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Kinetics of oxidation of nitrosodisulfonate anion radical with a metallo-superoxide[†]

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The metal bound superoxide in μ -superoxo-bis[pentaamminecobalt(III)]⁵⁺ (1) oxidizes the nitrosodisulfonate anion radical (NDS²⁻) by two electrons. Oxidized NDS²⁻ quickly decomposes to SO₄²⁻ and NO. 1 is itself reduced to the corresponding hydroperoxo complex which also decomposes fast to Co(II), NH₄⁺ ions and oxygen. 1.5 moles of volatile products formed per mole of 1 mixed with excess NDS²⁻. In the absence of superoxide in a bridged complex, *e.g.* the μ -amido-bis [pentaamminecobalt(III)]⁵⁺ complex fails to oxidize the nitroxyl radicals, NDS²⁻, TEMPO and 4-oxo TEMPO. With excess NDS²⁻ over 1, the reaction is first-order with respect to [1], [NDS²⁻] and inverse first order in [H⁺]. The activation entropy, ΔS^{\neq} , is largely negative, increased ionic strength decreased the

rate and a Brønsted plot is fairly linear with a negative slope. Oxidant μ -superoxo-bis[(ethylenediamine) (diethylenetriamine)cobalt(III)]⁵⁺ has ligands sterically more crowded though more basic than ammonia in **1**. It oxidizes NDS²⁻ much more slowly. No solvent kinetic isotope effect ($k_{H_2}O/D_2O \approx 1$) could be seen; a spin-adduct formation by the conjugate base of **1** followed by electron transfer is postulated.

Introduction

The persistent odd-electron species, nitrosodisulfonate anion radical, $ON(SO_3)_2^{2-}$ (NDS²⁻) forms by virtually complete homolysis of Fremy's salt (potassium nitrosodisulfonate dimer) in polar solvent media.¹ Many groups utilized mild oxidizing capacity of this comparatively stable, water-soluble nitroxyl radical in kinetic studies² and preparation³ related to a wide range of natural products.⁴ Some closed ring nitroxyl radicals like TEMPO and its derivatives have also been oxidized to oxoammonium salts, and in some cases, to their decomposition products. The kinetics⁵ and catalytic activities⁶ of these reactions are well studied. In comparison, the reducing action of NDS²⁻ is little known.

Reactive oxygen species (ROS)⁷ are a class of radical or nonradical oxygen-containing molecules and display high reactivity with lipids, proteins and nucleic acids.⁸ Depending on concentration, location and context, ROS can be either "friends" or "foes".⁹ Accumulative and systemic ROS damage underlies cell senescence and aging. However, increasing evidence indicates that homeostatic and physiological levels of ROS are indispensable in regulating diverse cellular processes.¹⁰

Superoxide is one of the ROS. Even its metal complexes have substantial unpaired spin density on the oxygen, which makes it quite reactive towards radicals.⁵ Nevertheless, its reactivity can be controlled by metal coordination.¹¹ Again, NDS^{2-} is an

important probe for reactive oxygen species (ROS) in biology.¹² The superoxo moiety of the complex, μ -superoxo-bis [pentaamminecobalt(π)]⁵⁺ (1) oxidizes the nitroxyl radical NDS²⁻ at a measurable rate, and here we report its kinetics and plausible mechanism.

The primary objective of this work is to see how the metalcoordinated superoxide oxidizes NDS^{2-} , and to what products? We wish thus to add further details to the oxidation chemistry of NDS^{2-} with a metal-bound radical. It can be here mentioned that electron-transfer reactions involving radicals and radical ions have attracted much attention.¹³

In this context, it is interesting to note that the superoxo complex 10xidizes hydroxylamine disulfonate, $HON(SO_3K)_2$ · $2H_2O$ (HDS), faster than NDS^{2-} under comparable reaction conditions. Its preparative implications have also been discussed.

Experimental

Materials

2,2,6,6-Tetramethylpiperidine-*N*-oxyl radical (TEMPO) and 2,2,6,6-tetramethyl-4-oxopiperidine-*N*-oxyl radical (4-oxo TEMPO) were of analytical grade (Aldrich) and were used as received.

