Kinetic and thermodynamic aspects of the chain-breaking antioxidant activity of ascorbic acid derivatives in non-aqueous media

Riccardo Amorati, Gian Franco Pedulli and Luca Valgimigli

University of Bologna, Department of organic Chemistry "A. Mangini", via S. Giacomo 11, 40126 Bologna Italy.

ELECTRONIC SUPPLEMENTARY INFORMATION

1 Gauss
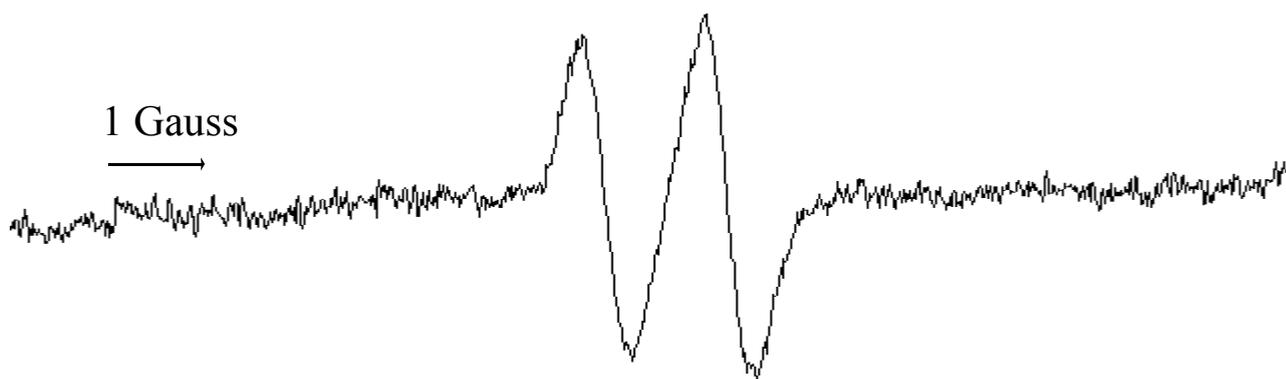
Figure S1. Experimental X-band EPR spectrum (of the ascorbate radical anion) recorded upon continuous UV irradiation at 298K of a solution of ascorbyl palmitate in *tert*-butanol, containing 5% (v/v) di-*tert*-butylperoxide. The visible HFSC is a(H)=1.7G; measured line-width is LW=0.5G ($g = 2.0054$).

