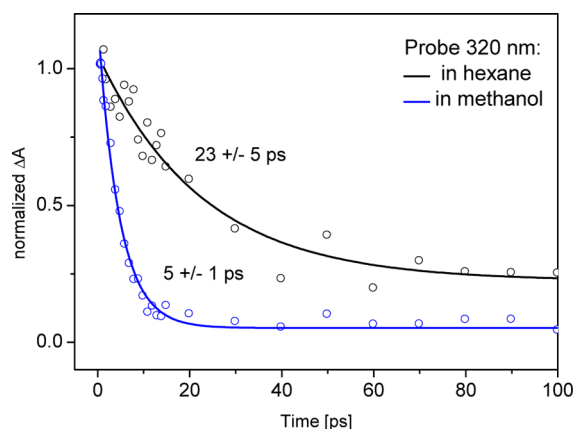

Figure 7. Kinetic traces for 2-chlorophenol (6 × 10^{-3} M) in hexane and methanol photoexcited at 266 nm (points) fitted to one-exponential function (solid lines).

As expected, a 5-fold lower yield of ketene formation is observed in methanol as compared to hexane or chloroform, assuming that the quantum yield of carbene formation does not depend on solvent (Figure 8). Interestingly, the time-resolved ketene IR spectra are very similar for 2-chlorophenol (**3**) and *o*-phenylene thioxocarbonate (**2**). Again the area of the ketene band is important at early delays (~2 ps, Figure 8A), so it is reasonable to assume that ketene is formed on a fast time-scale from hot carbenes and at longer time-scale from more thermalized and less reactive carbenes.

According to B3LYP/6-31+G* calculations, the triplet carbene (^{3}**4**) is the ground state of the molecule (~16 kcal/mol lower in energy than the open-shell singlet). In our time-resolved experiments, we have not observed a band that can be attributed to the carbene in the triplet state and that could hypothetically be formed by intersystem crossing from the singlet state (^{1}**4**). Obvious reasons for this negative result might be due to either a low absorption cross section or low yield for triplet formation. In the aqueous phase, the triplet state of the carbene has not been directly observed in laser flash photolysis experiments.[16] The presence of fast channels of singlet carbene deactivation, as a fast WR process and reaction with solvent (methanol), and a low rate of the intersystem crossing process (typically $10^9 - 10^{10}$ s^{-1} for keto carbenes),[2] seem to be main factors resulting in a small yield of triplet carbene formation. The failure to observe triplet carbene formation in time-resolved UV−vis transient absorption experiments with 2-chlorophenol is not surprising, since the quantum yield of triplet-state formation in aqueous solution is known to be low ($\Phi_T \sim 0.003$) and, furthermore, the transient absorption band with its maximum at 388 nm has a relatively small molar absorption coefficient of only $\varepsilon = 2100 \pm 500$ M^{-1} cm^{-1}.[16]

Conclusions. Cyclopentadienyl ketene formation has been observed upon photolysis of diazocyclohexadienone, *o*-phenylene thioxocarbonate, and 2-chlorophenol in solution. Three routes of WR process are observed: RIES, isomerization of hot carbenes (fast), and thermalized carbenes (relatively slow). As expected, RIES is the major path of WR for diazocyclohexadienone, as demonstrated by an only slightly decreased ketene band amplitude in methanol (a carbene trapping solvent) compared to that in chloroform. For *o*-phenylene thioxocarbonate and 2-chlorophenol, WR proceeds through two parallel paths from: vibrationally excited (fast) and thermalized (slow) carbene species. The carbene lifetime in hexane (23 ps) decreases
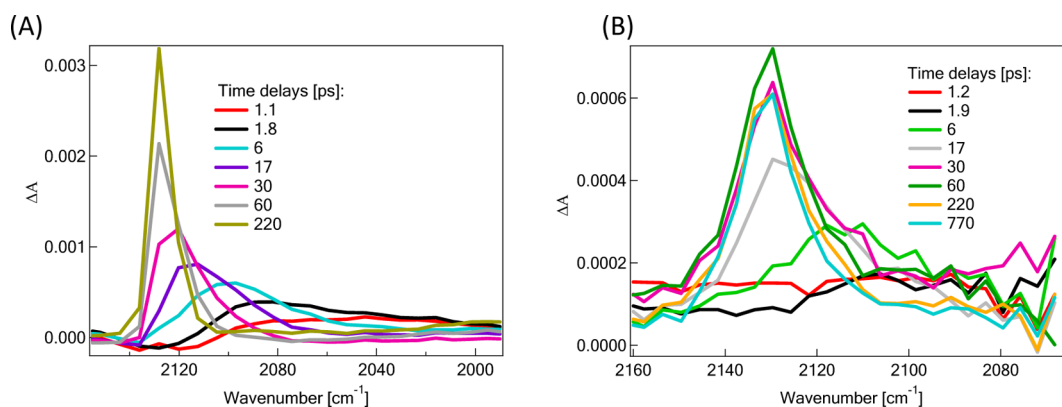
Figure 8. Time-resolved infrared transient absorption spectra after photoexcitation of 2-chlorophenol (2×10^{-3} M) at 266 nm in hexane (A) and methanol (B).