Fremy's salt was prepared by the reported procedure¹⁴ and stored below 5 °C in an ammonia environment. Freshly prepared samples were pure ($\varepsilon^{545} = 20.8 \text{ M}^{-1} \text{ cm}^{-1}$ on the basis¹⁵ of NDS²⁻) but slowly decomposed on storage. Therefore, fresh samples were prepared regularly and samples with $\varepsilon \ge 19.5$ were only used.

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The pentachloride salt of μ -superoxo-bis[pentaamminecobalt(III)]⁵⁺ (1) was synthesized following a literature process.¹⁶ The chloride salt was converted to the corresponding perchlorate salt¹⁷ and re-crystallized from 10% HClO₄ (ε , M⁻¹ cm⁻¹ at 670 nm = 835; lit. value: 838¹⁸).

 μ -Amido-bis[pentaamminecobalt(III)] pentaperchlorate monohydrate was prepared as described in the literature¹⁹ (ε , M⁻¹ cm⁻¹ at 360 nm = 705, at 505 nm = 426; lit. value: at 360 nm = 708, at 505 nm = 428). The compound is stable against autodecomposition.²⁰

The superoxo complex, μ -superoxo-bis[(ethylenediamine) (diethylenetriamime)cobalt(III)] pentaperchlorate was synthesized following a literature procedure²¹ and re-crystallized from 0.3 M HClO₄. Its purity was checked by measuring its absorbance at 708 nm (ε , M⁻¹ cm⁻¹ at 708 nm = 1200; lit. value: 1210).

HDS was prepared by a reported procedure.²² Its purity was checked by H, N microanalyses (Anal. Calc. for HON(SO₃K)₂· $2H_2O$: H, 1.63; N, 4.50. Found: H, 1.60; N 4.41%).

Physical measurements, kinetics and stoichiometry

The pH values of the reaction solutions were measured with a Toshniwal pH meter (CL-54), having electrodes calibrated²³ with standard pH 4, 7 and 9 buffers. In D₂O media, the relation pD = pH + 0.4 was used.^{24,25} H, N microanalyses were done on a Perkin-Elmer 240C elemental analyzer. Absorbance, UV-Vis spectra and kinetics were recorded with a Jasco (V-1700) spectrophotometer using 1.00 cm quartz cells. The kinetics was monitored at 670 nm, observing the decay of 1 in aqueous acetate buffer media ($T_{OAc} = 0.10$ M) in the range pH, 4.85–5.85 at 25 (±0.1) °C in an electrically controlled thermostated cell-housing of the instrument. Ionic strength (1) of the reaction media was maintained at 1.5 M. A large excess of NDS²⁻ over 1 was used to maintain the pseudo first-order conditions. NDS²⁻ has a small contribution to the total absorbance at 670 nm. It was subtracted from the observed total absorbance, assuming essential constancy of $[NDS^{2-}]$. The absorbance vs. time (t) data fitted a firstorder decay equation (ORIGIN 7.0). The reported first-order rate constants (k_{obs}) are the averages of 2–3 independent measurements. It was verified that purging the reaction media with Ar gas had practically no effect on kinetics and, therefore avoided.

With $[NDS^{2-}]$ in excess over [1], the amount of sulfate formed was measured gravimetrically. The volume of gas(es) evolved during the reaction was collected by downward displacement of water and corrected to NTP as usual. NO gas was qualitatively tested in the ensuing gas by passing it through a fresh FeSO₄ solution acidified with sulfuric acid. The consumption ratio, $\Delta[NDS^{2-}]/\Delta[1]$, was measured at 670 nm with [1] in excess over $[NDS^{2-}]$. Doubly distilled water was used all throughout the reaction.

Results and discussion

The consumption ratio, Δ [1]/ Δ [NDS²⁻] \approx 2 and NDS²⁻ is a two electron donor (see ESI, Table S1a⁺) in contrast to some other nitroxyl radicals like TEMPO and its derivatives which are known to be one electron donors.⁵ With excess NDS²⁻, each mole of **1** produces 1.5 moles of gaseous products (see ESI, Table S1b⁺) and one mole of SO₄²⁻ (see ESI, Table S1c⁺). The

amount of sulfate captured as barium salt did not change in the presence of NH_4Cl ; it eliminated any chance¹⁵ for accumulation of a detectable amount of HDS formed by the acid degradation of NDS^{2-} . These observations suggest the following stoichiometric equation (eqn (1)).¹⁶

$$21 + \text{NDS}^{2-} \rightarrow \text{NO} + 2\text{SO}_4^{2-} + 2\text{O}_2 + \text{other product}$$
 (1)