1 Gauss
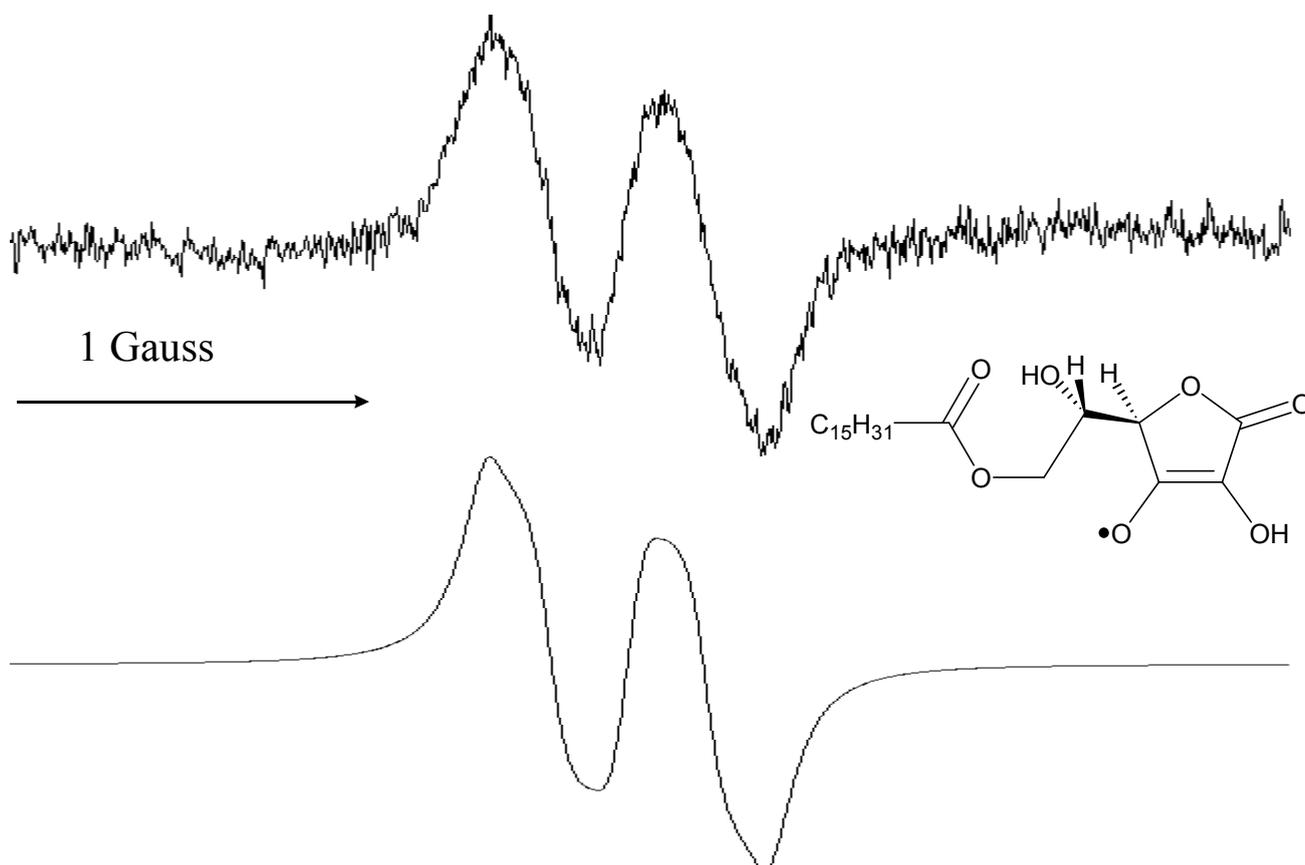
Figure S2. Experimental (top) and simulated (bottom) X-band EPR spectrum of the ascorbyl radical recorded upon continuous UV irradiation at 310K of a solution of ascorbyl palmitate in *tert*-butanol, containing 5% (v/v) di-tert-butylperoxide and 5% (v/v) concentrated (36% in water) hydrochloric acid (g=2.0050).
Simulation was obtained with the following parameters: a(H)=0.45G; a(H)=0.14G; a(H)=0.11G; a(H)=0.05G; LW = 0.28G.

