

Evidence of a Nitrene Tunneling Reaction: Spontaneous Rearrangement of 2-Formyl Phenylnitrene to an Imino Ketene in Low-Temperature Matrixes

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S Supporting Information

ABSTRACT: Triplet 2-formyl phenylnitrene was generated by photolysis of 2-formyl phenylazide isolated in Ar, Kr, and Xe matrixes and characterized by IR, UV-vis, and EPR spectroscopies. Upon generation at 10 K, the triplet nitrene spontaneously rearranges in the dark to singlet 6-imino-2,4-cyclohexadien-1-ketene on the time scale of several hours. The intramolecular [1,4] H atom shift from the nitrene to the imino ketene occurs by tunneling, on the triplet manifold, followed by intersystem crossing. This case constitutes the first direct evidence of a tunneling reaction involving a nitrene.

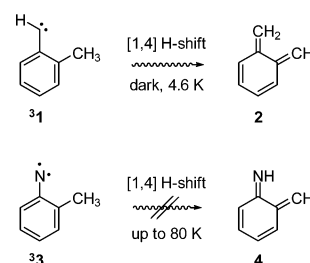
Nitrenes are fascinating reactive intermediates bearing a neutral monovalent nitrogen atom (R–N).^{1–6} The first direct observation of a nitrene was achieved in 1962 by electron paramagnetic resonance (EPR) spectroscopy in an organic glass at 77 K.⁷ Since then, a comprehensive body of data concerning the structure, spectroscopy, kinetics, and thermodynamic properties of numerous nitrenes has been acquired.^{1–6} These data have provided crucial knowledge to develop the field of nitrene chemistry and to boost the range of nitrene applications.⁸ Nevertheless, several questions about nitrene reactivity are not yet clearly understood.

The lack of reactivity of triplet nitrenes toward H-abstraction, even for intramolecular reactions, contrasts with the reactivity of triplet carbenes.^{9–20} This uniqueness has been interpreted as a result of thermodynamic and electronic factors. Triplet nitrenes are ~20 kcal mol⁻¹ more stable than the comparably substituted triplet carbenes.^{21–23} Moreover, the singlet–triplet gap ($\Delta E_{S,T}$) in nitrenes is generally much larger than in carbenes. The $\Delta E_{S,T}$ in phenylnitrenes is ~18 kcal mol⁻¹, and therefore, the intersystem crossing (ISC) in phenylnitrenes to their triplet ground-state is often considered irreversible. In phenylcarbenes $\Delta E_{S,T}$ is less than 5 kcal mol⁻¹,^{6,24,25} and consequently, the triplet ground-state phenylcarbenes can serve as a reservoir for the highly reactive singlet phenylcarbene.^{13,26,27}

An interesting type of H-abstraction in triplet carbenes occurs via quantum tunneling mechanism.^{11,15,17,28–31} In particular cases, the spin-forbidden H-abstraction tunneling from triplet carbenes to singlet products has been observed at cryogenic temperatures in the dark.^{17,28,29} A carefully studied example is the direct spectroscopic observation of the spontaneous intra-

molecular [1,4] H-shift reaction from triplet 2-methyl phenylcarbene ³1 to *o*-xylylene 2 at 4.6 K.¹⁷ This contrasts with the lack of reactivity of the corresponding triplet 2-methyl phenylnitrene ³3, which was found to be thermally stable up to 80 K in Xe matrix (Scheme 1).¹⁴

Scheme 1. Contrasting Chemistry of Triplet Phenylcarbene ³1 and Triplet Phenylnitrene ³3



