

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

The role of carbonate as a catalyst of Fenton like reactions in AOP processes, CO_3^- as the active intermediate.

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

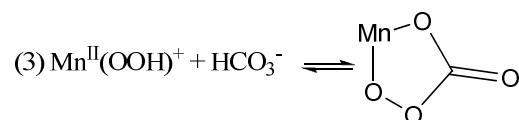
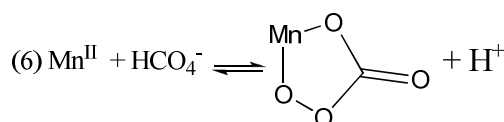
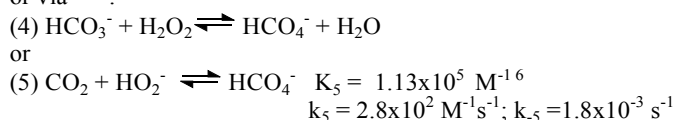
Ariela Burg^{*a}, Dror Shamir^b, Inna Shusterman^c, Haya Kornweitz^d, Dan Meyerstein^{*c,d}

Kinetic and DFT results for the carbonate catalysed $\text{Co}(\text{H}_2\text{O})_6^{2+} + \text{H}_2\text{O}_2$ Fenton like reaction suggest that a mechanism involving the formation of the cyclic transient $\text{cyclic}(\text{CO}_4)\text{Co}^{\text{II}}(\text{OOH})(\text{H}_2\text{O})_2^-$ that decomposes into $\text{Co}^{\text{II}}(\text{H}_2\text{O})(\text{OOH})(\text{OH})_2 + \text{CO}_3^-$, i.e. no OH^\cdot radicals are involved. Plausible biological implications are pointed out.

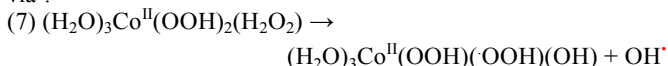
The development of advanced oxidation processes, AOPs, requires the use of cheap reagents soluble in neutral aqueous solutions. The Fenton like reactions are in principle optimal for AOPs but as $\text{Fe}(\text{III})$ precipitates in neutral solutions the use of other first row transition metals is desired. Thus AOPs based on $\text{Mn}(\text{II})^1$, $\text{Co}(\text{II})^2$ and even $\text{Cu}(\text{II})^{1b, 1d, 1c, 3}$ were developed. As the reactions:

(1) $\text{M}(\text{H}_2\text{O})_6^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{M}(\text{H}_2\text{O})_6^{3+} + \text{OH}^\cdot + \text{OH}^-$
are endothermic for these metals, usually their complexes with ligands that stabilize the trivalent complexes are employed. However, organic ligands have the disadvantage that the radicals formed might oxidize them^{1a, 1b, 2-4}. Therefore, perhaps carbonate is often the ligand of choice^{1a, 1b, 2-4, 4j, 4l, 4n, 4p, 4q, 4s, 4u, 4w, 5}. Though carbonate is expected to stabilize high-valent transition metal complexes it has been suggested that its catalytic role might be due to the formation of percarbonate complexes, either via^{1a, 4d}:

(2) $\text{Mn}^{2+} + \text{HO}_2^- \rightleftharpoons \text{Mn}^{\text{II}}(\text{OOH})^+$

or via^{1a, 4d}:

Recently it was shown that the Fenton like reaction of $\text{Co}(\text{H}_2\text{O})_6^{2+}$ proceeds via the binding of three H_2O_2 molecules to the cobalt(II) ion forming the transient $(\text{H}_2\text{O})_3\text{Co}^{\text{II}}(\text{OOH})_2(\text{H}_2\text{O}_2)^7$ that decomposes via⁷:

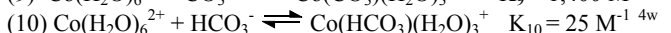
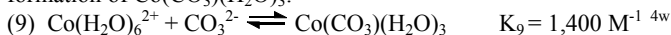


It seemed of interest to check how the addition of bicarbonate to the system affects this mechanism, i.e. whether analogous intermediate complexes to those proposed in the $\text{Mn}(\text{II})$ catalyzed process are formed.