1 Gauss
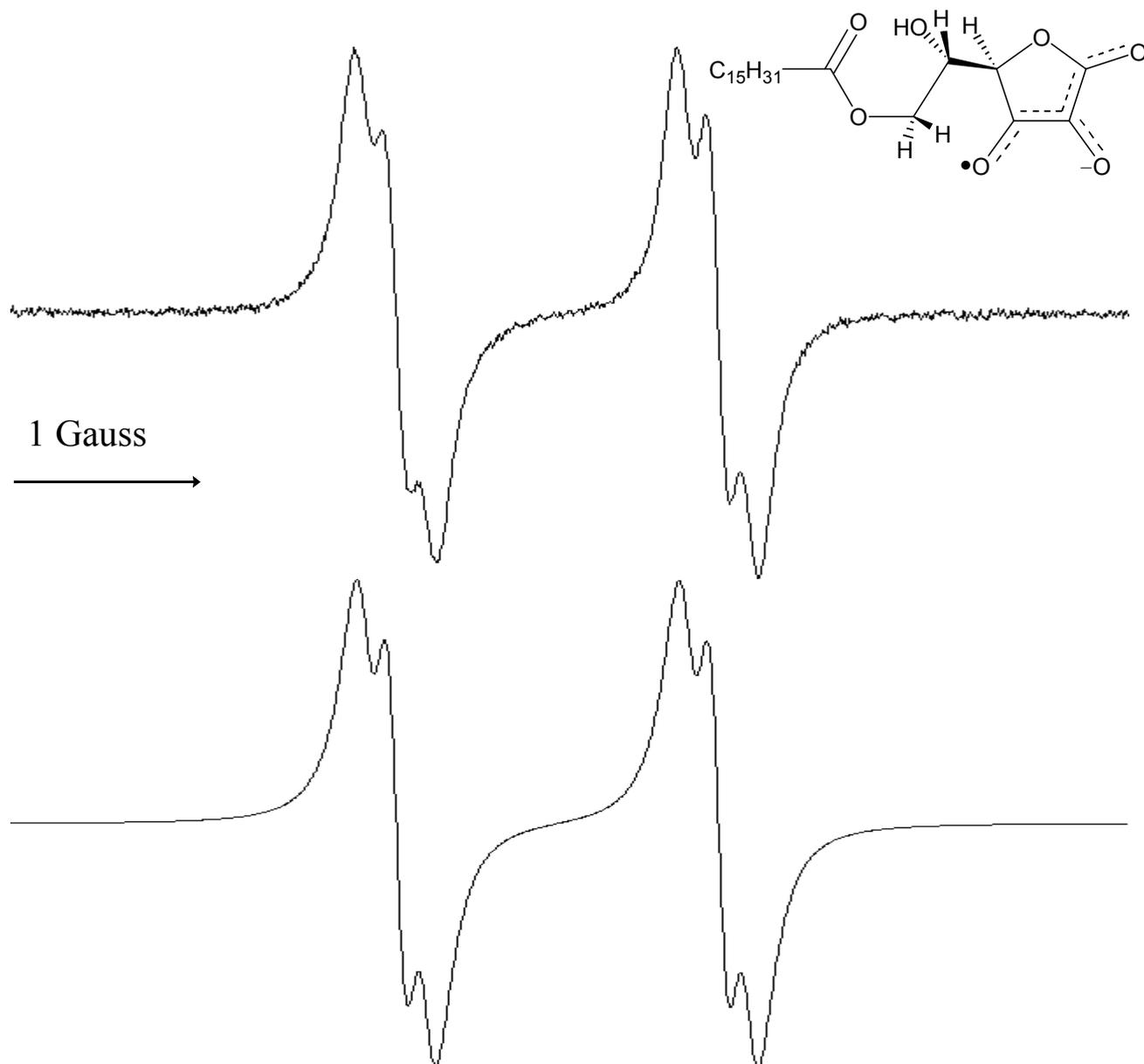
Figure S3. Experimental (top) and simulated (bottom) X-band EPR spectrum of the ascorbate radical anion recorded upon short (5 sec) UV irradiation at 310K of a 3mM solution of ascorbyl palmitate in *tert*-butanol, containing 3mM DBU (1 equiv.) and 5% (v/v) di-*tert*-butylperoxide (*g*=2.0054).
Simulation was obtained with the following parameters: a(H)=1.85G; a(H)=0.18G; a(H)=0.16G; a(H)=0.05G; LW = 0.22G.