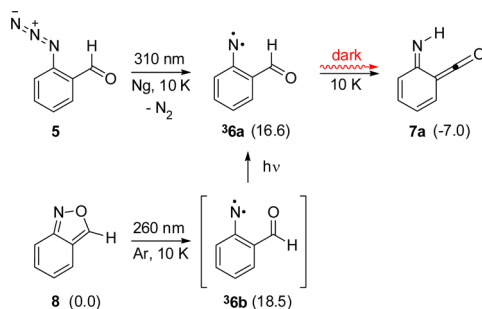
Indications of H-abstraction in phenylnitrenes were obtained by the capture of *o*-quinoid compounds in the photochemistry of phenylazide derivatives bearing active hydrogens in the proximity of the reactive center.^{12,32–36} However, these intramolecular H-shift reactions are likely to occur via the singlet excited state nitrene or hot (triplet) ground-state formed immediately upon photolysis of the corresponding azide precursor. This reactivity would compete or even suppress the formation of the corresponding triplet ground-state nitrene, preventing their capture in low-temperature matrixes.^{34,35,37}

Here, we report the observation of an intramolecular H-abstraction in a triplet nitrene, namely, the transformation of 2-formyl phenylnitrene ³6a into imino ketene 7a (Scheme 2). This transformation occurs spontaneously in low-temperature matrixes and is the first direct evidence of a tunneling reaction in nitrene chemistry.

Monomeric 2-formyl phenylazide 5 was isolated in an argon matrix at 10 K (Figure S1). Irradiation of matrix-isolated 5 with $\lambda = 308$ nm³⁸ yields two products, A and B (Figure S2). The first few seconds of irradiation generate almost exclusively photo-product A, while with the increase of irradiation time, product B accumulates and the B/A ratio increases. Therefore, A must be a

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Scheme 2. Transformations Involving Triplet Nitrene $^3\mathbf{6}$ and Relevant Computed Relative Energies^a

^aEnergies (kcal mol⁻¹; zero-point vibrational energies [ZPVE] included) calculated at the B3LYP/6-311++G(d,p) level of theory are shown in parentheses. Ng = noble gas (Ar, Kr, Xe).

primary photoproduct of **5**, whereas **B** is most likely a secondary product formed via **A**. Interestingly, we discovered that **A** also transforms to **B** when the sample is kept in the dark at 10 K. This spontaneous transformation of **A** to **B** was followed by IR and UV spectroscopy, and the IR and UV signatures of these two species were obtained. As shown below, these data allow the unequivocal identification of **A** as triplet 2-formyl phenylnitrene ($^3\mathbf{6a}$) and **B** as singlet 6-imino-2,4-cyclohexadien-1-ketene (**7a**).

The experimental IR spectrum of **A** agrees well with the theoretical IR spectrum of triplet nitrene $^3\mathbf{6a}$ (Figure 1a,b).

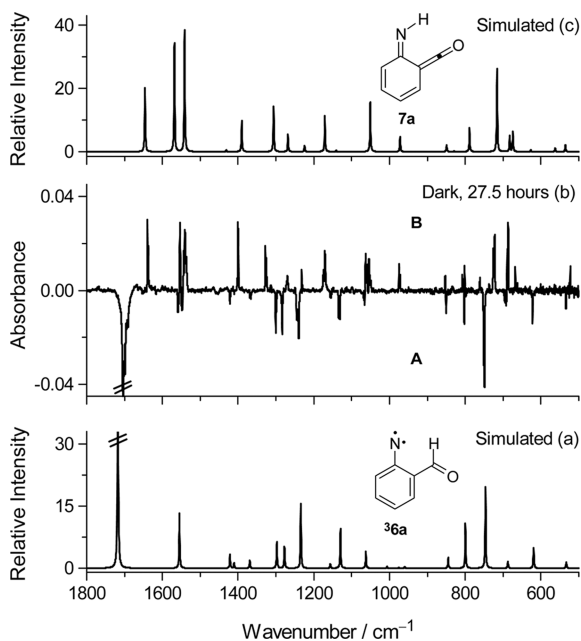


Figure 1. B3LYP/6-311++G(d,p) simulated IR spectra of (a) triplet 2-formyl phenylnitrene $^3\mathbf{6a}$ and (c) singlet 6-imino-2,4-cyclohexadien-1-ketene **7a**. (b) Spontaneous changes in the IR spectrum upon keeping the sample for 27.5 h in the dark, after UV-irradiation ($\lambda = 308$ nm) of 2-formyl phenylazide **5** isolated in Ar matrix at 10 K.