The mechanism of reaction (8) was studied by stopped flow and by DFT calculations. The reaction order and the observed rate constant for each kinetic run were fitted by Pro-data SX software that is connected to the Stopped-flow, see supplementary information⁸.

All measurements were performed at pH 6.5, the highest pH at which no cobalt precipitation occurs in the presence of low concentrations of bicarbonate.

(8) $\text{Co}(\text{H}_2\text{O})_6^{2+} + \text{H}_2\text{O}_2 + \text{HCO}_3^- \rightarrow \text{Products}$
After mixing H_2O_2 , with a solution containing HCO_3^- and $\text{Co}(\text{ClO}_4)_2$, two kinetic processes are observed, the first being a fast decrease in absorbance, followed by an increase in absorbance. As the reactions are ligand exchange reactions, see below, the absorbance changes are very small, Figure S-1 supplementary information⁸. Both these processes obey first order rate laws and are orders of magnitude faster than reaction (5)⁶, therefore this reaction clearly does not contribute to the processes observed. The initial absorbance depends on the concentration of NaHCO_3 due to the formation of $\text{Co}(\text{CO}_3)(\text{H}_2\text{O})_3$:



As in the present study $[\text{Co}(\text{H}_2\text{O})_6^{2+}] \geq 0.01 \text{ M}$ and $[\text{HCO}_3^-] \leq 6 \times 10^{-4} \text{ M}$ at pH 6.5 clearly only a small fraction of the cobalt ions are ligated to carbonate.

It should be noted that the initial absorbance, prior to the first reaction observed, is considerably higher than that expected from the molar absorption coefficients of the reactants. This indicates that the first reaction between hydrogen peroxide and $(\text{CO}_3)\text{Co}(\text{H}_2\text{O})_3$ is too fast to be observed. The dependencies of the observed rate constants of the two processes observed on $[\text{HCO}_3^-]$; $[\text{Co}(\text{H}_2\text{O})_6^{2+}]$ and on $[\text{H}_2\text{O}_2]$ are presented in Figures 1-3 respectively.

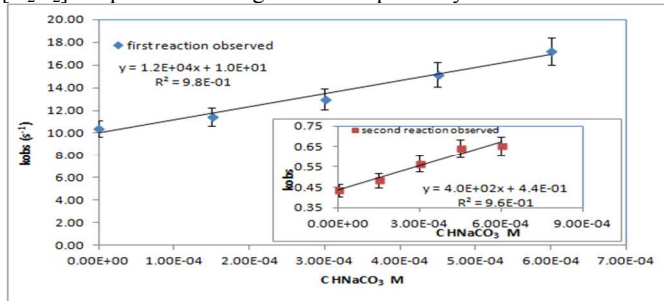


Fig. 1 - Dependence of k_{obs} on $[\text{HCO}_3^-]$.

1.00×10^{-2} M $\text{Co}(\text{ClO}_4)_2$, 2.50×10^{-3} M H_2O_2 , pH 6.5, PIPES 1.00×10^{-1} M ionic strength 2.31×10^{-1} M controlled by adding NaClO_4 .

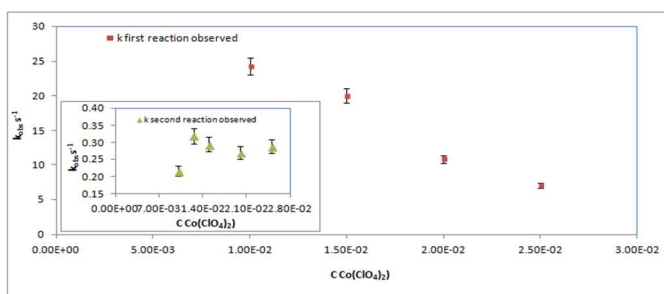


Fig. 2 - Dependence of k_{obs} on $[\text{Co}(\text{H}_2\text{O})_6^{2+}]$.

7.50×10^{-4} M H_2O_2 , 1.50×10^{-4} M NaHCO_3 , pH 6.5, PIPES 1.00×10^{-1} M ionic strength 2.31×10^{-1} M controlled by adding NaClO_4 .

