Facile Aerial Oxidation of a Porphyrin. Part 5.† Unsymmetrical *meso*-Tetra-aryl Porphyrins with 3,5-Di-t-butyl-4-hydroxyphenyl and 3-Hydroxyphenyl Substituents

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The aerial oxidation in basified dichloromethane (DCM) solutions of porphyrins (**2b**)–(**4b**), unsymmetrically *meso*-substituted with 3,5-di-t-butyl-4-hydroxyphenyl (DtB4HP) and 3-hydroxyphenyl (3-HP) groups, has been investigated using u.v.–visible spectroscopy and cyclic voltammetry. As in the analogous series (**2a**)–(**4a**), basification with 1 mol dm^{-3} tetrabutylammonium hydroxide (tnBAH) in MeOH produces very little aerial oxidation. However, basification with 1 mol dm^{-3} potassium hydroxide (KOH) in MeOH leads to aerial oxidation of (**2b**)–(**4b**), but to a lesser extent than in the series (**2a**)–(**4a**). Except for porphyrin (**3b**), this trend in lowered oxygen reactivity in base is not reflected in increased first half-wave oxidation potentials (E°) from cyclic voltammetry, compared to the series (**2a**)–(**4a**). An explanation of these differences is offered in terms of the relative availability to oxygen of DtB4HP electron density in the two sets of porphyrins.

The facile aerial oxidation of porphyrin (**1**), to give the macrocyclic diquinomethide (**7**),[1a–c] has recently been extended to include metal complexes of (**1**),[1d–h] different *meso*-substituted porphyrins,[1i] and, latterly, porphyrins unsymmetrically substituted with both redox-active (DtB4HP) and functional (4-HP) moieties (**2a**)–(**5a**).[2] This last group of compounds has potential applications, *e.g.*, in fuel cells[3] and for the *in situ* generation of hydrogen peroxide, by virtue of their possible immobilisation on solid supports.

We were able to demonstrate, using u.v.–visible spectroscopy and cyclic voltammetry, that in basified DCM solution (1 mol dm^{-3} KOH/MeOH; 10 drops) unsymmetrical porphyrins (**2a**)–(**5a**) undergo aerial oxidation to a lesser extent than the symmetrically substituted parent porphyrin (**1**).[2] This behaviour could be broadly rationalised in terms of the relative deprotonating ability of the two bases used,[4] the decreased acidity of phenols with bulky *ortho* substitutents,[5] and competition between the different electron-releasing power onto the macrocycle, of the two types of phenoxide anions that are generated.[6]

In order to test these rationalisations, we synthesised an analogous series of unsymmetrical porphyrins (**2b**)–(**4b**) in which the 4-HP groups of the original series were replaced by 3-HP groups.[2] Phenoxide electron density from these latter groups is now unable to delocalise onto the porphyrin macrocycle [*e.g.*, in (**6b**)].[7] We reasoned that this family of porphyrins in basified DCM solutions should have redox and u.v.–visible characteristics determined solely by the interaction of DtB4HP groups with the porphyrin macrocycle: they should be less amenable to aerial oxidation than the series (**2a**)–(**4a**). Preliminary experiments tend to confirm this.[2] In this paper, we report more fully on the behaviour of porphyrins (**2b**)–(**4b**) in basified DCM solutions.

Results and Discussion

The preparation and separation of porphyrins (**2b**)–(**4b**) were described in the previous paper.[2] In neutral DCM, these porphyrins give u.v.–visible spectra typical of *meso*-tetra-aryl-substituted porphyrins,[8] *i.e.*, a strong B band (around 420 nm) and four less intense Q bands (500–650 nm). Addition of base to the DCM solutions (1 mol dm^{-3} solutions in MeOH of either tnBAH or KOH; 10 drops) led to colour and spectroscopic changes that were less drastic than those observed for the analogous series of porphyrins (**2a**)–(**4a**).[2] Thus, (**2b**)–(**4b**) show similar spectral changes in both bases. In particular, some B band absorption is retained in all bases, albeit in (**3b**) and (**4b**) of much reduced intensity. Except in (**2b**), the Q bands become ill-defined, and there is a weak, very broad absorption in the region 750–800 nm (see Figure 1). This is broadly similar to the spectral changes observed for the series (**2a**)–(**4a**) in DCM basified with 1 mol dm^{-3} KOH/MeOH. However, in DCM basified with 1 mol dm^{-3} tnBAH/MeOH, this last series shows marked differences to (**2b**)–(**4b**), in particular, the B bands are split and further reduced in intensity, while the broad band at 750–800 nm is increased.[2] These differences probably reflect the interaction of two different phenoxide chromophores with the porphyrin optical state in (**2a**)–(**4a**), as opposed to one phenoxide in (**2b**)–(**4b**).