Particularly characteristic are the bands observed at 2857, 1703, 1301, and 750 cm⁻¹, which correspond to the vibrational modes predicted at 2885 [$\nu(\text{OC-H})$], 1718 [$\nu(\text{C=O})$], 1298 [$\nu(\text{C-N})$], and 747 [$\gamma(\text{CH})$] cm⁻¹.³⁹ A more complete assignment of the mid-IR spectrum of triplet nitrene $^3\mathbf{6a}$ is given in Table S1. In the experimental difference UV-spectrum (Figure 2a) three bands at 216, ~235, and 326 nm decrease upon

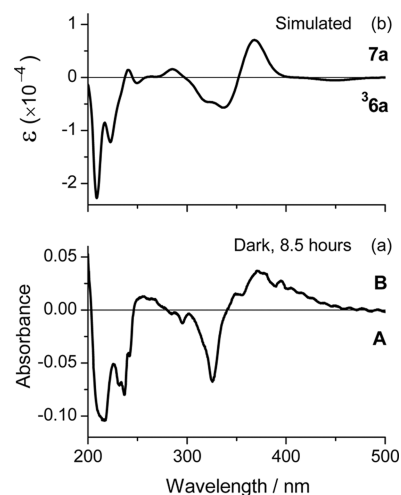


Figure 2. (a) Changes in the experimental UV-vis spectrum resulting from keeping the sample for 8.5 h in the dark, after irradiation of **5** isolated in Ar matrix at 10 K. (b) Simulated difference UV-vis spectrum obtained from vertical transition energies determined by TD-DFT calculations at the B3LYP/6-311++G(d,p) level, considering production of imino ketene **7a** at the cost of triplet nitrene $^3\mathbf{6a}$.

the consumption of **A**. These bands are well reproduced in the TD-DFT simulated UV-vis difference spectrum, where the vertical transitions with higher oscillator strengths were estimated at 209, 223, and 338 nm for the triplet nitrene $^3\mathbf{6a}$ (Figure 2b and Table S2). The band observed at 326 nm for **A** compares well with the strong absorption of triplet phenylnitrene at 308 nm or with the 336 nm absorption of the parent nitrene (NH), which are assigned mainly to the $n_z \rightarrow n_y$ transitions localized on the nitrogen atom.⁴⁰

The identity of **A** was also confirmed by EPR spectroscopy. Irradiation of azide **5** ($\lambda = 310 \pm 10$ nm, 40 min; methylcyclohexane glass, 4.2 K) afforded the EPR spectrum of triplet 2-formyl phenylnitrene ($^3\mathbf{6a}$) (Figure S3). The spectrum of $^3\mathbf{6a}$ is characteristic of many triplet aryl nitrenes in the X-band EPR spectrum.^{3,5} It exhibits a single XY_2 transition, rather than distinct X_2 and Y_2 transitions,⁷ which reveals that the local electronic environment at the nitrene center is axially symmetric and establishes that the magnitude of the zero-field splitting parameter E is very small ($|E/hc| < 0.002$ cm⁻¹). The value of the zero-field splitting parameter D ($|D/hc| = 0.979$ cm⁻¹) is in good agreement with those of other triplet aryl nitrenes, which typically fall in the range 0.9–1.2 cm⁻¹.

In the case of **B**, the experimental IR spectrum compares well with the theoretical IR spectrum of imino ketene **7a** (Figure 1c). The most distinctive bands are observed at 3266, 2110, 1553, and ~724 cm⁻¹ and readily assigned to the vibrational modes predicted at 3283 [$\nu(\text{N-H})$], 2149 [$\nu(\text{C=C=O})_{\text{as}}$], 1568 [$\nu(\text{C=N})$], and 716 [$\gamma(\text{CH})$] cm⁻¹. The frequency and very high intensity of the band observed at 2110 cm⁻¹ are especially characteristic of a ketene moiety and compare well with the frequency of the $\nu(\text{C=C=O})_{\text{as}}$ band reported at 2125 cm⁻¹ for the methylimino ketene analogue.⁴¹ A comprehensive assignment of the observed IR bands for **7a** is given in Table S3.