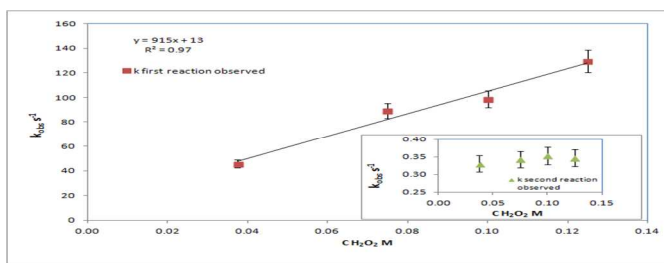


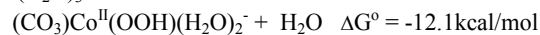
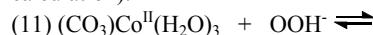
Fig. 3 - Dependence of k_{obs} on $[\text{H}_2\text{O}_2]$.

1.50×10^{-2} M $\text{Co}(\text{ClO}_4)_2$, 1.50×10^{-4} M NaHCO_3 , pH 6.5, PIPES 1.00×10^{-1} M ionic strength 2.31×10^{-1} M controlled by adding NaClO_4 .

The results presented in Figure 1 point out that though less than 1% of the cobalt ions are ligated to carbonate the observed rate constants increase by a factor of 2. (At considerably higher $[\text{HCO}_3^-]$ the processes are too fast to be measured). These results clearly demonstrate that the processes observed are catalysed by bicarbonate.

The results concerning the first reaction observed, presented in Figures 2 and 3 are analogous to those reported for the reaction of $\text{Co}(\text{H}_2\text{O})_6^{2+}$ with H_2O_2 ⁷, *i.e.* the observed rate constants depend

linearly on $[\text{H}_2\text{O}_2]$ when the latter is present in excess and decrease with the increase in $[\text{Co}(\text{H}_2\text{O})_6^{2+}]$ when the latter is in excess. These results, remembering that the initial absorbance is higher than expected, in analogy to the $\text{Co}(\text{H}_2\text{O})_6^{2+}$ system⁷, are in accord with the following mechanism (ΔG° values are results of DFT calculation):



Reaction (11) is too fast to be followed and causes the higher initial absorbance observed. DFT calculations were performed in order of checking whether $(\text{CO}_3)\text{Co}^{\text{II}}(\text{OOH})(\text{H}_2\text{O})_2^-$ might isomerise into a percarbonate complex. The results, see the supporting information, table S-1⁸, point out that indeed the final product is cyclic- $(\text{CO}_4)\text{Co}^{\text{II}}(\text{OH})(\text{H}_2\text{O})^-$, Figure 4. The free energy gain in the isomerisation of $(\text{CO}_3)\text{Co}^{\text{II}}(\text{OOH})(\text{H}_2\text{O})_2^-$ into cyclic- $(\text{CO}_4)\text{Co}^{\text{II}}(\text{OH})(\text{H}_2\text{O})^-$ is 6.2 kcal/mol.

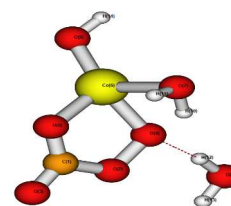
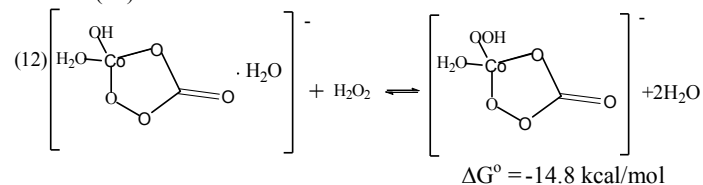
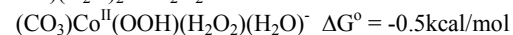
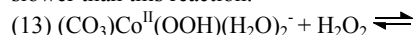


Fig. 4 - B3LYP optimized of cyclic- $(\text{CO}_4)\text{Co}^{\text{II}}(\text{OH})(\text{H}_2\text{O})^- \cdot \text{H}_2\text{O}$. Color of the atoms: white – H, brown – C, red – O, yellow Co.

The first reaction observed, which clearly is a reaction between the product of reaction (11) and H_2O_2 can be one of two possibilities, reaction (12):

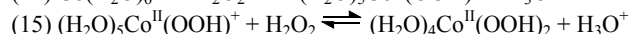
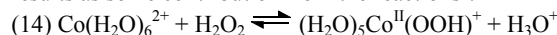


or reaction (13), if the isomerisation of the product of reaction (11) is slower than this reaction.



