Photo-control of bimolecular reactions: reactivity of the long-lived Rhodamine 6G triplet excited state with 'NO.

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Scheme S1. Proposed mechanism leading to the radical losses of Me⁺ and Et⁺ from ³Rh6G⁺. Radicals and charge are formalized for the sake of the representation but are stabilized by delocalization over the whole aromatic system

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Figure S2. Comparison between CID spectra of Rh6G⁺ cations after 500 ms without (top: singlet only) and with (bottom: triplet is formed) irradiation at 488 nm. Intensities are relative to the precursor (indicated with a "*")

Figure S3. (left) LID mass spectra after 500 ms irradiation at 488 nm followed by (respectively top to bottom) (i) isolation of Rh6G⁺ with a large selection window ($\Delta m/z = 20$), (ii) a small selection window ($\Delta m/z = 1$), and (iii) a large selection window but 10 ms at 10 NCE activation before the 600 nm pulse. (right) Evolution of the LID yield at 600 nm as a function of the NCE value

Figure S4. Relative intensity of the nitroso-product [Rh6G -H +NO]⁺ (in ppm with regards to the precursor ion intensity). Error bars indicate 2σ uncertainty windows. The mass spectra acquisitions all follow the same sequence: 500 ms with or without activation, followed by isolation ($\Delta m/z = 20$) and 500 ms reaction time with *NO. Collisional activation (green) with 1 NCE for 500 ms yields ~ 67 % fragmentation, *i.e.* ~ 10 times the fragmentation ratio obtained with 10 mW of 488 nm (data not shown). Nevertheless, the product ion intensity is significantly higher after laser activation, which is particularly apparent at 30 mW

Figure S5. Dataset #5. Fit performed separately on data from series in in Helium: NO. Photo-fragments and NO-Products are fitted simultaneously for each dataset

Figure S6. Dataset #6. Fit performed separately on data from series in in Helium: NO. Photo-fragments and NO-Products are fitted simultaneously for each dataset

Figure S7. Dataset #7. Fit performed separately on data from series in in Helium: NO. Photo-fragments and NO-Products are fitted simultaneously for each dataset

List of ESI-Tables

Coordinates of NO Coordinates of NO2 Coordinates of HNO Coordinates of HONO Coordinates of [Rhodamine 6G] + singlet Coordinates of [Rhodamine 6G - H] + Coordinates of [Rhodamine 6G - H + NO] + Coordinates of [Rhodamine 6G - H + NO2] + Coordinates of [Rhodamine 6G - 2H] +

Experimental and Theoretical Methods

Material

All compounds were used as received: Rh6G chloride salt was purchased from Lamba Physics GMBH, Goettingen, Germany; Nile blue perchlorate salt was purchased from Exciton Chemical Co., Dayton, Ohio. All dyes solutions were made up 10⁻⁵ M in methanol. A Crystal quality (Alphagaz mix series) helium: NO bottle was purchased from Air Liquide (Bagneux, France) with 'NO composition of 1,056 ± 0,021 Mol-%.

Instruments and experimental sequences

A linear quadrupole ion trap mass spectrometer (LTQ Velos, Thermo Fisher Scientific, San Jose, CA), previously modified to allow interaction with lasers,¹ was used to generate ¹Rh6G⁺ via ESI. The low-pressure ion trap of the instrument was used for ion trapping. During ion trapping, a sequence of reaction events can be carried out via multistage mass spectrometry experiments (MSⁿ) in which ions can be activated and fragmented by collisions (CID) or photons (LID) or allowed to react with neutral reagents (IMR). A fused silica window (3 mm thick, 1 in diameter) is positioned at the back end of the instrument and allows for the introduction of the laser beams in the UV-visible range along the axis of the linear ion traps.

Two lasers were used: (1) in order to form the triplets, a 488 nm continuous wave (CW) diode laser (COBOLT MLD 0488-06-01-200-100), typically set at 15 mW; (2) in order to probe the triplet population by LID, the 600 nm beam from a Horizon OPO pumped by the third harmonic (355 nm) of a Surelite I Nd:YAG laser (Continuum, Santa Clara, CA) operating at 10 Hz, and with pulse-widths on the order of 5 ns.