From the experimental difference UV-spectrum, the growing band of **B** at ~256 nm and a broad band at ~375 nm, extending to ~460 nm, can be assigned to **7a** (Figure 2a). In a good correspondence with the experimental data, TD-DFT calculations for imino ketene **7a** estimate three vertical transitions with higher oscillator strengths at 366, 242, and 234 nm (Figure

2b and Table S2). The experimental broad band of **B** that appears between 350–460 nm (assigned to the $\pi_{\text{HOMO}} \rightarrow \pi_{\text{LUMO}}^*$ transition) compares well with the broad band of the methylimino ketene analogue centered near 400 nm.^{41,42}

2,1-Benzisoxazole **8** (see Scheme 2) was also investigated as an alternative precursor to generate the 2-formyl phenylnitrene **6a**. The photochemistry of **8** in argon matrix is complex, due to the concomitant formation of several photoproducts, yet we have successfully identified the formation of triplet nitrene **36a** and observed its spontaneous rearrangement to imino ketene **7a** (Figures S4 and S5).

The kinetics of the spontaneous rearrangement of **36a** to **7a** was followed by monitoring the decrease and increase of the IR bands due to **36a** and **7a**, respectively (Figure S6, Ar matrix; Figure S7, Kr matrix). The observed decays follow equations of dispersive kinetics (see Supporting Information). About 50% of **36a** is converted into **7a** within 5.8 h in argon and 4.5 h in krypton. In a xenon matrix the spontaneous rearrangement was found to be much slower. Over a period of 7 days in the dark at 10 K only ~25% of **36a** was transformed into **7a**.

To verify that rearrangement of **36a** to **7a** is not stimulated by the IR radiation from the light source of the IR spectrometer, we performed independent measurements with the matrix sample kept in dark (protected from the spectrometer IR source) and using, when collecting IR spectra, a cutoff filter transmitting only below 2200 cm^{-1} . Since similar kinetic data were obtained (Figure S8), the influence of IR radiation on the spontaneous rearrangement of **36a** to **7a** was excluded. To verify that the rearrangement of **36a** to **7a** is not activated thermally, we carried out a similar experiment using xenon as matrix material. Even upon annealing up to 60 K the photogenerated nitrene was still present in the sample for hours.

It seems clear that the spontaneous rearrangement of triplet nitrene **36a** to imino ketene **7a** cannot be explained by the classical rate theory considering an over-the-barrier process. A rate constant on the order of $3 \times 10^{-5} \text{ s}^{-1}$ (a rough estimate based on the decay of **36a** in Ar) would correspond to an activation energy $\sim 0.2 \text{ kcal mol}^{-1}$;⁴³ such very low barrier is extremely improbable to exist. The observed spontaneous rearrangement must be caused by a tunneling effect, a conclusion supported by preliminary studies on the deuterated **36a-D**. We found that D-formyl phenylnitrene (**36a-D**) (photogenerated from deuterated D-formyl azide **5-D**) is stable against spontaneous decay at 10 K (Figures S9 and S10).

Two mechanisms can be envisaged for the transformation of triplet **36a** into singlet **7a**.²⁹ One hypothesis is the H atom migration occurring concomitantly with the crossing from the triplet to the singlet surface. In such case, the triplet **36a** should be upconverted by ISC into a low-lying excited singlet state, probably before reaching the barrier top on the triplet surface. This is unlikely because $\Delta E_{\text{S,T}}$ of phenylnitrenes is considerably high ($\sim 18 \text{ kcal mol}^{-1}$), making the ISC less plausible. Also, experiments in Xe matrixes show a decrease in the reaction rate, contrary to the expected increase of rate that would result from the external heavy atom effect.⁴⁴

Another hypothesis is the H atom migration occurring on the triplet surface, from triplet **36a** to triplet **37a**, which then internally converts to the singlet ground state of **7a**. The feasibility of such mechanism was investigated by carrying out a potential energy scan between **36a** and **37a** as a function of the NH distance (Figure 3). The calculations indicate that triplet **36a** and triplet **37a** (resembling a biradical formed by abstraction of H atom from triplet **36a**) are essentially isoenergetic (Table S4).