To understand what these spectral changes could mean in terms of aerial oxidation of the porphyrins (**2b**)–(**4b**), we repeated the previously reported procedure[1h,2] of acidifying aliquots of the basified porphyrin solutions with trifluoroacetic acid (TFA) and observing reappearance of the porphyrin dication B band. Any significant reduction in the magnitude of this absorption with time, compared with the original dication B band absorption prior to basification, was taken to mean that some aerial oxidation of the porphyrins had taken place. Figure 2 shows the effect of the two different bases on the susceptibility to aerial oxidation of the porphyrins (**2b**)–(**4b**), while Table 1 indicates the percentage reduction in dication B band intensity (and therefore extent of aerial oxidation) calculated from Figure 2, and compares this with results obtained from the previous series of porphyrins (**2a**)–(**4a**). Our results indicate (*a*) that the amount of aerial oxidation of both series of porphyrins using 1 mol dm^{-3} tnBAH/MeOH is

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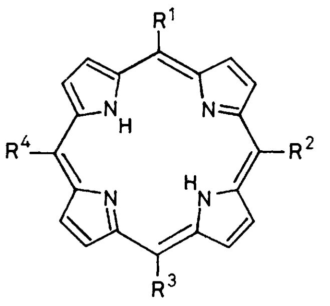
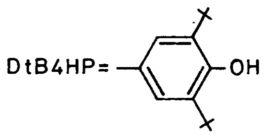
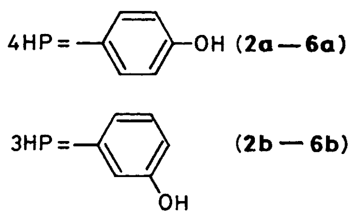
† For Part 4, see ref. 2.



	R^1	R^2	R^3	R^4
(1)	DtB4HP	DtB4HP	DtB4HP	DtB4HP
(2)	HP	DtB4HP	DtB4HP	DtB4HP
(3)	HP	HP	DtB4HP	DtB4HP
(4)	HP	DtB4HP	HP	DtB4HP
(5)	HP	HP	HP	DtB4HP
(6)	HP	HP	HP	HP





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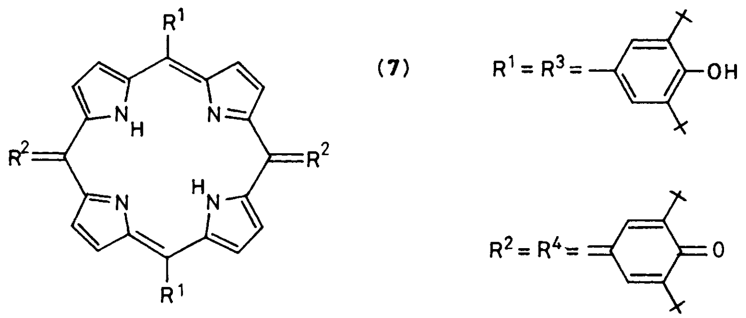

Table 1. Maximum reduction in returned B band absorption[a] after having acidified[b] aliquots of basified porphyrin solutions.

	Base[c]	
Porphyrin	1 mol dm^{-3} tnBAH/MeOH (%)	1 mol dm^{-3} KOH/MeOH (%)
(2a)	<10	70
(2b)	<10	45
(3a)	<10	75
(3b)	Nil	12
(4a)	<10	47
(4b)	<10	46

[a] This is a direct indication of the percentage aerial oxidation that has taken place. [b] TFA. [c] 10 Drops added to a neutral DCM stock solution of the porphyrin.

Table 2. First half-wave potentials (*V versus* s.c.e.[a]) of porphyrins in neutral and basified[b] DCM.