Several experimental sequences were used and are described here. In order to generate triplet cations, the intrinsically charged molecular ions at m/z 443 are mass selected ($\Delta m/z = 1$, normalized collision energy (NCE) = 0) and submitted to 500 ms irradiation at 488 nm / 15 mW (CW laser). A second selection event (MS³, $\Delta m/z = 10$ -20, NCE = 0) is carried out to allow ions to relax to the ground state and/or react with neutral reagents for a variable amount of time. In order to monitor the dynamics of the triplet population (triplet lifetime) and reaction products, the length of this MS³ event is adjusted from 10 ms to 10 s. Reaction products may be mass detected at this stage. Alternatively, a third selection event (MS⁴, $\Delta m/z = 10$ -20) may be included before mass detection in order to monitor the remaining triplet population by LID. For LID, a single 8 mJ pulse of 600 nm photons is used. The resulting fragmentation ratio is calculated as $I_{Fragments}/IIC$, where the "fragments" intensity results from signal integration between m/z 120 and m/z 442, *i.e.* excludes the precursor intensity at m/z 443. In order to minimize noise and measure standard deviations, 150 mass spectra (600 for IMR) are recorded for each delay (*i.e. per* MS³ length).

For the ion-molecule reactions with 'NO, the regular helium line was replaced with a line connected to a helium cylinder that was seeded with 1 % 'NO. Nitrogen dioxide ('NO₂) was formed from reaction between 'NO and initial traces of adventitious O₂ in the Helium line, which enabled the reactivity of Rh6G⁺ towards 'NO₂ until the line was fully flushed. CID spectra and lifetime measurements in the presence of 'NO were performed as described above. The mass selection in step 2 was used to select the triplet and clean the trap from any fragment and/or product formed during irradiation at 488 nm. It was performed with $\Delta m/z = 20$ in order to avoid activation and quenching of the triplet. This necessarily large selection window is unfortunately not compatible with the ejection of the -H and -2H product ions formed by reaction with 'NO and 'NO₂. Thus the reaction time was not properly re-initialized by the selection step for these products.

The optical spectra of Rh6G⁺ ions were recorded following an MS³ experimental scheme. In step 1, the mass-selected rhodamine ions are irradiated at 488 nm for a period of 500 ms. During step 2, Rh6G⁺ is again selected and irradiated with a single pulse of photons from the Horizon OPO. In order to measure the optical spectrum of the singlet alone, all acquisition parameters remain identical but the CW laser is switched off during step 1. The optical photo-fragmentation spectrum of Rh6G⁺ cations is measured by continuously scanning the OPO output wavelength from 550 nm to 650 nm over ~16 min (0.1 nm.s⁻¹) while recording mass spectra. The optical spectra are reported in terms of fragmentation yield (FY), which is calculated as:

$$FY = \frac{-\ln(I_{precursor}/TIC)}{ProbeLaserPower/ProbeLaserWavelength}$$
(S0)

Details of the calculation of the ion-molecules collision rate

This collision rate between Rh6G ions and neutral, polar 'NO was calculated by multiplying the capture rate constant (in cm³. s⁻¹) by the number density (in cm³.molec⁻¹) of the neutral 'NO in the ion trap.

The capture rate constant between the ion and polar 'NO was calculated using the Colrate program² with the "Average Dipole Orientation" (ADO) theory which is well adapted to describe ion-polar molecule collisions.³ The requested parameters are: the ion mass (443 amu) and charge (+1), and the neutral mass (30 amu), dipole moment (0.15 D), polarizability (1.7 Å³) and moment of inertia (10 amu.Å²). The resulting capture rate constant k_{ADO}^{NO} amounts to 5.8 x 10⁻¹⁰ cm³. s⁻¹.

The number density of 'NO was (roughly) approximated to 10×10^{10} cm⁻³ based on the known partial pressure of 'NO in the Helium: 'NO supply (1 %) and the pressure specified in the low pressure ion trap (LPT): 3.5×10^{-4} Torr.⁴

