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The Oxidation of Bis(salicylhydrazonato)manganese(II) to Bis(salicylhydrazonato)peroxymanganese(IV)monopyridine and Bis(salicylhydrazonato)oxomanganese(IV)monopyridine

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Abstract

Bis(salicylhydrazonato)manganese(II) in dimethylformamide solution containing pyridine takes up molecular oxygen to form bis(salicylhydrazonato)-peroxymanganese(IV)monpyridine while reaction of the manganese(II) chelate with iodosylbenzene leads to the formation of bis(salicylhydrazonato)oxomanganese(IV)monopyridine. Bis(salicylhydrazonato)-peroxymanganese(IV)monopyridine oxidizes benzyl alcohol to benzaldehyde and acts as a catalyst in the autoxidation of benzyl alcohol to benzaldehyde in dimethylformamide.

Introduction

Current views of the photosynthetic electron transport chain involve the interaction of various cytochromes with the chlorophyll linked primary electron acceptors and donors of photosystem I and II and a number of iron sulfur proteins involved in non-cyclic and possibly cyclic electron transfer pathways. The accumulation of four redox equivalents leads to the oxidation of water to yield molecular oxygen by a water splitting metalloenzyme which involves at least two manganese atoms per molecule of enzyme [1–3]. ESR measurements of chloroplasts indicate the presence of a pair of antiferromagnetically coupled manganese ions or possibly a tetramer of manganese ions in which Mn(III) and Mn(IV) oxidation states are present [4].

The developments in the role of manganese in the photosynthetic apparatus have stimulated chemical interest in the formation, photochemistry and chemical properties of compounds containing manganese in high oxidation states [5–8]. The present investigation is concerned with the oxidation states of manganese in the products formed by the reaction of the manganese(II) chelate of the hydrazone of salicylaldehyde with molecular oxygen and the oxygen-atom transfer agent iodosylbenzene in organic solvents.

Experimental

The ESR spectra were recorded at 77 K using the X-band of a Varian E12 spectrometer. Infrared spectra were obtained on a Perkin-Elmer model 521 spectrophotometer with sodium chloride optics. Infrared measurements at lower frequencies were made with a Perkin-Elmer 180 spectrophotometer. Absorption spectra in the visible region were recorded on a Unicam SP700 spectrophotometer. Magnetic susceptibility measurements were made at room temperature by the Gouy method with a glass sample tube calibrated for dimagnetism. All organic solvents were freshly distilled before use and dried over Linde 4A molecular sieves.

Preparation of Salicylaldehyde Hydrazone and Phenylhydrazone

Salicylaldehyde hydrazone was prepared as follows [9]. Salicylaldehyde (12.2 g) was added to an ice-cold solution of hydrazine hydrate (5.0 g) in ethanol (50 ml). Ice-cold water (50 ml) was added to the reaction mixture with constant stirring. The white product was filtered, washed with ice-cold water and recrystallized from ethanol (yield 87%). Salicylaldehyde phenylhydrazone was prepared similarly using salicylaldehyde and phenyl hydrazine.

Preparation of Bis(salicylhydrazonato)manganese(II)-dihydrate

The manganese(II) chelate was prepared as described previously [10].

Reaction of Bis(salicylhydrazonato)manganese(II)-dihydrate with Molecular Oxygen

Manganese(II)dihydrate (1 g) was dissolved in dimethylformamide (50 ml) containing pyridine (5 ml) under nitrogen atmosphere. The reaction mixture was exposed to a stream of dried molecular oxygen for 10 min. The solvent was removed by distillation at diminished presence to recover the manganese chelate which was washed with two portions of benzene (50 ml).

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TABLE I. Analytical and Magnetic Susceptibility Data for the Manganese Chelates

Compound	Calculated (%)			Found			μ_{eff} (BM)
	C	H	N	C	H	N	
$Mn(II)(salhy)_2 \cdot 2H_2O$	46.50	4.90	15.50	46.25	5.10	15.05	6.03
$Mn(IV)(salhy)_2 \cdot py \cdot O_2$	52.29	4.36	16.05	51.93	4.64	16.51	3.96
$Mn(IV)(salhy)_2 py \cdot O$	54.28	4.52	16.6	55.45	4.34	16.10	3.75

Oxidation of Manganese(II)salicylaldehyde Hydrazone by Iodosylbenzene

Bis(salicylhydrazonato)manganese(II)dihydrate (0.5 g) was dissolved in dimethylformamide (50 ml) containing pyridine (5 ml) under nitrogen atmosphere. A solution of iodosylbenzene (1.0 g) in dimethylformamide (25 ml) was added to the solution of the manganese(II) chelate and the reaction mixture warmed gently for 20 min under a stream of nitrogen. The solvent was removed at diminished pressure and the remaining solid washed with absolute ethanol to remove any excess iodosylbenzene and finally with hexane.