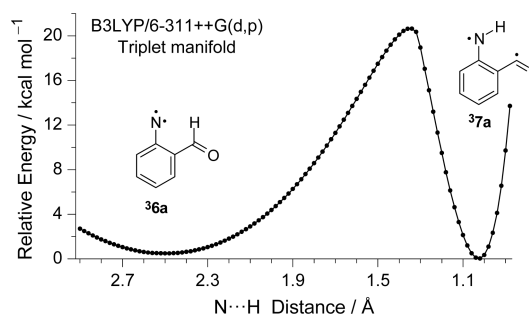


Figure 3. Relaxed potential energy scan, as a function of the NH distance, connecting phenylnitrene **36a** and the corresponding imine **37a**, calculated at the B3LYP/6-311++G(d,p) level on the triplet manifold. All relative energies are with respect to the triplet **37a**.

The calculated barrier for this reaction is above 17 kcal mol^{-1} (Figure 3, Figure S11, Table S4), which clearly rules out the possibility of an over-the-barrier thermal reaction at 10 K. However, conditions for the occurrence of quantum tunneling seem to be satisfied: the barrier is rather narrow, no more than 2.1 Å (Figure S11), and the reaction is associated with the movement of the light H atom.^{45,46} Indeed, considering this hypothesis, the tunneling half-lives for H-formyl (**36a-H**) and D-formyl (**36a-D**) phenylnitrene were computed on the order of tens-of-minutes/hours and 10^5 years, respectively (see Supporting Information), in agreement with experimental results. Moreover, [1,2] H-shift tunneling in hydroxycarbenes is known to occur at 10 K through a comparable barrier on the time scale of 1–4 h, whereas their deuterated analogues are stable against tunneling.^{31d}

Summarizing, triplet 2-formyl phenylnitrene (**36a**) was generated in cryogenic matrixes by photolysis of two different precursors. We found that it spontaneously rearranges in dark, at 10 K, to singlet 6-imino-2,4-cyclohexadien-1-ketene (**7a**). This reaction involves intramolecular [1,4] H atom shift from the nitrene to the corresponding imine. It is the first report of a tunneling reaction involving a nitrene, and we believe it opens a new chapter in the nitrene chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07368.

Materials and methods, spectroscopic data, and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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- (37) It is also known that irradiation of the isolated triplet nitrene may induce H-abstraction reaction.^{10,18,32} This supports the idea that H-abstraction occurs via excited singlet or hot (triplet) ground-state.
- (38) The irradiation wavelength of 308 nm was chosen to match the first absorption maximum of **5** and also to avoid the absorption of photoproduct **36a** with a maximum at 326 nm. The UV-vis spectrum of matrix-isolated **5** is given in Figure S12. The UV-vis spectrum of photoproduct **36a** is discussed in the text and given in Figure 2.
- (39) The experimental absorptions at 1298 [$\nu(\text{C}-\text{N})$] and 747 [$\gamma(\text{CH})$] cm $^{-1}$ of triplet 2-formyl phenylnitrene **36a** correlate well with similar bands observed at 1287 [$\nu(\text{C}-\text{N})$] and 746 [$\gamma(\text{CH})$] cm $^{-1}$ for triplet phenylnitrene.^{39a,b} Note that $\nu(\text{C}-\text{N})$ mode is coupled with the $\nu(\text{C}-\text{C})$ ring and $\delta(\text{CH})$ modes. (a) Kim, S.-J.; Hamilton, T. P.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1992**, *114*, 5349. (b) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879.
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- (46) The scan connecting **33** to **34** on the triplet manifold shows a barrier of ~ 27 kcal mol $^{-1}$, but **34** is ~ 8 kcal mol $^{-1}$ higher in energy than **33**, making the tunneling virtually impossible (Figure S13). This can explain why triplet 2-methyl phenylnitrene **33** does not rearrange to the corresponding imine **4** up to 80 K in Xe matrix (Scheme 1).