	DCM	
Porphyrin	Neutral	Basic
(1)[c]	0.81	0.28
(2a)[c]	0.82	0.35
(2b)	0.82	0.35
(3a)[c]	0.75	0.42
(3b)	0.87	0.51
(4a)[c]	0.78	0.46
(4b)	0.89	0.34

[a] Saturated calomel electrode. [b] By addition of sodium ethoxide. [c] See ref. 2.

very small; (*b*) using 1 mol dm^{-3} KOH/MeOH, (**2b**) and (**3b**) undergo significantly less aerial oxidation than (**2a**) and (**3a**); (*c*) (**4b**) is oxidised to the same extent as (**4a**).

Cyclic voltammetry was performed on nitrogen-degassed DCM solutions of (**2b**)–(**4b**), under neutral and basified (10^{-2} mol dm^{-3} NaOEt/EtOH) conditions (Table 2). In neutral DCM, there is a small increase in the first half-wave potentials for oxidation ($E^{\ominus}$) with decreasing number of DtB4HP groups on the porphyrin—the reverse of the trend found for (**2a**)–(**4a**).[2]

In basified DCM solutions, the $E^{\ominus}$ values are markedly decreased, compared with those in neutral solution, with the '*cis*'-di-DtB4HP-substituted porphyrin (**3b**) having a much larger $E^{\ominus}$ value than the '*trans*'-di-DtB4HP-substituted porphyrin (**4b**). Again, this contrasts with the series (**2a**)–(**4a**) where it is the '*trans*'-di-DtB4HP-substituted porphyrin (**4a**) which has the slightly larger value of $E^{\ominus}$. The ease of one-