The analytical results and magnetic susceptibility data for the manganese chelates is summarised by Table I.

Catalytic Autoxidation of Benzyl Alcohol

Bis(salicylhydrazonato)peroxymanganese(IV)monopyridine (0.5 g) obtained from the reaction of bis(salicylhydrazonato)manganese(II) with dioxygen in the presence of pyridine was dissolved in dimethylformamide (50 ml). Benzyl alcohol (1 g) was added to this solution along with a drop (0.05 ml) of pyridine. Molecular oxygen was bubbled through the solution for 5 min and the solvent and liquid components recovered from the reaction mixture by distillation, followed by separation of the components by fractional distillation to recover benzaldehyde (0.85 g, 85% yield, boiling point (b.p.) 179 °C, MS *m/e* 106 (74%)).

Results

The high spin manganese(II) chelate of salicylaldehyde hydrazone ($Mn(II)(salhy)_2 \cdot 2H_2O$) dissolves in dimethylformamide (dmf), dimethylsulphoxide (dmso) and tetrahydrofuran (thf) to form yellow solutions. The addition of pyridine to these solutions in a dinitrogen atmosphere does not lead to any marked colour change.

The ESR spectrum due to the manganese(II) chelate doped (0.5% *w/w*) into the corresponding nickel(II) chelate consists of a group of six hyperfine lines in the $g = 2$ region, typical of that expected from a compound containing high spin manganese(II). An almost identical ESR spectrum is obtained from a frozen solution (77 K) of the manganese(II) chelate in dmf containing acetonitrile (25% *v/v*). However, the ESR spectrum due to $Mn(II)(salhy)_2$ in pure dmf as indicated by Fig. 1 shows resonances at field values other than in the $g = 2$ region. The occurrence of resonances at higher and lower field positions [11] is enhanced greatly by the addition of a small amount (5% *v/v*) of methanol to the dmf solution containing the manganese chelate as shown by Fig. 2a. The ESR spectrum due to a frozen solution (77 K) of $Mn(II)(salhy)_2$ in dmf containing a little water (5% *v/v*) is shown by Fig. 2b which shows a close resemblance to that of Fig. 2a but in addition shows super-hyperfine lines with peak to peak spacing of about 18 gauss. The number of such lines and their spacing is consistent with the interaction of the manganese(II) centre with two ^{14}N nuclei as anticipated from the binding of manganese(II) to two ligand anions each containing a nitrogen donor atom. The occurrence of resonances at the high and low field positions is even more marked in the second derivative ESR spectrum due to a frozen solution of bis(salicylphenylhydrazonato)manganese(II) ($Mn(II)(phensalhy)_2$) in dmf containing methanol (5% *v/v*) as indicated by Fig. 3.

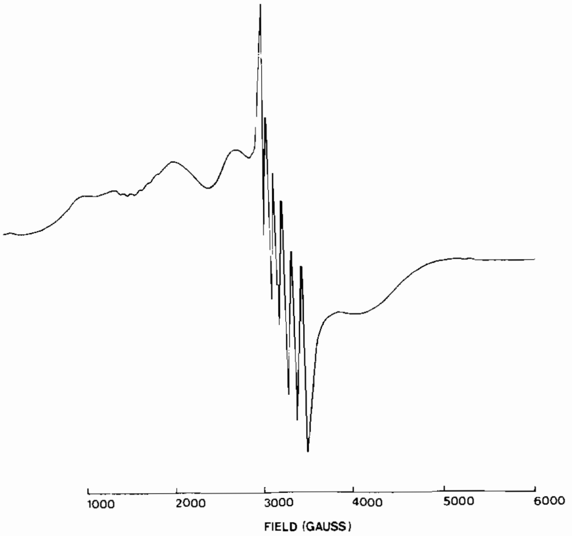


Fig. 1. ESR spectrum due to manganese(II)(salhy)$_2$ (1.0×10^{-3} M) in dmf. 77 K, microwave frequency 9.147 GHz.

