Supporting Information for "Disproportionation Pathways of the Hyponitrite Radical ($HN_2O_2^{\bullet}/N_2O_2^{\bullet-}$)" by Gregory A. Poskrebyshev, Vladimir Shafirovich, and Sergei V. Lymar.

Kinetic Modeling.

The absorbance-time kinetic profiles were modeled by numerical integration using rate, spectral, and yield data compiled in Tables S1 and S2. During fitting, these parameters were not allowed to deviate beyond 10% from their nominal values; in most cases, good fits were obtained by adjusting parameters within 5%.

TABLE S1. Reactions and their nominal rate constants.

N	Reaction	k, M^{-1} s^{-1}	Reference
6a	$N_2O_2^{\bullet-} + N_2O_2^{\bullet-} \rightarrow N_2O_2^{2-} + 2NO^{\bullet}$	4.1×10^{7} [a]	This work
10	$N_2O_2^{\bullet-} + NO^{\bullet} \rightarrow N_3O_3^{-}$	5.4×10^{9}	*[1]*
11	$N_3O_3^{-} \rightarrow NO_2^{-} + N_2O$	300[b]	This work and *[1]*, *[2]*, *[3]*
17	$NO + O_2^{\bullet-} \rightarrow ONOO^{-}$	4.8×10^{9}	*[4]* and refs. therein

[a] At zero ionic strength; appropriate Debye-Hückel corrections were applied for modeling. [b] In units of s^{-1}.

TABLE S2. Nominal molar absorptivities and radiation yields (in number of radicals per 100 eV absorbed energy).

Absorbing species	Wavelength, nm	ε, M^{-1} cm^{-1}	Reference	Radiation yield	
				O_2-saturated solution	N_2O/O_2-saturated solution
$N_2O_2^{\bullet-}$	290	5900	*[5]*	2.8	6.0
	300	3100			
	380	820			
$N_3O_3^-$	290	450	*[1]*	N/A	N/A
	300	400			
	380	3760			
$O_2^{\bullet-}$	290	520	*[6, 7]*	3.4	0.6
	300	410			
$ONOO^-$	290	1520	*[8]*	N/A	N/A
	300	1650			

References:

[1] S. V. Lymar, V. Shafirovich, G. A. Poskrebyshev, *Inorg. Chem.* **2005**, *44*, 5212.
[2] W. A. Seddon, M. J. Young, *Can. J. Chem.* **1970**, *48*, 393.
[3] W. A. Seddon, J. W. Fletcher, F. C. Sopchyshyn, *Can. J. Chem.* **1973**, *51*, 1123.
[4] S. V. Lymar, G. A. Poskrebyshev, *J. Phys. Chem. A* **2003**, *107*, 7991.
[5] G. A. Poskrebyshev, V. Shafirovich, S. V. Lymar, *J. Am. Chem. Soc.* **2004**, *126*, 891.
[6] B. H. J. Bielski, D. E. Cabelli, R. L. Arudi, A. B. Ross, *J. Phys. Chem. Ref. Data* **1985**, *14*, 1041.
[7] B. H. J. Bielski, *Photochem. Photobiol.* **1978**, *28*, 645.
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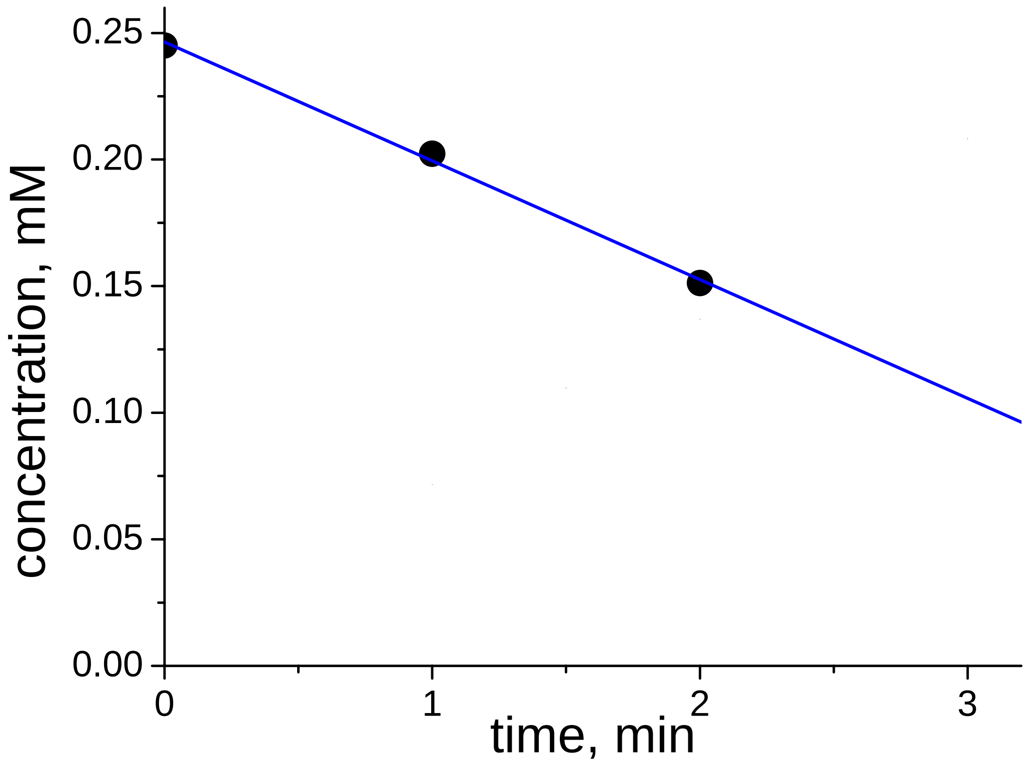