$(\text{CO}_3)\text{Co}^{\text{II}}(\text{OOH})(\text{H}_2\text{O}_2)(\text{H}_2\text{O})^-$, the product of reaction (13), might isomerise into six products, species S-13a – S-13f see supporting information table S-2⁸. The DFT calculations indicate that the product of reaction (12) is the most stable one, Figure 5. Clearly we cannot determine whether it is formed via reaction (12) or reaction (13) and an isomerisation process.

In the present system K_{11} , k_{12} and k_{-12} cannot be derived from the results as some contribution from the reactions⁷:



clearly contributes to the results.

The rate constant of the second reaction observed, insets in Figures 2 and 3 does not depend on either $[\text{H}_2\text{O}_2]$ or $[\text{Co}(\text{H}_2\text{O})_6^{2+}]$, however it depends on $[\text{HCO}_3^-]$, inset of Figure 1. These observations suggest that this reaction is the decomposition of the intermediate formed in reactions (12) or (13), cyclic- $(\text{CO}_4)\text{Co}^{\text{II}}(\text{OOH})(\text{H}_2\text{O})_2^-$.

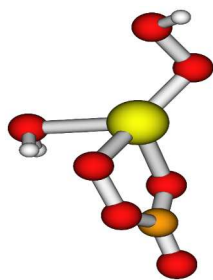
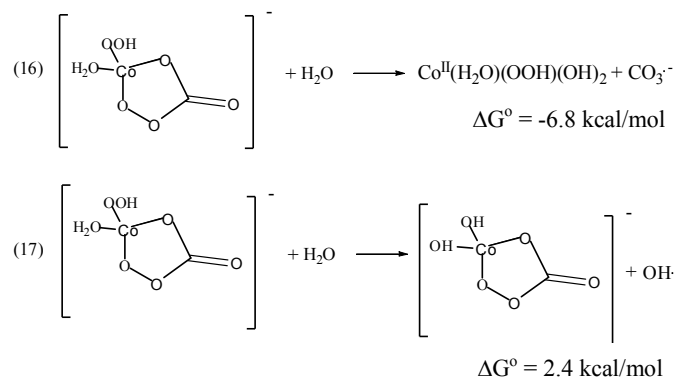


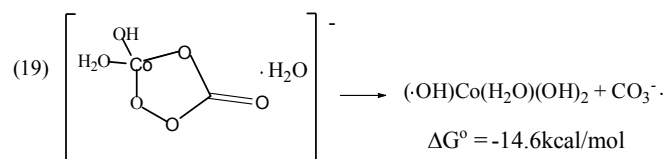
Fig 5: The DFT calculated structure of cyclic-(CO₄)-Co^{II}(OOH)-(H₂O)₂⁻.

This decomposition reaction might proceed either via reaction (16) or via reaction (17):



As reaction (16), the formation of CO₃^{·-} radical anion, is exothermic, this is probably the reaction which occurs. The conclusion that the CO₃^{·-} radical anion is formed is not surprising as reaction (18) is fast and clearly exothermic.

(18) OH[·] + HCO₃⁻ → CO₃^{·-} + H₂O $k_{18} = 8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ⁹
CO₃^{·-} could also be formed via reaction (19) *i.e.* via the direct decomposition of the isomerisation of the product of reaction (11).



Reactions (12) and (19) are both exothermic. However as the kinetic results point out that two H₂O₂ molecules are involved in the process clearly reaction (12) followed by reaction (16) is the mechanism of the process under the present experimental conditions.

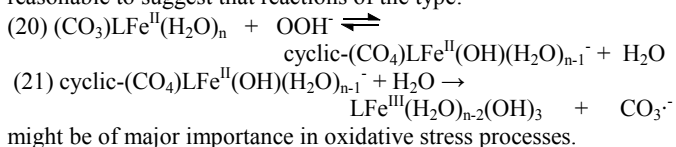
The Mulliken atomic spin densities¹⁰ of the reactants and products of reactions (16) and (19) were calculated, the results are summed up in table S-3⁸. The results clearly point out that already in cyclic-(CO₄)Co^{II}(OH)(H₂O)⁻ and cyclic-(CO₄)Co^{II}(OOH)(H₂O)₂⁻ a considerable spin density on the peroxide-oxygens bound to the central cobalt cation, is present. These spin densities are the result of partial electron transfer from the peroxides to the cobalt and decrease the spin density on the cobalt. The spin densities on the products Co^{II}(H₂O)(OOH)(OH)₂ and Co^{II}(H₂O)(OH)₃ clearly point out that the cobalt oxidation state is +2 and a spin density of one is distributed on the oxygen atoms bound to the central cobalt cation.