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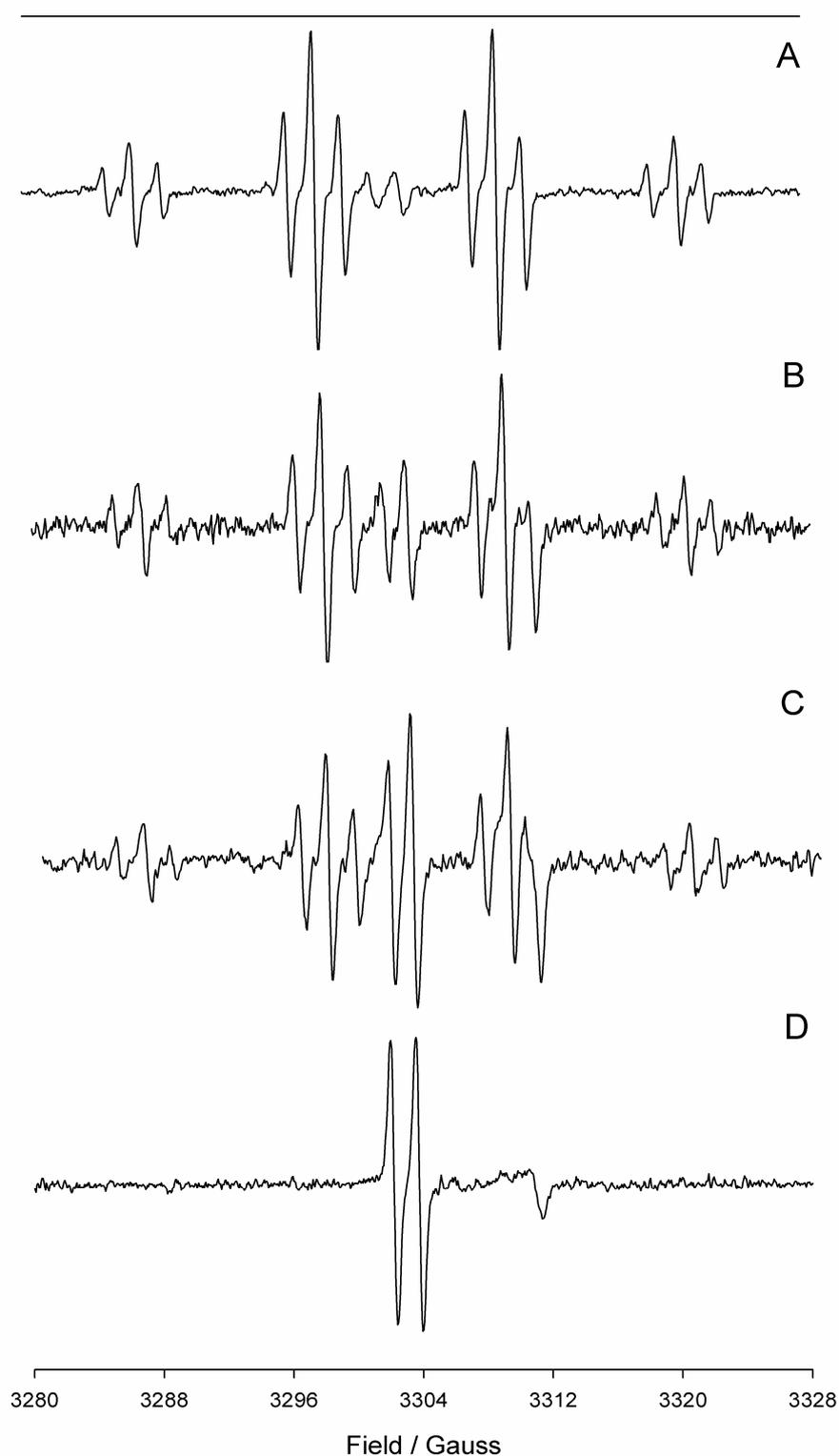
Figure S4. Experimental X-band EPR spectra recorded upon continuous UV irradiation at 298K of a mixture of ascorbyl palmitate (22 mM) and 2,6-di-*tert*-butyl-4-methylphenol (12 mM) in *tert*-butanol, containing: (A) 5% (v/v) di-*tert*-butylperoxide; (B) 5% (v/v) di-*tert*-butylperoxide and 3% (v/v) pyridine; (C) 5% (v/v) di-*tert*-butylperoxide and 7% (v/v) pyridine; (D) 5% (v/v) di-*tert*-butylperoxide and 7% (v/v) triethylamine.

Table S1. Sum of electronic and thermal enthalpies for the model of ascorbic acid **4H₂** and relative energies of the conformers for its molecule and radical in the various protonation states. All calculations are at the B3LYP/6-31g+(d,p) level.

		E+H (Hartree)	ΔH (kcal/mol)
Closed-shell molecule		-455.638582	+7.1
		-455.643475	+4.0
		-455.649842	0
Neutral radical		-455.025314	+4.3
		-455.032194	0
		-455.031465	+0.5
anion[a]		-455.133200	0
		-455.131628	+1.0
Radical anion		454.533082	
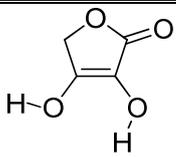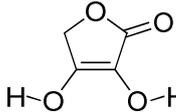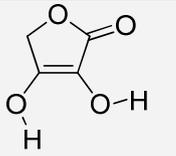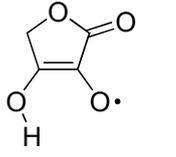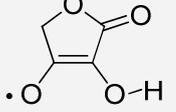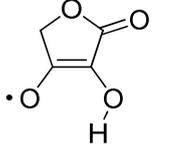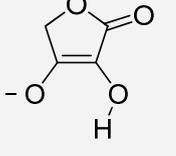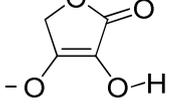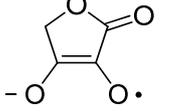
a In the anion, the H+ is lost from the 4-OH group, as reported in ref. 17.