Extracting the triplet lifetime from experimental datasets

In the simple kinetics model presented in the manuscript, the effective triplet lifetime is $1/(k_r^{NO} + k_q)$. Triplet and singlet ions are undistinguishable by mass spectrometry, however photo-fragments (F) are triplet-specific and follow the same mono-exponential evolution as their triplets precursors. Thus, $k_r^{NO}+k_q$ and k_q^{He} (quenching rate in helium only) were determined by fitting the fragmentation ratio (in practice the log of it). Since the triplet formation as well as the triplet fragmentation yield strongly depend on experimental conditions, due to varying ion cloud size and overlap for both CW and pulsed lasers, complete time series were recorded within single experimental sessions in order to avoid inconsistencies. Then, all independent datasets were fitted simultaneously (within given buffer gas condition), modelling the log of the fragmentation ratio with a linear function sharing the rate parameter (= 1/slope, which ought to be independent from the alignment) but keeping prefactors independent. Fits were performed with least-square optimization using the LMFIT package for python,⁵ weighting the residuals, for each delay, with the uncertainty calculated on the 150 or 600 mass recordings. A bootstrap approach was implemented where such fit was performed on resampled data (10⁴ draws). The lifetime values discussed in the manuscript (Figure 3) are the mean of bootstrap distribution of optimized slopes. The uncertainty window reported in the text and Figure 3 are estimated from the dispersion of optimized slopes in the bootstrap distribution and are set at 2σ (*i.e.* uncertainty window 95.4 %).

Extracting the branching ratio between 'NO reaction vs. 'NO quenching of triplets

The determination of branching ratios between relaxation paths represents an important objective in order to finely understand the physical-chemistry of molecular systems. Here, the branching ratio between *NO reaction and *NO quenching of the triplet (BR, Eq. S1a) can be extracted from the experimental datasets. In the simple model exposed in the manuscript, this ratio appears hidden in the prefactor of the products population P while using the rate difference in helium and He:NO to estimate $\frac{k}{r} + \frac{k}{q}$ (see Eq.1b and Eqs.S1b).

$$BR = \frac{k_{r}^{\bullet NO}}{k_{r}^{\bullet NO} + k_{q}^{\bullet NO}} = \frac{k_{r}^{\bullet NO}}{k_{r}^{\bullet NO} + k_{q} - k_{q}^{He}}$$
(S1a)

$$= \frac{P \operatorname{prefactor}}{\frac{k^{\bullet NO} \cdot T_{0}}{k^{\bullet NO} \cdot r_{0} + k_{q}}} \times \frac{k^{\bullet NO} + k_{q}}{\frac{k^{\bullet NO} + k_{q}}{r_{1} + k_{q}} - \frac{k^{He}}{r_{1} + k_{q}}} \times \frac{\operatorname{not directly fitted}}{\frac{1}{T_{0}}}$$
(S1b)

However, in order to determine the branching ratio, it is necessary to normalize this expression by T_0 (Eq. S1b). Unfortunately, it is not possible to directly quantify triplets on the mass spectrum due to contribution of singlets at the same m/z. However, since all ions are singly charged and 600 nm photo-fragments are specific for the triplets, there can only be one charged fragment ion per precursor triplet ion. As a consequence, the total number (or intensity) of photo-fragments (F) is proportional to the population of triplet ions, for given probe laser irradiation conditions (Φ the laser fluence, Eq. 1c). In the most favorable (ideal) case, with 100 % efficiency of the triplet fragmentation, $(1 - e^{-\sigma.\Phi})$ may be close to 1 but the photo-fragmentation yield is also limited by the quality of the laser/ion cloud overlap. Thus, the photo-fragments prefactor only provides a lower bound, relative quantification proxy for the initial rhodamine triplets population (Eq. S2).

$$BR \leq \frac{P \operatorname{prefactor}}{\frac{k^{\bullet N0} T_{0}}{k^{\bullet r}_{r} + k_{q}}} \times \frac{k^{\bullet N0} + k_{q}}{\frac{k^{\bullet N0} + k_{q}}{r_{r} + k_{q}}} \times \frac{F \operatorname{prefactor}}{\frac{1}{T_{0} \cdot (1 - e^{-\sigma \cdot \Phi})}}$$
(S2)

Due to the very low relative intensity of product ions, their S/N is somewhat low compared to photo-fragments. In order to maximize the accuracy of the product prefactor, fits were performed simultaneously, *per* dataset, on fragments and products, sharing only the rate constant $(k_r^{NO}+k_q)$ in the exponent of the expression of F and P. Fits are graphically presented in Figures S5, S6 and S7. Optimized variables are listed in Table 1 in the manuscript. From these optimized variables (and the decay rates measured in helium and He:NO), it is possible to extract an upper bound for the reaction/quenching branching ratio (Eq. S2 and Table 1).