The reduced form of **1** has been previously suggested to be **3**, the hydroperoxo derivative¹⁸ of **1** which rapidly decomposes²⁶ to Co^{II}, NH₄⁺ ion and O₂. A blue color appeared by boiling the product mixture with HCl that confirms the presence of Co²⁺ ions in the product solution. Co²⁺ ions, as with O₂, had no effect on the kinetics. Simple Co(II) species (hexaaqua) are d⁷ ions and radicals on their own, which may react quickly with excess NDS²⁻. Probably Co²⁺ and NDS²⁻ experience ionic interaction only and do not take part in kinetics which were not first-order as observed if Co²⁺ takes part in kinetics (kind suggestion of one referee).

Kinetics and mechanism

In the range pH 4.85–5.85, individually neither 1 nor NDS^{2–} suffer any bleaching, even in 3 h, but on mixing them the reaction is completed in less than 1.5 h. Murib *et al.*¹⁵ reported that at pH 4.96 the decomposition time of NDS^{2–} is 19 h. If we consider the possibility that very small amounts of decomposition products of NDS^{2–} may act as chain propagators, one would then expect complex auto-catalytic kinetics instead of the first-order kinetics observed here. Hence this possibility is not further taken up. The complex ion μ -amido-bis[pentaamminecobalt (m)]⁵⁺ has no superoxo moiety and it does not react with NDS^{2–}, TEMPO or 4-oxo-TEMPO. This observation strongly suggests that reaction of 1 with NDS^{2–} is actually the reaction of the superoxo group in 1. Other researchers^{17,27} also presumed the same.

Spectral changes after mixing excess NDS^{2-} with 1 are shown in Fig. 1. The reactions were found to be first-order in [1] (Fig. 2), first-order in $[NDS^{2-}]$ and inverse first order in $[H^+]$



Fig. 1 Spectra at different times of 0.20 mM of **1** reacting with 4 mM of NDS^{2–}. pH = 5.60. $T_{OAc} = 0.10$ M, I = 1.5 (NaCl) M and T = 25.0 ($\pm = 0.1$) °C. Spectra (a–h) are reaction mixtures at 0, 60, 120, 180, 240, 300, 360 and 720 s, respectively.



Fig. 2 Kinetic profile at 670 nm for the oxidation of NDS^{2–} (4.0 mM) with **1** (0.2 mM). pH = 5.6, $T_{OAc} = 0.10$ M, I = 1.5 (NaCl) M and $T = 25.0 (\pm 0.1)$ °C. The solid line is the first-order fit of the experimental values (shown in solid circles). Absorbance of NDS^{2–} was subtracted from the observed total absorbance, assuming essential constancy of [NDS^{2–}].



Fig. 3 Plot k_{obs} vs. 1/[H⁺] at different concentrations of NDS²⁻. [1] = 0.20 mM, $T_{OAc} = 0.10$ M, I = 1.5 (NaCl) M and $T = 25.0 (\pm 0.1)$ °C. (1)–(4) are at [NDS²⁻] = 2.0, 3.0 4.0 and 5.0 mM respectively. Corresponding values of $K_1K_2k_1$ are fairly constant = 5.1 (± 0.3) × 10⁻⁶ s⁻¹. Previously¹¹ for H₂O₂ the value was found to be 5.26 (± 0.2) × 10⁻⁸ s⁻¹. A comparison for the reduction of 1 by different reducing agents is given later in Table 3.

(Fig. 3). Some representative values of the rate constant (k_{obs}) are summarized in Table 1. k_{obs} of the reaction decreases with increasing ionic strength of the media.