These results point out that the unpaired electron resonates between these oxygens, *i.e.* the products are stabilized by resonance.

Conclusions

The results presented here suggest that the role of bicarbonate/carbonate in the catalytic process may be a multi-faceted one. On this proposal, it accelerates the ligand exchange process, as expected. Second, it facilitates the decomposition of the H₂O₂, thus only two ligated peroxides are required prior to its decomposition, as compared to three peroxides in the absence of carbonate⁷. More importantly, we propose that the active species formed is not the OH[·] radical or Mⁿ⁺²=O, as commonly assumed^{7, 11}, but the CO₃^{·-} anion radical. This radical anion is a very strong oxidizing agent, E° = 1.5 V¹², but considerably weaker than OH[·] and therefore considerably more selective in its redox processes⁹. The mechanism involves the formation of cyclic-cobalt(II)-percarbonate as intermediates.

Finally it is tempting to wonder whether analogous processes are involved in the formation of oxidative stress in biological processes. Oxidative stress is commonly attributed mainly to reaction of OH[·] radicals formed in Fenton like reactions¹³. However as in the body HCO₃⁻ is present at considerable concentrations, 4 – 40 mM¹⁴ it is reasonable to suggest that reactions of the type:



might be of major importance in oxidative stress processes.

Notes and references

- Chemical Engineering Department, SCE – Shamoon College of Engineering, Beer-Sheva, Israel.
E-mail: arielab@sce.ac.il
 - Nuclear Research Centre Negev, P.O.B. 9001, Beer-Sheva, Israel.
 - Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel.
 - Biological Chemistry Department, Ariel University, Ariel, Israel.
e-mail: Danm@ariel.ac.il
- (a) B. S. Lane, M. Vogt, V. J. DeRose and K. Burgess, *Journal of the American Chemical Society*, 2002, **124**, 11946; (b) M. Chen, K. Peng, H. Wang, Z. Yang, Q. Zeng and A. Xu, *Chemical Engineering Journal*, 2012, **197**, 110; (c) G. B. Shulpin and G. V. Nizova, *Reaction Kinetics and Catalysis Letters*, 1992, **48**, 333; (d) G. B. Shul'pin, *Dalton Transactions*, 2013, **42**, 12794.
 - X. Long, Z. Yang, H. Wang, M. Chen, K. Peng, Q. Zeng and A. Xu, *Industrial & Engineering Chemistry Research*, 2012, **51**, 11998.
 - L. Cheng, M. Wei, L. Huang, F. Pan, D. Xia, X. Li and A. Xu, *Industrial & Engineering Chemistry Research*, 2014, **53**, 3478.
 - (a) K. G. Tikhonov, O. M. Zastrizhnaya, Y. N. Kozlov and V. V. Klimov, *Biochemistry (Moscow)* 2006, **71**, 1270; (b) E. Ember, H. A. Gazzaz, S. Rothbart, R. Puchta and R. van Eldik, *Applied Catalysis, B: Environmental*, 2010, **95**, 179; (c) C. A. Wegermann, P. Strapasson, S. M. M. Romanowski, A. Bortoluzzi, R. R. Ribeiro, F. S. Nunes and S. M. Drechsel, *Applied Catalysis, A: General* 2013, **454**, 11; (d) E. Ember, S. Rothbart, R. Puchta and R. van