Figure S1. Consumption of $N_2O_2^{2-}$ measured spectrophotometrically and using ε_{248} = 6550 M^{-1} cm^{-1} in alkaline (25 mM NaOH), N_2O-saturated solution of $Na_2N_2O_2$ under continuous gamma-radiolysis with a Co-60 source at an 110 Gy/min dose rate. The line slope corresponds to a 0.047 mM/min consumption rate. The rate of $OH^{\bullet}$ radical generation calculated from Fricke dosimetry and using radiation yield of 6.1 $OH^{\bullet}$ radicals per 100 eV of absorbed radiation energy amounts to 0.070 mM/min, which yields the rate ratio of 0.67.

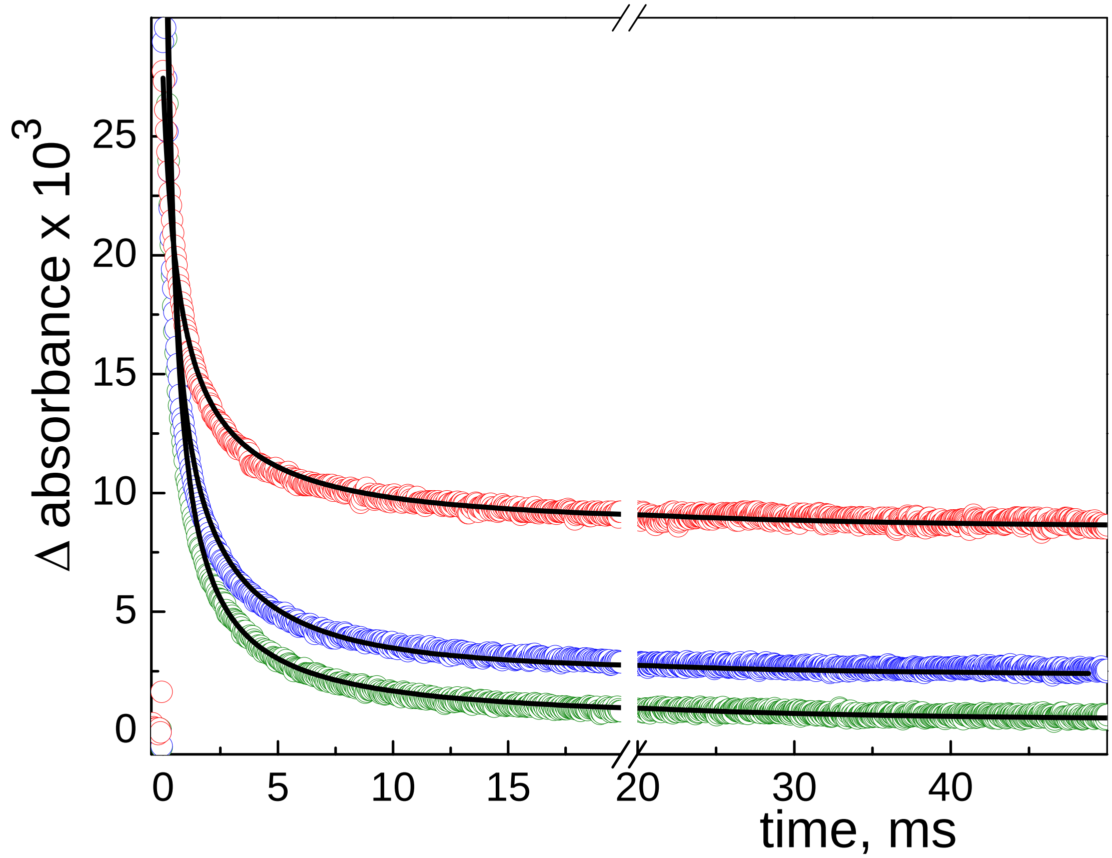
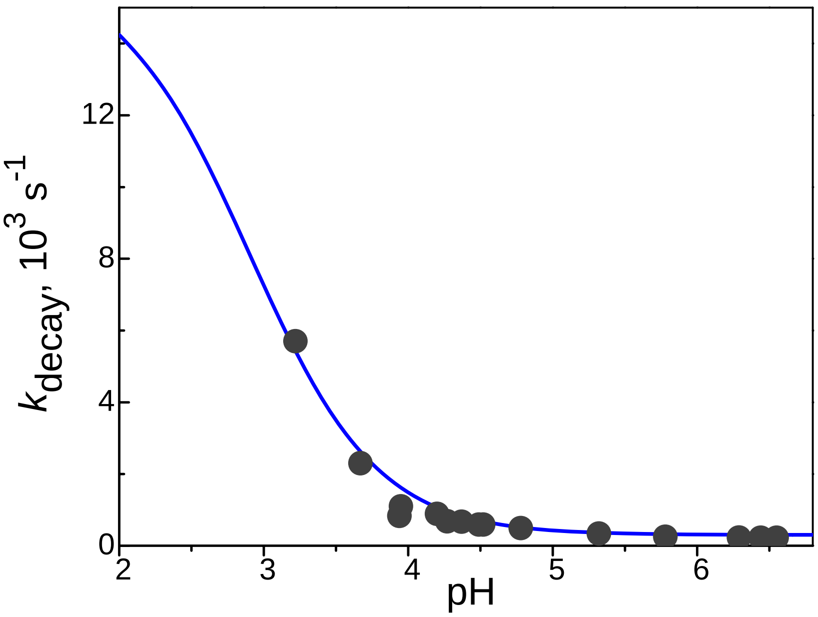


Figure S2. Kinetic traces recorded at 300 nm (open circles) following pulse radiolysis (doses 26–28 Gy) of 4.8 mM $Na_2N_2O_2$ in 5 mM Borax buffer (pH 9.2). Green trace: N_2O-saturated solution; blue trace: solution saturated with 9:1 N_2O/O_2 mixture; red trace: pure O_2-saturated solution. Black lines show fits by kinetic simulations using rates, molar absorptivities, and radiation yields data from Tables S1 and S2. Note the time scale break.



$HN_3O_3 \leftrightarrows H^+ + N_3O_3^-$ $\qquad K_a$

$N_3O_3^- \rightarrow N_2O + NO_2^-$ $\qquad k_{base}$

$HN_3O_3 \rightarrow N_2O + HNO_2$ $\qquad k_{acid}$

$$k_{\mathrm{decay}} = \frac{k_{acid}[\mathrm{H}^+] + k_{base}K_a}{K_\mathrm{a} + [\mathrm{H}^+]}$$

Figure S3. pH dependence of the $HN_3O_3/N_3O_3^-$ decay observed at 380 nm (circles) following pulse radiolysis of N_2O-saturated hyponitrite solutions. The blue line shows the expected dependence for p*K*a = 2.9, $k_{\mathrm{base}} = 320\ \mathrm{s}^{-1}$ and $k_{\mathrm{acid}} = 1.6 \times 10^4\ \mathrm{s}^{-1}$.