The superoxo moiety in **1** has no acidic proton and cannot explain the inverse proton dependence of k_{obs} . NDS²⁻, in basic media may add to water²⁸ or a nucleophile²⁹ and thus can act as a source for the inverse proton dependence. In the acetate buffer media, such a function for NDS²⁻ is unexpected. Absence of

Table 1 Representative rate constants for the oxidation of NDS^{2–} with 1 (0.20 mM) at different pH. $T_{OAc} = 0.10$ M, I = 1.5 (NaCl) M and $T = 25.0 (\pm 0.1)$ °C

[NDS ²⁻]/mM	$10^3 k_{\rm obs} ({\rm s}{\rm -}^{-1})$ at pH					
	4.85	5.10	5.35	5.60	5.85	
2.0	0.46	0.71	1.35	2.05	3.74	
3.0	0.60	0.95	1.71	3.15	4.87	
4.0	0.82	1.41	2.55	4.09	7.75	
5.0	1.15	1.71	3.02	5.01	8.81	
6.0	1.44	1.97	3.45	6.05	10.41	

solvent kinetic isotope effect (see ESI, Table S2[†]) supports this proposition. Therefore rate-enhancement with pH is ascribed to the dissociation of an H⁺ ion from one of the coordinated NH₃ molecules in **1**, thus forming the conjugate base¹¹ $[(NH_3)_5Co(O_2)Co(NH_3)_4(NH_2)]^{4+}$ (**2**) as the kinetically reactive species (eqn (2)). Decomposition of **1** by base hydrolysis¹⁶ supports the formation of **2** and inverse first order in [H⁺]. Kinetically reactive conjugate bases like **2** have been sufficiently demonstrated to participate³⁰ in the base-catalysed hydrolysis reactions of acidopentaamminecobalt(III) complexes.³¹

Other mechanistic possibilities for $[OH^-]$ dependence may arise by attack of OH^- ion at the superoxide bridge or by an equilibrium attack of OH^- ion on NDS^{2-} (suggestion of a referee). But attack by OH^- ion on the superoxo-bridge in **1** needs catenation of three oxygen atoms and seems improbable. Also, attack of OH^- on NDS^{2-} requires^{28,29} much higher pH of the solution. We prefer conjugate base formation by **1** because of the reasons stated above and because (a) several Co^{III} -amines deprotonate^{31b,c} at acidic pH to show base catalysis and (b) formation of the conjugate base appears easier for a dinuclear complex than for its mononuclear analogue.³⁰

The reduction potential of NDS^{2-} is much lower (see Table 2) than the reduction potential of 1 under similar conditions. So

 Table 2
 A comparison of the reduction potentials

Reagent	pН	Reduction potential (Volt vs. NHE)	Source
μ-Superoxo-bis [pentaamminecobalt(III)] ⁵⁺ NDS ²⁻ NDS ²⁻ NDS ²⁻	4.0 5.9 4.9	1.00 0.70 0.76	Ref. 27 <i>c</i> Ref. 37 Ref. 37
NDS ^{2–} NDS ^{2–} 4-Oxo-TEMPO TEMPO	4.0 1.0 1.0 1.0	0.81 0.98 0.91 0.73	Ref. 37 Ref. 37 Ref. 5 Ref. 5

$$[(NH_{3})_{5}Co(O_{2}^{-})Co(NH_{3})_{5}]^{5} + \frac{K_{1}}{2} [(NH_{3})_{5}Co(O_{2}^{-})Co(NH_{2})(NH_{3})_{4}]^{4+} + H^{+}$$

$$2 + NDS^{2} + NDS^{2} + [(NH_{3})_{5}Co(O_{2}^{-})Co(NH_{2})(NH_{3})_{4}]^{2+}$$
Spin adduct
$$[NDS^{2-} \# [(NH_{3})_{5}Co(O_{2}^{-})Co(NH_{2})(NH_{3})_{4}]^{2+} \frac{k_{1}}{slow} [(NH_{3})_{5}Co(O_{2}^{-2})Co(NH_{2})(NH_{3})_{4}]^{3+} + NDS$$

$$2 + NDS - \frac{fast}{2H_{2}O} [(NH_{3})_{5}Co(O_{2}^{-2})Co(NH_{2})(NH_{3})_{4}]^{3+} + 2 SO_{4}^{2-} + NO + 4 H^{+}$$

$$[(NH_{3})_{5}Co(O_{2}^{-2})Co(NH_{2})(NH_{3})_{4}]^{3+} \frac{fast}{2 H^{+}} [(NH_{3})_{5}Co(HO_{2}^{-})Co(NH_{3})_{5}]^{5+}$$
fort

3 $\xrightarrow{\text{tast}}$ Decomposion products like Co^{II}, NH₄⁺, O₂

Scheme 1

 NDS^{2-} should act as a reductant for 1 according to the thermodynamics.