to 5 ps in methanol, as deduced from time-resolved measurements performed with 2-chlorophenol. The singlet carbene decays through parallel pathways: ketene formation, insertion product formation (in methanol) and possibly by intersystem crossing to form the lower energy triplet, although the triplet state was not detected.

3. EXPERIMENTAL AND COMPUTATIONAL METHODS

6-Diazo-2,4-cyclohexadienone (**1**) was synthesized according to procedures described in the literature.[20,24] 2-Chlorophenol (**3**), *o*-phenylene thioxocarbonate (**2**) and solvents were used as obtained without further purification. The ultrafast time-resolved infrared laser system consists of a short-pulse titanium-sapphire oscillator (Coherent, Vitesse, 50 fs) followed by a high-energy titanium-sapphire regenerative amplifier (Coherent, Positive Light, Legend HE USP). The 800 nm beam is split into two beams to pump BBO harmonic crystals (266 and 400 nm generation) and OPA (OPerA Coherent). The OPA with a DFG module produces IR pulses (tunable from 2 to 10 μm, 5 μJ at 4 μm). A Ge beamsplitter splits the IR beam into reference and probe beams and both are focused into a 1 mm path length sample cell (Harrick Scientific), but only the probe beam overlaps with the pump beam in the sample. After passing through the sample the probe and reference beams were spectrally dispersed in a grating spectrometer (iHR 320) and independently imaged on a liquid nitrogen cooled HgCdTe detector (2 × 32 elements) with 17 nm resolution. IR beams are permanently purged with dry air. Every other UV pump pulse is blocked by a synchronized chopper to eliminate long-term drift effects. The pump pulse energy was about 3 μJ at the sample position. Femtosecond TRIR experiments on diazocyclohexadienone (time resolution 300 fs) were performed at Center for Chemical and Biophysical Dynamics at The Ohio State University,[8] while some experiments on *o*-phenylene thioxocarbonate were performed at the University of Zürich.[25] The broadband UV−vis femtosecond transient absorption system has been described elsewhere.[26,27] The sample concentration was adjusted for an optical density of 1.0 at the excitation wavelength with a 1 mm path length. A sample volume of 50 mL was continuously flowed through the sample cell to ensure that fresh sample was photoexcited. The entire set of pump−probe delay positions is repeated at least three times, to ensure data reproducibility. To avoid rotational diffusion effects, the angle between polarization of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces are analyzed by fitting to a sum of exponential terms. Convolution with a Gaussian response function is included in the global fitting procedure. The instrument response was approximately 300 fs (fwhm). Fluorescence measurements for *o*-phenylene thioxocarbonate were performed at Center For Ultrafast Laser Spectroscopy at Adam Mickiewicz University using the picosecond laser system and time-correlated single-photon counting (TCSPC) detection systems.[28] All experiments were performed at ambient temperature.

Calculations. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed using the Gaussian 03 suite of programs at the Ohio Supercomputer Center. Geometries were optimized at the B3LYP/6-31G(d) level of theory with single-point energies obtained at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. Vibrational frequency analyses at the B3LYP/6-31G(d) level were utilized to verify that stationary points obtained corresponded to energy minima. The calculated frequencies were scaled by a factor of 0.9614.[29] The electronic spectra were computed using TD-DFT with Gaussian 03 at the TD-B3LYP/6-311+G(d,p) level, and 20 allowed electronic transitions were calculated. To explore the excited state potential energy surfaces, we performed calculations using Turbomole-6.0.0 software at the B3LYP/TZVP level of theory (and TD-B3LYP/TZVP level of theory for the excited states). All of the stationary points determined at the ground and excited state surfaces were verified to be minima by computing the second derivatives analytically and numerically, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Stationary UV−vis absorption spectra; DFT and TD-DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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