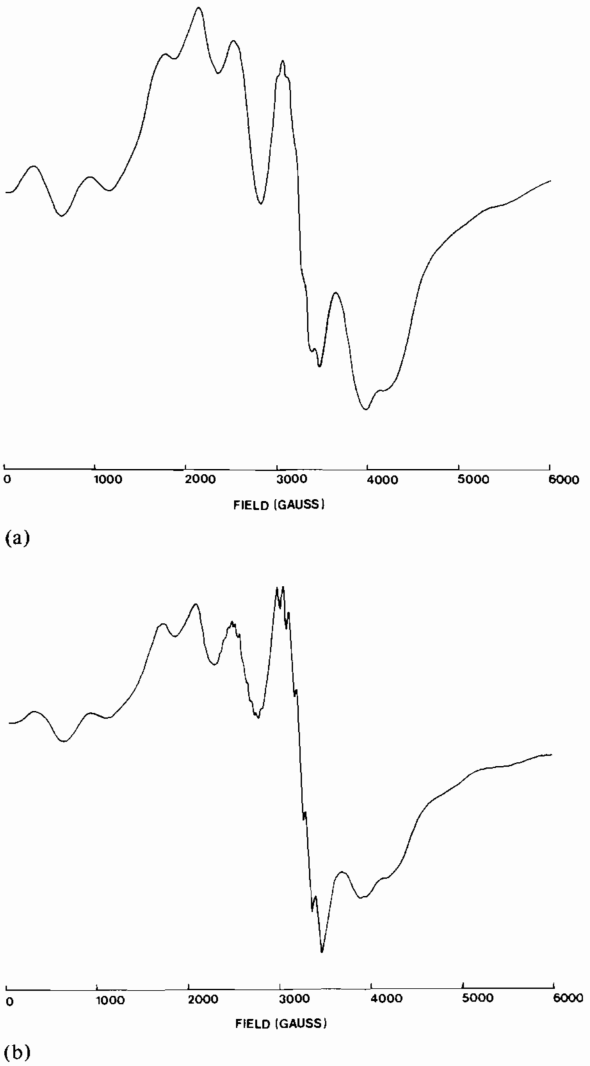


Fig. 2. ESR spectra due to manganese(II)(salhy)$_2$ (1.0×10^{-3} M) in dmf containing (a) methanol (5% *v*/*v*), (b) water (5% *v*/*v*), 77 K, microwave frequency 9.147 GHz.

The admission of dry molecular oxygen to a dmf solution of Mn(II)(salhy)$_2$ containing pyridine (10% *v*/*v*) leads to an immediate colour change to dark brown the intensity of which is not reduced by subsequent passage of dinitrogen through the solution. The electronic absorption spectrum due to the oxygenated solution of Mn(II)(salhy)$_2$ is shown by Fig. 4a which may be compared with the spectra (Fig. 4b) due to the chelate in different solvents. The infrared spectrum of the manganese chelate isolated from the oxygenated solution shows that the ligand structure is unchanged while the elemental analysis and magnetic susceptibility data are consistent with the formulations of the isolated product as bis(salicylhydrazonato)peroxomanganese(IV)monopyridine (Mn(IV)O$_2$(salhy)$_2$·py). The ESR spectrum due to a frozen solution of the peroxo compound in dmf containing some pyridine (5% *v*/*v*) is shown by Fig. 5.