Based on the kinetic and stoichiometric observations, we propose the Scheme 1 for the oxidation of NDS^{2-} .

Two moles of **1** are consumed by one mole of NDS^{2–}, so it is a non-complementary reaction and stoichiometric factor is two. Assuming $K_1K_2 \ll 1$ the proposed scheme leads to $k_{obs} = 0.5K_1K_2k_1[NDS^{2-}]/[H^+]$ (see ESI[†]), in accord with the observations. Some values of $K_1K_2k_1$ are summarized in Fig. 3. From this figure it is clear that composite $K_1K_2k_1$ regenerated k_{obs} values reasonably well.

Previously Goldstein et al.32 suggested adduct formation before electron transfer between the reaction of NO2[•] and nitroxyl radical. Also, Bakac⁵ showed that LMOO²⁺ undergoes adduct formation with nitroxyl radicals. Such adducts are innersphere spin adducts and involve distinct chemical bonding between the reactants.³³ We found that NDS²⁻ reacts 10⁴ times slower with µ-superoxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)]⁵⁺ ion than with **1**. The p K_a of ammonia is 9.3 while that of ethylenediamine³⁴ and diethylenetriamine³⁵ are respectively 10.0 and 9.9. So K_1 , and k_1 are expected to be larger in the µ-superoxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)]⁵⁺ complex but the reverse has been found. Possibly, steric factors dominate over pK_a values and steric congestion in the µ-superoxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)]⁵⁺ complex slows down the adduct formation equilibrium prior to the electron transfer.

Since K_1 , K_2 and k_1 are inseparable, Erying plot with the third order rate constants, $k_{obs}[H^+]/[NDS^{2-}]$, has been constructed (Fig. 4). This gives an activation enthalpy $\Delta H^{\neq} = 83.8 \text{ kJ mol}^{-1}$ and the activation entropy $\Delta S^{\neq} = -54.3 \text{ JK}^{-1} \text{ mol}^{-1}$. Such a highly negative value of ΔS^{\neq} indicates close approach of the reagents, and supports the K_2 step in the Scheme 1.

Ionic strength (*I*) plays an important role in reactions between charged species. We investigated the effect of ionic strength on the reaction by varying NaCl concentration in the reaction media. The Brønsted plot of $\log(k_{obs})$ vs. $I^{1/2}$ (at pH = 5.35 and [NDS^{2–}] = 4 mM) is fairly linear with a negative slope (see ESI,



Fig. 4 Eyring plot at pH = 5.85, [1] = 0.20 mM, $[NDS^{2-}] = 10.0$ mM, $T_{OAc} = 0.10$ M and I = 1.5 (NaCl) M. Third-order rate constants (k) = $k_{obs}[H^+]/[NDS^{2-}]$.

Fig. S1[†]) probably due the interaction of opposite charges in the K_2 step.

1 reacts with TEMPO almost immediately. In comparison, its reaction with 4-oxo-TEMPO is slow (Table 3) but faster than that of NDS^{2-} . From the reduction potential data shown in Table 2, we conclude that thermodynamically weaker reducing agents react at a slower rate. So electron transfer appears to be through outer sphere, after the spin-adduct formation.

As expected, no solvent kinetic isotope effect is observed for the oxidation of NDS²⁻ with **1** and $k_{\rm H_2}O/D_2O \approx 1$. Therefore this accounts to describe a pathway in which concerted electron– proton transfer occurs, but involves more than one site, *i.e.* electron transfer from NDS²⁻ and proton transfer from the solvent at different time.

All the observations support the proposed Scheme 1, where 2, the conjugate base of 1 accepts electron from NDS²⁻; μ -super-oxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(\mathfrak{m})]⁵⁺ ion is