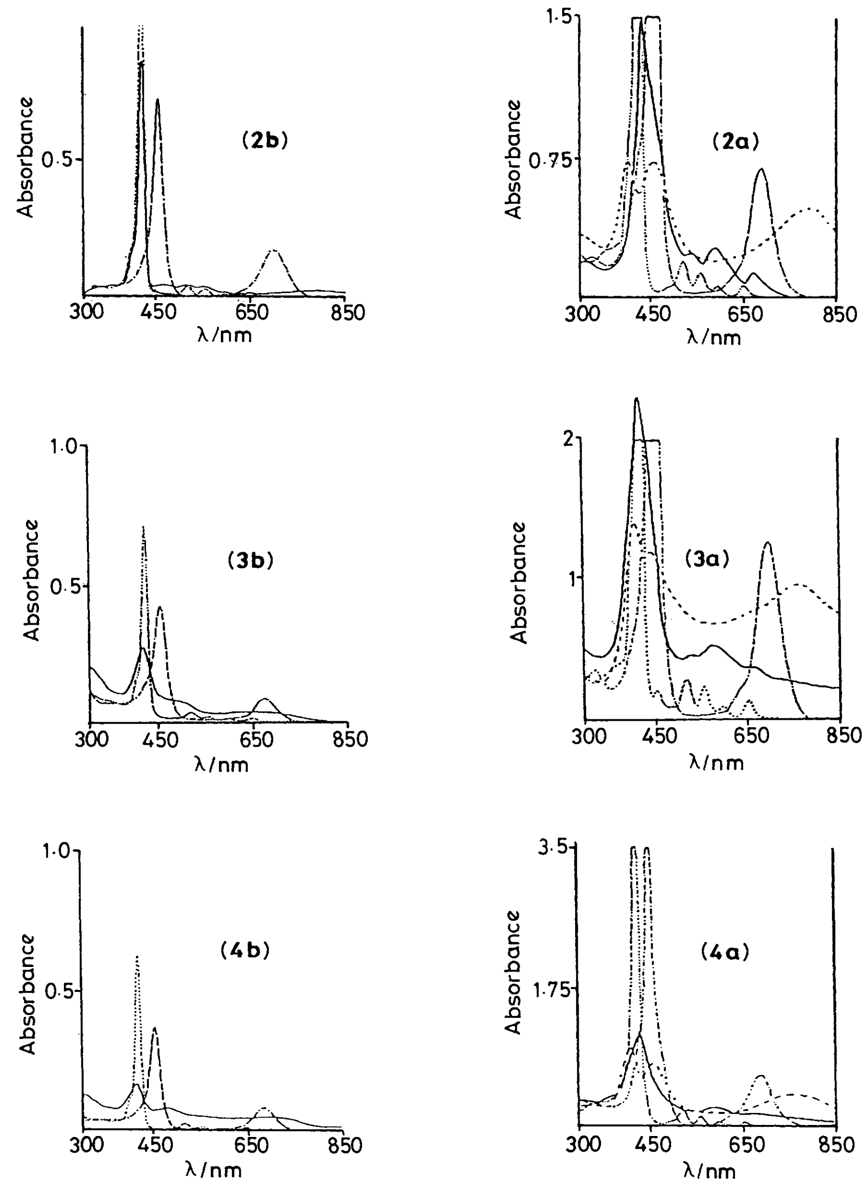

Figure 1. U.v.–visible spectra of porphyrins (**2b**)–(**4b**) in neutral (· · · ·), acidified (— · — · —), and basified (1 mol dm^{-3} KOH/MeOH or 1 mol dm^{-3} tnBAH/MeOH, ——) DCM. For (**2a**)–(**4a**), 1 mol dm^{-3} KOH/MeOH is (——), while 1 mol dm^{-3}) tnBAH/MeOH is (– – – –). Concentration of (**2b**) is 6 × 10^{-6} mol dm^{3}, (**3b**) and (**4b**) unknown but probably about 10^{-6} mol dm^{-3}. Concentration of (**2a**)–(**4a**) is 2 × 10^{-5} mol dm^{-3} (ref. 2).

electron oxidation of the two series of porphyrins in basified DCM may be summarised as:

$$(\mathbf{3b}) \ll (\mathbf{4b}) = (\mathbf{2b}) < (\mathbf{1})^*$$

In the previous paper,[2] we rationalised the autoxidation behaviour of porphyrins (**2a**)–(**5a**) in basified DCM solutions in terms of competing electron donation onto the macrocycle by the two types of phenolic substituent.[6] The relative deprotonating power of the two bases,[4] and differences in phenolic acidity[5] were central issues in this argument. Thus, bulky *ortho*-alkyl substituents lower the redox potential of a phenol[9] and decrease its acidity.[5] Also, we considered that 1 mol dm^{-3} tnBAH/MeOH would deprotonate both types of phenolic substituent, while 1 mol dm^{-3} KOH /MeOH initially deprotonates the 4-HP groups only. In this last base, it would mean that when the DtB4HP groups eventually did deprotonate, they would be less able to delocalise their electron density onto the now electron-rich porphyrin macrocycle and, consequently, would be more readily oxidised by air. In the present series of porphyrins (**2b**)–(**3b**), the 3-HP phenoxides are unable to delocalise their negative charge onto the macrocycle.[7] Therefore, they cannot oppose the delocalisation of DtB4HP electron density onto the macrocycle. With less electron density around them, the DtB4HP groups, and therefore the porphyrins, should be harder to oxidise aerially. This seems to be born out by the u.v.–visible data, which shows that, in 1 mol dm^{-3} KOH/MeOH, porphyrins (**2b**) and (**3b**) undergo far less aerial oxidation than (**2a**) and (**3a**), as judged by the absorption of the dicationic B band produced by TFA acidification (see Table 1). Porphyrin (**3b**) also has a larger $E^{\ominus}$ value than (**3a**), indicating increased difficulty of removal of an electron (Table 2). Interestingly, (**2b**) has the same $E^{\ominus}$ value as (**2a**), yet shows less aerial oxidation by u.v.–visible spectroscopy, while (**4b**) has a lower $E^{\ominus}$ value than (**4a**) but undergoes aerial oxidation to the same extent.

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* Compare with the series obtained in the previous paper[2] in which (**4a**) < (**3a**) < (**2a**) < (**1**).