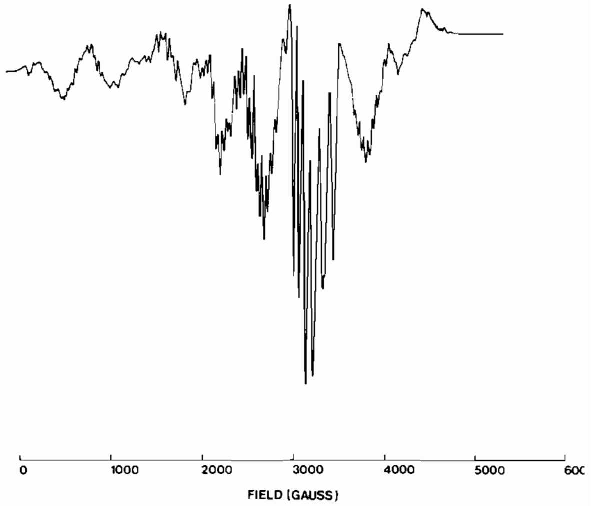
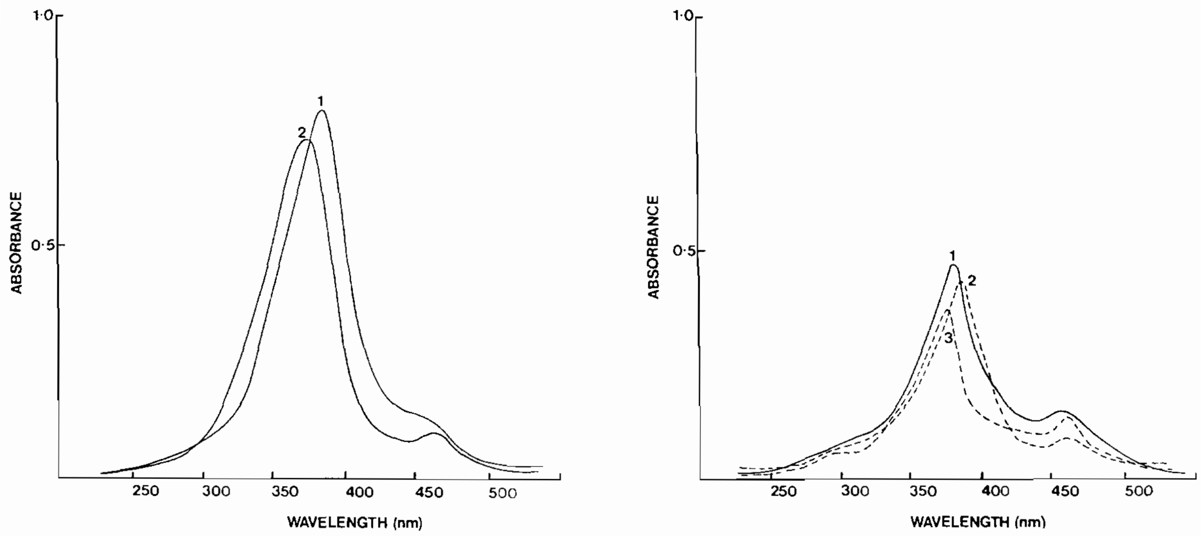


Fig. 3. Second derivative ESR spectrum due to manganese(II)(phensalhy)$_2$ (1.0×10^{-3} M) in dmf containing methanol (5% *v*/*v*), 77 K, microwave frequency 9.147 GHz.

An alternative route to the synthesis of a salicylhydrazone chelate containing manganese(IV) is afforded by reaction of the oxygen atom transfer reagent iodosylbenzene with manganese(II)(salhy)$_2$ whereby a two electron transfer to the oxygen atom removed from the iodosylbenzene and acquired by the manganese(II) centre results in the formation of bis(salicylhydrazonato)oxomanganese(IV). A spectrophotometric titration of iodosylbenzene with manganese(II)(salhy)$_2$ in dmf solution shows that the reaction leading to the formation of an oxomanganese(IV) chelate is almost complete when a one to one mole ratio of reactants is reached. The isolated product of the reaction possesses an IR spectrum characteristic of the salicylhydrazone ligand and in addition a new IR absorption at 1060 cm^{-1} attributable to the Mn(IV) = 0 group. The composition of the compound as bis(salicylhydrazone)oxomanganese(IV) is confirmed by elemental analysis while the ESR spectrum to the chelate in frozen dmf solution is shown by Fig. 6.