Computations

Coordinates are fully listed below. In brief, standard computational chemistry calculations were carried out with Gaussian 16.⁶ Geometries were optimized using the N12/6-31G(d) procedure.⁷ The choice of this level of theory is based on the our previous

studies into the use of efficient computational chemistry methods for obtaining reliable molecular geometries and thermochemical quantities related to vibrational frequencies.^{8,9} To obtain zero-point vibrational energies (ZPVEs) and thermal corrections to 298 K enthalpies, we used N12/6-31G(d) frequencies scaled by 0.9849 and 1.0205, respectively. For the calculation of single-point energies, we used the higher-level MN15 functional¹⁰ in conjunction with the larger 6-311G(2df,p) basis set. Unless otherwise noted, computed relative energies in the text are given as MN15/6-311G(2df,p) enthalpies at 298 K in kJ.mol⁻¹.

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Scheme S1. Proposed mechanism leading to the radical losses of Me⁺ and Et⁺ from ³Rh6G⁺. Radicals and charge are formalized for the sake of the representation but are stabilized by delocalization over the whole aromatic system.



Figure S1. Evolution of the CID fragmentation yield of Rh6G⁺ as a function of the normalized collision energy (NCE), under various ion preparation conditions: after 500 ms irradiation at 488 nm (red), after 500 ms without irradiation (blue) and without irradiation but immediately after selection (cyan). Activation time was set to 10 ms for all conditions.

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Figure S2. Comparison between CID spectra of Rh6G⁺ cations after 500 ms without (top: singlet only) and with (bottom: triplet is formed) irradiation at 488 nm. Intensities are relative to the precursor (indicated with a "*").



Figure S3. (left) LID mass spectra after 500 ms irradiation at 488 nm followed by (respectively top to bottom) (i) isolation of Rh6G⁺ with a large selection window ($\Delta m/z = 20$), (ii) a small selection window ($\Delta m/z = 1$), and (iii) a large selection window but 10 ms at 10 NCE activation before the 600 nm pulse. (right) Evolution of the LID yield at 600 nm as a function of the NCE value.



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Figure S5. Dataset #5. Fit performed separately on data from series in in Helium: *NO. Photo-fragments and NO-Products are fitted simultaneously for each dataset.



Figure S6. Dataset #6. Fit performed separately on data from series in in Helium:*NO. Photo-fragments and NO-Products are fitted simultaneously for each dataset.





Figure S7. Dataset #7. Fit performed separately on data from series in in Helium: *NO. Photo-fragments and NO-Products are fitted simultaneously for each dataset.

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•NC)			
02				
Ν	0.000000	0.000000	-0.617615	
0	0.000000	0.000000	0.540413	
•NC) ₂			
02				
Ν	-0.000000	0.329920	0.000000	
0	1.103548	-0.144340	-0.000000	
0	-1.103548	-0.144340	0.000000	
HN	0			
01				

Ν	0.063220	0.580626	0.000000
0	0.063220	-0.622749	0.000000
Н	-0.948293	0.917608	0.000000

HONO

01			
Ν	0.000000	0.548901	0.000000
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0	1.084034	0.059079	0.000000
н	-0.567626	-1.253579	0.000000

[Rhodamine 6G](+) singlet

11			
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н	2.221961	-3.363366	0.492345
С	2.316355	-2.347193	0.149290
С	2.491442	0.291015	-0.740507
С	1.174043	-1.616863	-0.086512
С	3.652604	-0.397501	-0.518731
С	1.210206	-0.275816	-0.538704
н	2.545527	1.312500	-1.084893
С	-1.174193	-1.616778	-0.086484
С	-2.316551	-2.347029	0.149340
С	-1.210272	-0.275731	-0.538680
н	-2.545493	1.312660	-1.084897
С	-0.000010	0.411137	-0.737542
С	-3.571156	-1.755642	-0.057940
н	-2.222222	-3.363208	0.492395
С	-3.652677	-0.397259	-0.518698
С	-2.491472	0.291178	-0.740489
0	-0.000095	-2.237325	0.129805
Ν	-4.706252	-2.443028	0.166041
н	-5.575013	-1.969886	0.004362
Ν	4.706050	-2.443352	0.165953
С	-4.785109	-3.808733	0.634212
н	-4.270862	-3.891654	1.594836
н	-4.260568	-4.461849	-0.067484
С	-6.228410	-4.245997	0.775171
н	-6.760759	-3.625821	1.495040
н	-6.272571	-5.273327	1.127023
н	-6.750694	-4.199538	-0.179410
С	4.784826	-3.809058	0.634135