- Eldik, *New J. Chem.*, 2009, **33**, 34; (e) S. Rothbart, E. Ember and R. van Eldik, *Dalton Transactions*, 2010, **39**, 3264; (f) H. H. Monfared, V. Aghapoor, M. Ghorbanloo and P. Mayer, *Applied Catalysis, A: General* 2010, **372**, 209; (g) B. K. Shin, M. Kim and J. Han, *Polyhedron*, 2010, **29**, 2560; (h) G. B. Shul'pin, Y. N. Kozlov, L. S. Shul'pina, T. V. Strelkova and D. Mandelli, *Catalysis Letters* 2010, **138**, 193; (i) T. K. Saha, H. Frauendorf, M. John, S. Dechert and F. Meyer, *From ChemCatChem*, 2013, **5**, 796; (j) S. Rothbart, E. E. Ember and R. van Eldik, *New Journal of Chemistry*, 2012, **36**, 732; (k) T. S. Sheriff, S. Cope and D. S. Varsani, *Dalton Transactions*, 2013, **42**, 5673; (l) J. Wisniewska, P. Rzesnicki and A. Topolski, *Transition Metal Chemistry* 2011, **36**, 767; (m) W.-L. Wong, K.-P. Ho, L. Y. S. Lee, M.-H. So, T. H. Chan and K.-Y. Wong, *Applied Catalysis, A: General* 2013, **453**, 244; (n) X. Li, Z. Xiong, X. Ruan, D. Xia, Q. Zeng and A. Xu, *Applied Catalysis, A: General*, 2012, **411** - **412**, 24; (o) Z. ang, H. Wang, M. Chen, M. Luo, D. Xia, A. Xu and Q. Zeng, *Industrial & Engineering Chemistry Research*, 2012, **51**, 11104; (p) A. Xu, X. Li, S. Ye, G. Yin and Q. Zeng, *Applied Catalysis, B: Environmental* 2011, **102**, 37; (q) J. J. Kukor and K. Nam, in *U.S. Pat. Appl. Publ.*, U.S., 2002; (r) L. Zhang, Z. Zhang, C. Lu and J.-M. Lin, *Journal of Physical Chemistry C*, 2012, **116**, 14711; (s) D. Sannino, V. Vaiano, P. Ciambelli and L. A. Isupova, *Catalysis Today* 2011, **161**, 255; (t) G. P. Anipsitakis and D. D. Dionysiou, *Environmental Science and Technology*, 2003, **37**, 4790; (u) M. Luo, L. Lv, G. Deng, W. Yao, Y. Ruan, X. Li and A. Xu, *Applied Catalysis, A: General*, 2014, **469**, 198; (v) A. Xu, X. Li, Z. Xiong, Q. Wang, Y. Cai and Q. Zeng, *Catalysis Communications* 2012, **26**, 44; (w) B. Cosovic, D. Degobbi, H. Bilinski and M. Branica, *Geochimica et Cosmochimica Acta*, 1982, **46**, 151.
- 5 G. P. Anipsitakis and D. D. Dionysiou, *Environmental Science and Technology*, 2003, **37**, 4790.
- 6 E. V. Bakhmutova-Albert, H. Yao, D. E. Denevan and D. E. Richardson, *Inorg. Chem. (Washington, DC, U. S.)*, 2010, **49**, 11287.
- 7 A. Burg, I. Shusterman, H. Kornweitz and D. Meyerstein, *Dalton Transactions* 2014, **43**, 9111.
- 8 s. information.
- 9 N. N. S. K. D. o. t. web.
- 10 *Handbook of Metalloproteins*, 2001.
- 11 S. Goldstein, D. Meyerstein and G. Czapski, *Free Radical Biology and Medicine*, 1993, **15**, 435.
- 12 D. M. Stanbury, *Advances in Inorganic Chemistry*, 1989, **33**, 69.
- 13 (a) J. Carillon, J.-M. Rouanet, J.-P. Cristol and R. Brion, *Pharmaceutical Research*, 2013, **30**, 2718; (b) M. P. Murphy, A. Holmgren, N.-G. Larsson, B. Halliwell, C. J. Chang, B. Kalyanaraman, S. G. Rhee, P. J. Thornalley, L. Partridge and D. Gems, *Cell Metabolism*, 2011, **13**, 361; (c) B. Halliwell, *Trends in Pharmacological Sciences*, 2011, **32**, 125; (d) A. Terman and T. Kurz, *Antioxidants & Redox Signaling*, 2013, **18**, 888.
- 14 (a) D. C. Darrow, R. Schwartz, J. F. Iannucci and F. Coville, *Journal of Clinical Investigation*, 1948, **27**, 198; (b) L. J. J. L. E. J.; G. A. D.; L. J. R.; and R. A. S, *The Journal of clinical investigation*, 1965, **44**, 507.