Table 3 Kinetic data for the reduction of 1 in aqueous solution at T = 25.0 °C

Reductant	Concentration (mM)	pН	$k_{\rm obs},{\rm s}^{-1}$	Source
Ascorbic acid ^a	200	5.17	24.0	Ref. 17
Ascorbic acid ^a	200	4.94	20.1	Ref. 17
Ascorbic acid ^a	200	4.65	18.8	Ref. 17
Hydrazine ^b	150	6.10	26.0×10^{-4}	Ref. 38
Hydrazine ^b	150	5.80	16.0×10^{-4}	Ref. 38
Hydrazine ^b	100	6.10	18.0×10^{-4}	Ref. 38
Hydrogen peroxide ^{c}	50	5.01	2.7×10^{-3}	Ref. 11
Hydrogen peroxide ^c	50	5.30	5.3×10^{-3}	Ref. 11
Hydrogen peroxide ^{c}	30	5.01	1.7×10^{-3}	Ref. 11
HDS^{d}	2	5.01	8.1×10^{-3}	This work
HDS^d	2	5.48	25.0×10^{-3}	This work
HDS^d	5	5.01	14.2×10^{-3}	This work
TEMPO ^e	5	4.39	Instant	This work
4-Oxo-TEMPO ^e	5	4.39	32.5×10^{-3}	This work
NDS^{2-e}	5	4.39	0.5×10^{-3}	This work

^{*a*} At [1] = 0.01 mM, T_{OAc} = 0.20 M, I = 0.20 M (NaClO₄). ^{*b*} At [1] = 0.50 mM, [dipicolinic acid] = 0.10 mM, T_{OAc} = 0.20 M, I = 1.00 M (NaClO₄). ^{*c*} At [1] = 0.20 mM, T_{OAc} = 0.20 M, I = 0.50 M (NaClO₄). ^{*d*} At [1] = 0.20 mM, T_{OAc} = 0.10 M, I = 1.50 M (NaCl). ^{*e*} At [1] = 0.20 mM, T_{OAc} = 0.10 M, I = 1.50 M (NaCl). ^{*e*} At [1] = 0.20 mM, T_{OAc} = 0.10 M, I = 1.50 M (NaCl).

sterically congested and forms weaker adduct with NDS²⁻; so K_2 value is smaller leading to a smaller k_{obs} .

No attempt was taken to detect any intermediate such as 2 or the "spin adduct", since no saturation kinetics was observed, which tells us that no intermediate accumulates to a detectable extent.

1, under similar conditions, reacts with hydroxylamine disulfonate (HDS) almost ten times faster than NDS^{2-} (see ESI, Table S3†). HDS upon oxidation gives the radical NDS^{2-} , which itself is a mild oxidant. So strong oxidants "kill" NDS^{2-} as observed here and the yield of NDS^{2-} thus reduces.

Conclusions

NDS²⁻ radical is generally used as a mild oxidant, but it supplies electron to the O₂⁻ part of the conjugate base of μ -superoxo-bis [pentaamminecobalt(III)]⁵⁺ (1), *i.e* [(NH₃)₅CoO₂Co(NH₂) (NH₃)₄]⁴⁺ (2). NDS²⁻ first forms an intimate spin adduct with superoxo part of 2 and then supplies two electrons to two molecules of 2. NDS²⁻ thus converts 1 ultimately to its hydroperoxo form [(NH₃)₅Co(HO₂)Co(NH₃)₅]⁵⁺ (3) which quickly decomposes to Co(II), O₂, NH₄⁺ and other products. No solvent kinetic effect ($k_{H_2}O/D_2O \approx 1$) could be seen and the reaction appears to be non-electroprotic, *i.e.* necessary proton transfer and electron transfer occurs to different orbitals at different time. NDS²⁻ after electron transfer decomposes to NO and SO₄²⁻.

Another important conclusion pertains to the synthesis of Fremy's salt. Oxidation of hydroxylamine disulfonate (HDS) gives the radical NDS^{2–}, which decomposes after further oxidation. In these oxidations, **1** reacts with HDS faster than NDS^{2–}, which therefore appears to be a kinetically controlled product. Hence, NDS^{2–} should be taken out of the contact of the oxidant, as soon as NDS^{2–} is formed and the yield of Fremy's salt may be increased.

Thus we see that a nitroxyl radical can either donate or accept an electron. Although other nitroxyl radicals like TEMPO, 4oxo-TEMPO, HO-TEMPO also act in the same way, they are one electron agents,⁵ but NDS²⁻ is a two electron species, an important probe¹² for reactive oxygen species (ROS) and an efficient catalyst for the dismutation of superoxide.³⁶ Such a nitroxyl radical (NDS²⁻) may act as reducing agent as well as an oxidizing agent.

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