Bis(salicylhydrazonato)peroxymanganese(IV)monopyridine effects the oxidation of organic compounds containing oxidizable functional groups. For example benzyl alcohol is oxidized in a dmf solution containing the chelate to benzaldehyde in good yield with concomittant formation of the manganese(II) chelate. The ease of generation of the peroxymanganese(IV) in dmf containing pyridine (5% *v*/*v*) by the passage of dioxygen through the solution leads to the possibility of a catalytic autoxidation of compounds such as benzyl alcohol by the peroxymanganese(IV) chelate which would be reduced to the manganese(II) chelate then reoxidized by



(a) (b)

Fig. 4. Electronic spectra in the visible region of manganese(II)(salhy)$_2$ (5.0×10^{-4} M) in (a): curve 1, dimethylformamide containing 5% *v/v* of pyridine with nitrogen; curve 2, solution exposed to dry molecular oxygen; (b): curve 1, dimethyl formamide; curve 2, dimethyl sulphoxide; curve 3, tetrahydrofuran. 1 cm glass cells.

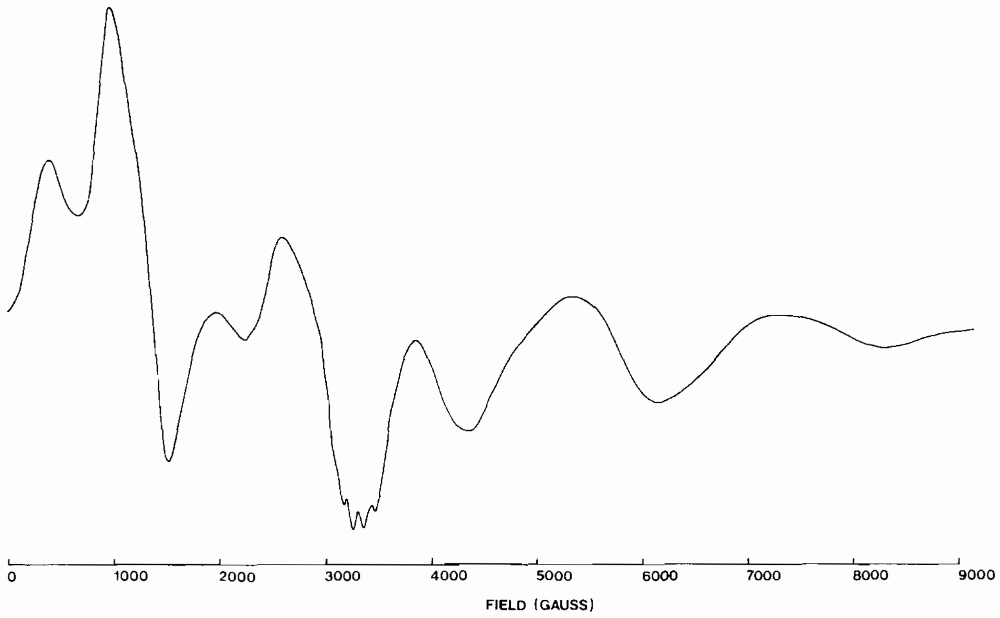


Fig. 5. ESR spectrum due to bis(salicylhydrazonato)peroxymanganese(IV)monopyridine (1.0×10^{-3} M) in dmf containing pyridine (5%). 77 K, microwave frequency 9.147 GHz.

dioxygen to continue the process. In fact it was found that a reaction mixture of bis(salicylhydrazonato)peroxymanganese(IV)monopyridine (0.5 g, 1 mmol) and benzyl alcohol (1 g, 10 mmol) in dmf (50 ml) containing a drop (0.05 ml) of pyridine through which dioxygen was bubbled for about 5 min gave, after separation of the products by fractional distillation, benzaldehyde (0.85 g, 85% yield). Similar results were obtained in the catalytic autoxidation of benzylamine and dibenzyl ether to benzaldehyde. In each case the bis(salicylhydrazonato)peroxymanganese(IV)monopyridine may be recovered from the dmf reaction mixture.

Bis(salicylhydrazonato)peroxymanganese(IV)monopyridine undergoes little chemical change in dmf solution when kept at room temperature (about 20 °C) for some hours. If the solution is heated to about 70 °C decomposition occurs within minutes to form some of the manganese(II) chelate, identified by its ESR spectral properties. Storage of the peroxy-