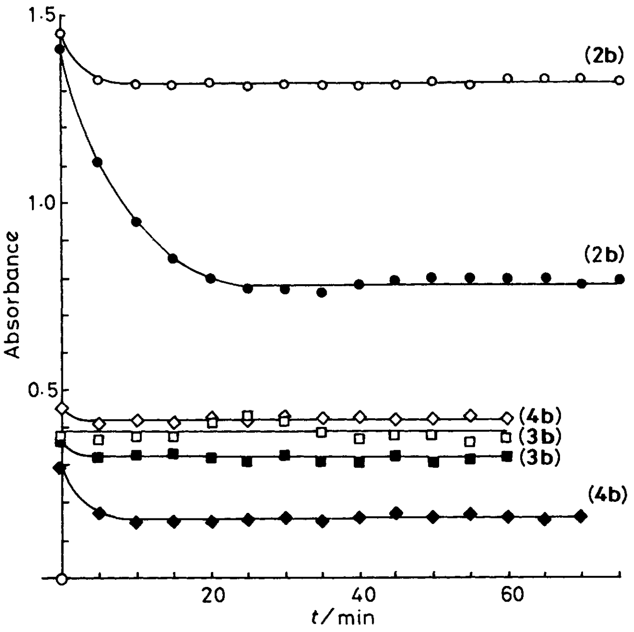

Figure 2. Decrease in regenerated porphyrin dicationic B band, the abscissa representing time elapsed after addition of base (open figures, 1 mol dm^{-3} tnBAH/MeOH; closed figures, 1 mol dm^{-3} KOH/MeOH: t = 0), before acidification with TFA.

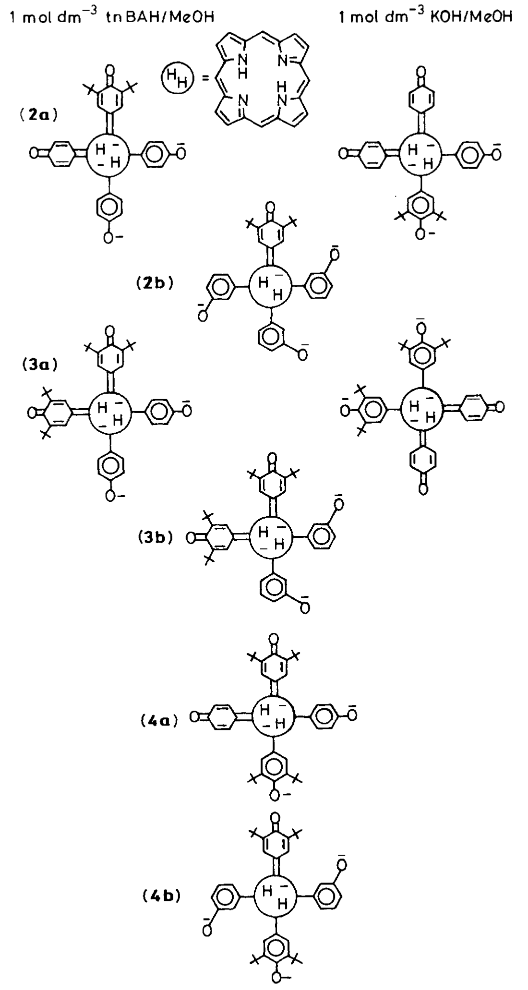

Figure 3. Possible diquinomethide resonance forms of (**2b**)–(**4b**) and (**2a**)–(**4a**) in DCM solutions basified with 1 mol dm^{-3} tnBAH/MeOH and 1 mol dm^{-3} KOH/MeOH.

Also, (**2b**) and (**4b**) have similar $E^\ominus$ values and undergo aerial oxidation to a similar extent.

The $E^\ominus$ value measures the ease of one-electron oxidation of a whole porphyrin molecule, *i.e.*, macrocycle and substituents. Aerial oxidation, on the other hand, probably most readily occurs at the substitutents, especially where these are antioxidant DtB4HP groups. If these groups are donating their electron density onto the macrocycle then, although basification lowers the $E^\ominus$ value of the whole system (relative to the porphyrin in neutral DCM), it may be more difficult for oxygen to oxidise the DtB4HP groups. If 1 mol dm^{-3} KOH/MeOH is deprotonating the DtB4HP groups less efficiently than other phenolic substituents, then DtB4HP electron density will be less readily donated onto the macrocycle. Consequently, aerial oxidation should be more favoured in this base. Fully deprotonated 4-HP groups, in the series (**2a**)–(**4a**) will increase this effect by prior donation of their electron density onto the macrocycle,[2] thereby blocking electron donation from the DtB4HP groups. Deprotonated 3-HP groups [in the series (**2b**)–(**4b**)], on the other hand, cannot donate onto the macrocycle,[7] leaving the way clear for the DtB4HP groups to delocalise their electron density even in the presence of the less efficient base, 1 mol dm^{-3} KOH/MeOH (see Figure 3). The presence of the band around 750–800 nm, absent in the porphyrins (**2a**)–(**4a**) in this base, might be indicative of such delocalisation. Ultimately, this will result in a local decrease of electron density around the DtB4HP groups that could mean porphyrins (**2b**) and (**4b**) undergoing less aerial oxidation than (**2a**) even though these porphyrins have similar $E^\ominus$ values.