н	4 260190	-1 162133	-0.067526
 Ц	4.200100	2 901024	1 504702
	4.270052	-5.691954	1.594792
C	6.228101	-4.246439	0.775004
н	6.750327	-4.200029	-0.179611
Н	6.272200	-5.273771	1.126861
Н	6.760548	-3.626303	1.494835
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С	0.000073	4.348173	-2.424417
С	-0.000045	2.934716	-0.463384
С	0.000141	1.952391	-2.667378
C	0.000159	3,220480	-3.236017
C	-0.000024	4 202707	-1 045761
ц	0.000197	1 077250	-3 300408
н ц	0.000137	2 222775	4 211242
п 	0.000240	5.522775	-4.511245
н	-0.000079	5.067446	-0.401827
н	0.000087	5.335028	-2.862455
С	-0.000100	2.765699	1.008687
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0	-0.000017	3.925299	1.659747
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н	0.878313	3.297795	3.409938
н	-0.877927	3.298202	3.410287
С	0.000681	5.268217	3.621951
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н	0.883913	5.810760	3,291813
н	0.000834	5 249085	4 710009
c	4 988740	0.234689	-0 743058
с u	4.388740	0.234089	1 404261
п 	5.572747	-0.301940	-1.494201
н	5.583108	0.266213	0.172972
н	4.879852	1.257821	-1.090864
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н	-5.572808	-0.301588	-1.494241
Н	-4.879819	1.258136	-1.090844
н	-5.583145	0.266575	0.172990
Н	5.574839	-1.970237	0.004339
·- ·			
[Rho	damine 6G	(+) triplet	
13			
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С	2.993950	-1.650768	0.260786
С	2.537699	0.978189	-0.519244
С	1.721066	-1.227789	-0.023789
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С	1.432804	0.099206	-0.438009
н	2.348594	1,999821	-0.809487
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н	-2.581349	0.665530	-1.188532
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С	-2.830432	-2.587505	-0.274823
Н	-1.129752	-3.805028	0.324440
С	-3.240511	-1.292009	-0.719401
C	-2 280690	-0 314167	-0 851988

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Ν

0.737930 -2.151405 0.117544

-3.753922 -3.564212 -0.127447

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С	-4.790585	-5.716281	0.363020
н	-5 503252	-5 278003	1 060017
н	-4 582753	-6 729515	0.696448
ц	-5 254866	-5 770017	-0 610963
C	5 7/2254000	2 474201	0.019903
L L	5.742250	2 100447	0.043370
н ц	5.420540 E 221200	-3.199447	1 771204
п С	7 241524	-2.752045	1.771594
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н	7.776611	-2.318547	0.127839
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н	7.568118	-1.847508	1.821827
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С	0.181433	2.173435	-2.492630
С	-0.095774	3.418990	-3.038558
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Н	0.710940	1.436376	-3.078973
Н	0.224419	3.646848	-4.044878
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Н	-1.015930	5.333184	-2.709702
С	-1.322745	2.520114	0.956334
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С	-1.110351	-0.477572	-0.615467
н	-2.644144	0.902858	-1.200687
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C	-3 499857	-0 976074	-0 725324
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0	0.564901	-2.259/16	0.001310
N	-4.292738	-3.123126	-0.172896
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С	-4.215755	-4.475155	0.268922
Н	-3.237945	-4.789964	0.646128
н	-4.431580	-5.095254	-0.609184
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Н	-5.107872	-4.173329	2.218964
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н	-6.274177	-4.478713	0.931487
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Н	-5.523754	-0.676763	-0.116284
Н	5.835814	-1.064391	0.145982

[Rhodamine 6G](+) -H + NO 1 1

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С	3.752557	-2.034254	-0.018508
н	2.239262	-3.504760	0.487365
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С	3.981770	-0.682141	-0.460511
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С	-4.843621	-2.951387	1.006440
н	-3.912660	-3.418697	1.307701
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С	0.870679	2.854564	0.960512
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