-695.730101   -695.116565

-484.090543   -483.489548
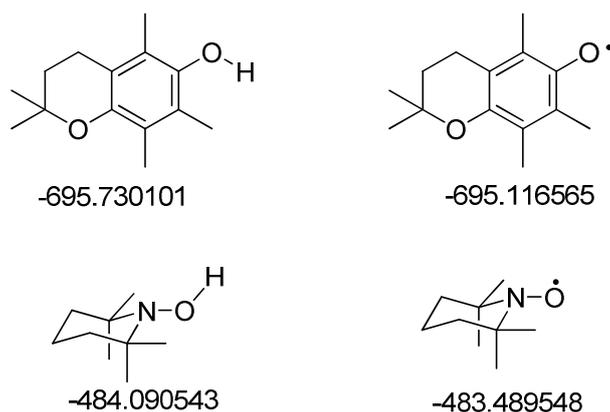
Figure S5. Sum of electronic and thermal enthalpies for PMHC (upper) and TEMPOH and for the respective radicals, at the B3LYP/6-31g+(d,p) level (in Hartree).

Table S2. Sum of electronic (E) and thermal enthalpies (H) for the simplified model of ascorbic acid **4H$_2$**, donating a H-bond to acetonitrile, and relative energies for the different binding sites in its molecule and radical. All calculations are at the B3LYP/6-31g+(d,p) level.

		E+H (Hartree)	ΔH (kcal/mol)
		-588.377236	0
		-588.373911	+2.1
		-587.757662	+2.6
		-587.761787	0

-307.384969   -132.716829   -440.109342
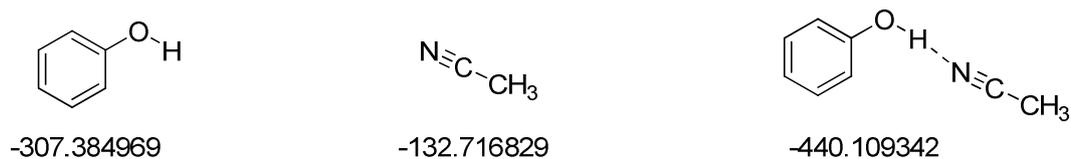
Figure S6. Sum of electronic and thermal enthalpies (Hartree) for phenol, acetonitrile and their complex.

Table S3. Differences between the total energies in solution for the investigated compounds and their radicals, calculated by using the polarized continuum model in MeCN, and with respect to TEMPOH.