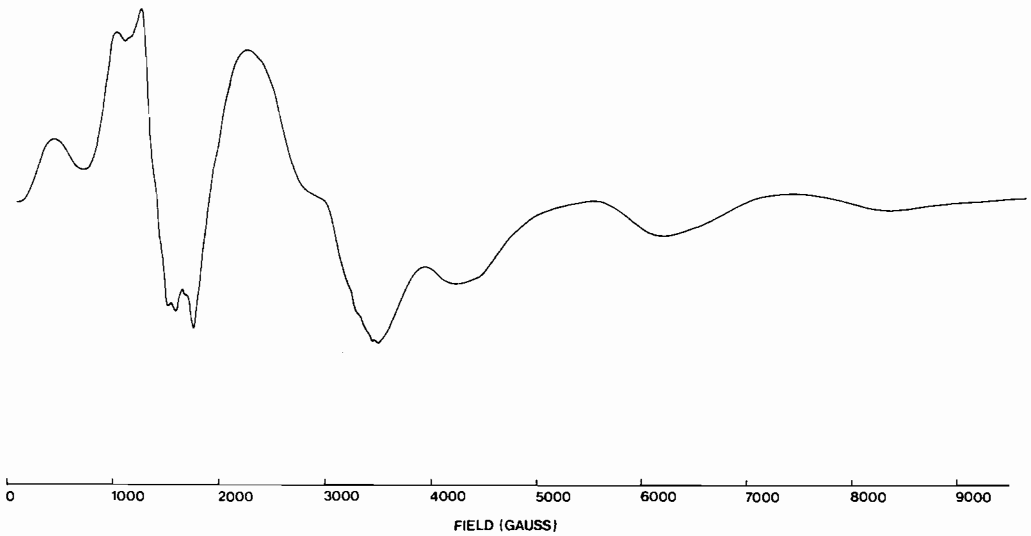


Fig. 6 ESR spectrum due to bis(salicylhydrazonato)oxomanganese(IV)monopyridine (1.0×10^{-3} M) in dmf containing pyridine (16% *v/v*). 77 K, microwave frequency 9.147 GHz.

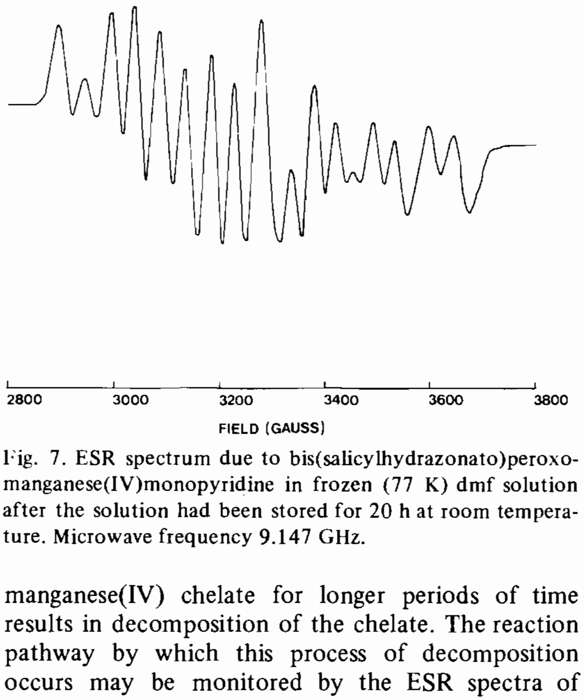


Fig. 7. ESR spectrum due to bis(salicylhydrazonato)peroxomanganese(IV)monopyridine in frozen (77 K) dmf solution after the solution had been stored for 20 h at room temperature. Microwave frequency 9.147 GHz.

manganese(IV) chelate for longer periods of time results in decomposition of the chelate. The reaction pathway by which this process of decomposition occurs may be monitored by the ESR spectra of frozen samples withdrawn from the stored dmf solution of the peroxymanganese(IV) chelate. Thus at the start, the ESR spectrum due to a frozen dmf solution containing the peroxymanganese(IV) chelate is as shown by Fig. 5. After 20 h standing the intensity of the ESR spectra is greatly diminished while the ESR spectrum shown by Fig. 7 makes its appearance. The instrumental gain was increased by a factor of five to observe this result. No further change occurs upon storage for a further 16 h whereafter an ESR spectrum consisting of six clearly resolved hyperfine lines of the relative intensity and spacing usually associated with high spin manganese(II) compounds becomes the dominant ESR spectral feature, therefore accounting for a minor portion of the total manganese present in solution, the major component being in an ESR undetectable form.