That (**4a**) undergoes aerial oxidation to the same extent as (**4b**), even though the former has a higher $E^\ominus$ value, might be explicable using a similar delocalisation argument. The '*trans*' arrangement of DtB4HP groups in (**4a**) and (**4b**) means that for both porphyrins with 1 mol dm^{-3} KOH/MeOH, these groups will be competing with each other for electron donation onto the macrocycle. The amount of electron density around these groups, therefore, should be the same in both porphyrins. Their difference in $E^\ominus$ values may reflect dissimilar polarisation within the molecules and hence differences in solvation. Alternatively, the stability of the two macrocycles could vary depending on the amount of donated electron density that resides on them (Figure 3).

Finally, it is worth noting that the split B band observed in the u.v.–visible spectra of porphyrins (**2a**)–(**4a**) in DCM basified with 1 mol dm^{-3} tnBAH/MeOH, is reminiscent of similar behaviour in the spectra of certain metal complexes of (**1**) under the same conditions.[1h] In the latter, the metal modulates the flow of electron density onto the macrocycle by interacting with the porphyrin π-system [presumably *via* vacant d (or p) orbitals on the metal and d (or p)-π^* backbonding onto the porphyrin]. Perhaps the 4-HP groups of (**2a**)–(**4a**), by similarly modulating the flow of DtB4HP electron density onto the macrocycle (albeit by a different mechanism), could produce similar optical states.

Conclusions

The porphyrins (**2b**)–(**4b**) undergo aerial oxidation in DCM basified with 1 mol dm^{-3} KOH/MeOH to a lesser extent than the previously reported series (**2a**)–(**4a**), even though there is no general correlation in the differences of $E^\ominus$ values, obtained by cyclic voltammetry, between the two sets of porphyrins. We propose that the availability to oxygen of electron density around the DtB4HP substituents may be the key to this behaviour.

It appears therefore, that the facile aerial oxidation of porphyrin (**1**) can be modulated, either by metallation or by replacement of some of the DtB4HP groups by other, weaker, electron-donating *meso*-substituents. In subsequent papers, we shall report on the effects on facile aerial oxidation of replacing DtB4HP groups with electron-withdrawing *meso*-substituents, and combining DtB4HP replacement with metallation. We shall also be reporting more fully on the e.s.r. data we have obtained on these porphyrins.

Experimental

The synthesis and separation of porphyrins (**2b**)–(**4b**) has been reported earlier.[2] Cyclic voltammograms were performed in neutral and basic, dried, nitrogen degassed, DCM with tetrabutylammonium fluoroborate (0.1 mol dm^{-3}) as the supporting electrolyte. For the basic solutions, sodium ethoxide in ethanol (10^{-2} mol dm^{-3}) was added, after purging with nitrogen. All u.v.–visible spectra were recorded on a Schimadzu UV-260 spectrophotometer. A stock solution of porphyrin (**2b**) was prepared in DCM (6×10^{-6} mol dm^{-3}; 100 cm^3). Porphyrins (**3b**) and (**4b**) were sticky oils so that it proved impossible to prepare accurately solutions of known concentration. We prepared solutions of these porphyrins, however, such that their B band absorbances were in the range 0.5–1.0, *i.e.*, about 1×10^{-6} mol dm^{-3}. The spectra of the neutral solutions of all the porphyrins were run, and then these solutions were basified, either by 1 mol dm^{-3} tnBAH/MeOH or 1 mol dm^{-3} KOH/MeOH (10 drops), and their spectra recorded again. Aliquots of these basified solutions were withdrawn at regular intervals and acidified with TFA to test the amount of aerial oxidation in base, as reported earlier.[2]

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