	$-\Delta E$ / Hartree	$\Delta\Delta E$ resp TempoH / kcal/mol
TEMPOH	0.613936	-
PMHC	0.624842	+6.8
AscH2	0.632735	+11.8
AscH-	0.615192	+0.8
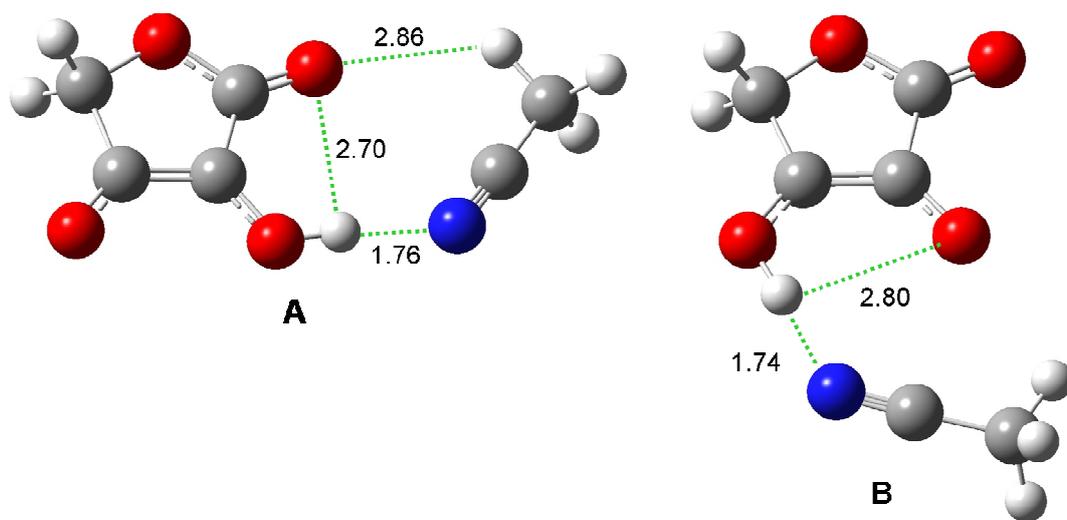
Figure S7. Optimized geometries (H-bond lengths are in Å) for the formation of the H-bond complex between **4H•** and acetonitrile.
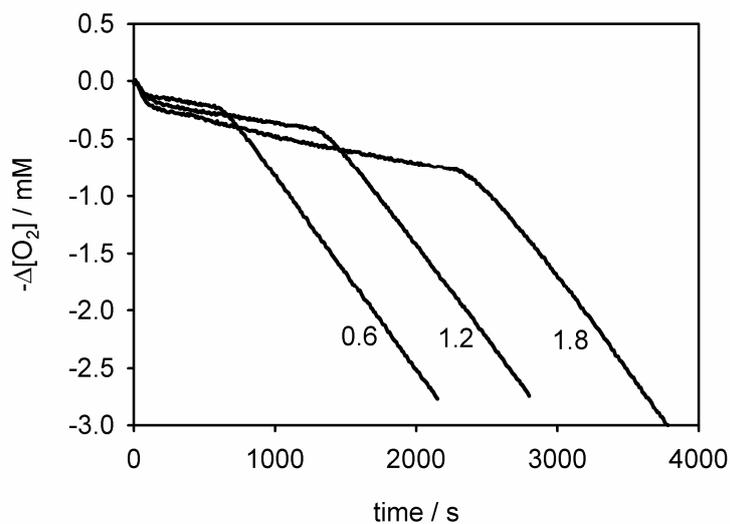
Figure S8. Oxygen consumption observed during the autoxidation of styrene (4.3 M) in MeCN initiated by AIBN (0.05 M) at 30 °C in the presence of acetic acid (44 mM) and of increasing amounts of **3H₂** (10^{-5} M).
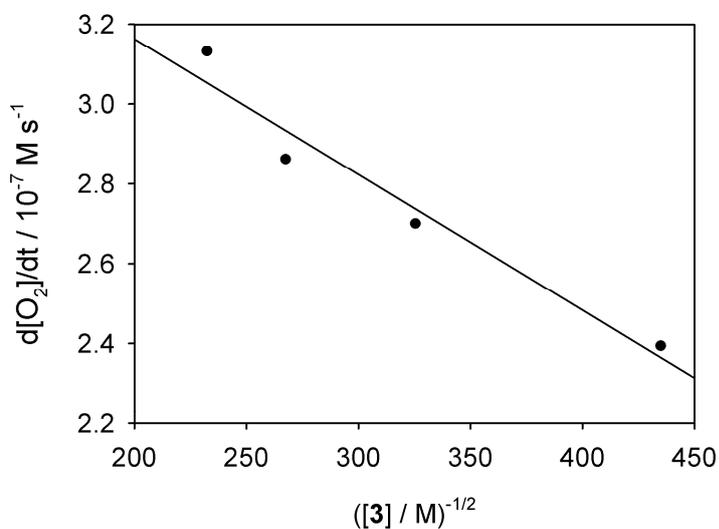
Figure S9. Dependence of the O_2 consumption rate during the inhibited period on the concentration of **3H₂**, in the presence of pyridine 30 mM.