Discussion

The reaction of dioxygen which a manganese(II) porphyrin chelate leads to the formation of a manganese(IV) porphyrin superoxide [12]. This reaction is paralleled by the formation of the product manganese(IV)O_2·(salhy)$_2$·py formed by the passage of oxygen through a dmf/pyridine solution of manganese(II)(salhy)$_2$.

The reaction of iodosylbenzene with manganese(II)tetraphenylporphyrin in methanol solution was reported to lead to the formation of oxomanganese(IV) porphyrin though the treatment of manganese(III)tetraphenylporphyrin acetate with iodosylbenzene in methanol did not result in spectral changes after 10 min [13]. It has also been reported that the manganese(III)tetraphenylporphyrin chloride reaction with iodosylbenzene in dichloromethanes leads to the formation of a solid product formulated as Mn(V)O·(tpp)·Cl containing occluded iodosyl benzene [14]. It has been shown, while recognizing the polymeric nature of iodosylbenzene, that this reagent leads to the formation of iodobenzene dimethoxide in methanol solution [15] and leads to the formation of dimethoxy(tetraphenylporphyrinato)manganese(IV) by reaction of tetraphenylporphyrinato manganese(II) with iodosylbenzene in methanol [16]. The reaction of (tetraphenylporphyrinato)manganese(III) derivatives with iodosylbenzene in chlorobenzene solution has been shown to lead to the formation of a dinuclear μ-oxo manganese porphyrin chelate containing one iodosylbenzene per manganese [17]. Magnetic susceptibility measurements on the diazido- and bis(isocyanato)(tetraphenylporphyrinato)manganese(IV) chelates show that the manganese(IV) has a high spin d^3 electronic ground state [18]. In the present work the reaction of manganese(II)(salhy)$_2$ with iodosylbenzene has been shown to result in the formation of the oxomanganese(IV) salicylaldehyde hydrazone chelate.

The oxidation of organic compounds by compounds containing manganese in a high oxidation state, usually manganese dioxide, has been described [19, 20] with mention of the possibility that the intermediate 5,10,15,20-tetraphenylporphyrinatooxomanganese(V) chloride is involved in the chlorination and hydroxylation of alkenes [21]. The use of hematoporphyrinatomanganese(IV) generated by the oxidation of the corresponding manganese(III) chelate by sodium hypochlorite, as an oxidizing agent capable of oxidizing benzyl alcohol, benzylamine, dibenzyl ether and benzylisopropyl ether to benzaldehyde has been described [22]. The reversible dioxygen addition to polymeric Schiff-base chelates of vanadium(II) and manganese(II) and their use as oxidation catalysts has been outlined [23] while the more general use of polymeric materials in oxidation reactions has been reviewed [24]. In the present circumstances the addition of molecular oxygen to the manganese(II) centre in the bis(salicylhydrazonato)manganese(II) chelate is critically dependent on the presence of pyridine in the axial position such that it may be envisaged that transfer of electron density from the pyridine in its axial interaction with the manganese(II) centre makes possible the loss of two electrons to the molecular oxygen with elevation of the oxidation state to manganese(IV) stabilized by coordination of the pyridine. The catalytic cycle involving bis(salicylhydrazonato)peroxymanganese(IV)monopyridinate in the autoxidation of benzyl alcohol to benzaldehyde in dmf solution may involve a two-electron oxidation of benzyl alcohol to benzaldehyde by the bis(salicylhydrazonato)peroxymanganese(IV)monopyridine which in turn is reduced to bis(salicylhydrazonato)manganese(II) with release of the peroxy anion and regeneration of the manganese(IV) state by reaction of the manganese(II) chelate with dioxygen. The final form of the peroxy anion is presumed to be hydrogen peroxide, the exact fate of which in the catalytic system has not been elucidated but it has been established in a separate experiment that hydrogen peroxide is rapidly decomposed in dmf solution containing bis(salicylhydrazonato)manganese(II). Thus bis(salicylhydrazonato)peroxomanganese(IV)monopyridinate offers the possibility of the catalytic autoxidation of organic compounds under mild conditions.

The monitoring of the thermal decomposition of bis(salicylhydrazonato)peroxymanganese(IV)-monopyridine using ESR spectroscopy shows that one of compounds formed possesses a complicated eighteen line spectrum which is unlike that usually encountered in compounds containing mixed oxidation states of manganese [25, 26] but is quite similar to that observed in a frozen solution of manganese(II) phthalocyanine in dimethylacetamide which had been exposed to molecular oxygen and attributed to a molecular oxygen complex of manganese(II) phthalocyanine [27]. The observation of such an ESR spectrum in the present circumstances provides at least spectroscopic evidence for the formation of a molecular oxygen complex of bis(salicylhydrazonato)manganese(II)monopyridine in the decomposition of the corresponding peroxymanganese(IV) compound.

References

1 J. Livorness and T. D. Smith, *Struct. Bonding (Berlin), 48,* 1 (1982).

2 K. Sauer, *Acc. Chem. Res., 13,* 249 (1980).

3 T. Wydrzynski and K. Sauer, *Biochim. Biophys. Acta, 589,* 56 (1980).

4 G. C. Dismukes and Y. Siderer, *Proc. Natl. Acad. Sci. U.S.A., 78,* 274 (1981).

5 W. M. Coleman and L. T. Taylor, *Coord. Chem. Rev., 32,* 1 (1980).

6 T. A. Furtoch and L. J. Taylor, *Inorg. Chim. Acta, 61,* 211 (1982).

7 L. A. Duncan, A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. II, 76,* 1415 (1980).

8 A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. II, 76,* 1429 (1980).

9 M. P. Jain and S. Kamer, *Talanta, 24,* 149 (1977).

10 T. D. Smith, I. M. Ruzic, S. Tirant and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.,* 363 (1982).

11 R. B. Birdy and M. Goodgame, *J. Chem. Soc., Dalton Trans.,* 1429 (1982).

12 (a) B. M. Hoffman, C. J. Weschler and F. Basolo, *J. Am. Chem. Soc., 98,* 5473 (1976); (b) B. M. Hoffman, T. Szymanski, T. G. Brown and F. Basolo, *J. Am. Chem. Soc., 100,* 7253 (1978). (c) L. K. Hanson and B. M. Hoffman, *J. Am. Chem. Soc., 102,* 4602 (1980).

13 I. Willner, J. W. Atvos and M. Calvin, *J. Chem. Soc., Chem. Commun.,* 964 (1980).

14 J. T. Groves, W. J. Kruper and R. C. Haushalter, *J. Am. Chem. Soc., 102,* 6375 (1980).

15 B. C. Schardt and C. L. Hill, *Inorg. Chem., 22,* 1563 (1983).

16 M. J. Camenzind, F. T. Hollander and C. L. Hill, *Inorg. Chem., 21,* 4301 (1982).

17 (a) J. A. Smegal, B. C. Schardt and C. L. Hill, *J. Am. Chem. Soc., 105,* 3510 (1983); (b) J. A. Smegal and C. L. Hill, *J. Am. Chem. Soc., 105,* 3515 (1983).

18 M. J. Camenzind, F. J. Hollander and C. L. Hill, *Inorg. Chem., 22,* 3776 (1983).

19 D. G. Lee, in R. L. Augustine (ed.), 'Oxidation' Marcel Dekker, New York, Chap. 2, p. 68.

20 J. S. Pizey, in 'Synthetic Reagents', Vol. 2, Ellis Horwood, Chichester, U.K., 1974, p. 152.

21 R. A. Sheldon and J. K. Kochi, in 'Metal-Catalyzed Oxidations of Organic Compounds', Academic Press, New York, 1981, p. 176.

22 I. Tabusai and N. Koga, *Tetrahedron Lett.,* 5017 (1978).

23 W. Sawodny, R. Grünes and H. Reitzle, *Angew. Chem., Int. Ed. Engl., 21,* 775 (1982).

24 A. Skorobogaty and T. D. Smith, *Coord. Chem. Rev., 53,* 55 (1984).

25 M. J. Camenzind, B. C. Schardt and C. L. Hill, *Inorg. Chem., 23,* 1984 (1984).

26 S. R. Cooper, G. C. Dismukes, M. P. Klein and M. Calvin, *J. Am. Chem. Soc., 100,* 7248 (1978).

27 A. B. P. Lever, J. P. Wilshire and S. K. Quan, *J. Am. Chem. Soc., 101,* 3668 (1979); *Inorg. Chem., 20,* 761 (1981).