Kinetics and Mechanism of the Autoxidation of Tris[biacetyl bis(methylimine)]iron(II)

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Tris[biacetyl bis(methylimine)]iron(II) undergoes autoxidation in acidic aqueous media through a free-radical process. Spectrophotometric and n.m.r. measurements show that molecular oxygen attacks the co-ordinated ligands without cleavage of the metal–ligand bond. The main product of the reaction is due to oxidation of a *C*-methyl group to a hydroperoxide group. Kinetic measurements show that the reaction is first order with respect to the complex and half order with respect to the oxygen concentration, and suggest that protonation is involved in a pre-equilibrium step. Iron(III) promotes the reaction, while iron(II) ions strongly inhibit it. A mechanism is proposed which involves an intramolecular electron transfer followed by a free-radical chain process.

THE oxidation by molecular oxygen of ligands co-ordinated to transition-metal ions can result in some cases in products which do not undergo metal–ligand bond rupture. For example, amines co-ordinated to Fe^{II},[1,2] Ru^{II},[3] Co^{II},[4] and Ni^{II} [5] give rise to stronger ligands (CN^- or imines), a fact which may account for these unusual reactions.

A novel kind of ligand activation was described in an earlier communication in which aliphatic di-imines co-ordinated to Fe^{II} are autoxidized without change of the basic ligand function.[6] In the present paper a full study is reported of the kinetics of the autoxidation of tris[biacetyl bis(methylimine)]iron(II), $[Fe(bmi)_3]^{2+}$, and related complexes. Oxidation is shown to occur primarily on the methyl, or methylene, groups attached to carbon and to lead to peroxide groups. A general mechanism is proposed for these reactions based on an intramolecular electron-transfer step followed by a radical-chain reaction.

EXPERIMENTAL

The perchlorate salts of tris[glyoxal bis(methylimine)]iron(II), $[Fe(gmi)_3][ClO_4]_2$, and tris[biacetyl bis(methylimine)]iron(II) were prepared by modification of the methods outlined by Krumholz.[7] The other iron(II) complexes were prepared as perchlorate salts according to the procedure of Krumholz *et al.*[8] The tris[biacetyl bis(methylimine)] complexes of Co^{II} and Ni^{II} were prepared according to

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[1] V. L. Goedken, *J.C.S. Chem. Comm.*, 1972, 207.

[2] V. L. Goedken and D. H. Busch, *J. Amer. Chem. Soc.*, 1972, **94**, 7355; D. Watkins, jun., D. P. Riley, J. A. Stone, and D. H. Busch, *Inorg. Chem.*, 1976, **15**, 387.

[3] J. D. Miller, J. B. Watts, and D. Y. Waddan, *Inorg. Chim. Acta*, 1975, **12**, 267.

[4] D. S. Back and A. J. Hartshorn, *Tetrahedron Letters*, 1974, 2157.

[5] E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, 1967, **6**, 2043.

[6] H. L. Chum, A. M. G. da Costa, and P. Krumholz, *J.C.S. Chem. Comm.*, 1972, 772.

[7] P. Krumholz, *J. Amer. Chem. Soc.*, 1953, **75**, 2163.

[8] P. Krumholz, O. A. Serra, and M. A. De Paoli, *Inorg. Chim. Acta*, 1975, **15**, 25.

Figgins and Busch.[9] Solutions were prepared with water redistilled from $K[MnO_4]$ in a glass apparatus in order to remove trace amounts of reducing impurities. Likewise, acid solutions were prepared from H_2SO_4 (95—98%, E. Merck), of low content in reducing agents and iron.

The consumption of oxygen was measured between 298.1 and 318.1 K (± 0.05 K) in a Warburg gas burette (B. Braun, model V166). The measurements were reproducible to within ± 3 μl of oxygen, and all the experiments were carried out at least three times. Visible-absorption spectra of aliquot portions of the oxidized solution diluted in succinate buffer solution (pH 5) were recorded on a Hitachi–Perkin-Elmer spectrophotometer. The reaction is quenched in this medium. N.m.r. spectra were recorded at 100 MHz on a Varian XL-100 spectrometer.

RESULTS

Manometric experiments carried out at 308.1 K to monitor the absorption of oxygen by acidic (0.5 mol dm^{-3} H_2SO_4) aqueous solutions of $[Fe(bmi)_3]^{2+}$ (10^{-3} mol dm^{-3}) revealed an induction period and a sigmoid curve (Figure 1). The uptake of oxygen continued for several hours (>50), although at a much slower rate after the first 10 h. The absorption spectra of these solutions, which initially displayed maxima at 567 nm ($\varepsilon_{max.}$ 10.7×10^5 dm^3 mol^{-1} m^{-1}) underwent noticeable changes as a function of time as previously reported.[7] A shift towards longer wavelengths (Figure 2) suggests that autoxidation of the complex results in species which maintain the iron(II)–di-imine chromophore structure.[10] By way of comparison, the iron(III) form of this complex, $[Fe(bmi)_3]^{3+}$, obtained by oxidation with Ce^{IV} at high acid concentration, has an absorption maximum at 374 nm ($\varepsilon_{max.}$ 3.1×10^5 dm^3 mol^{-1} m^{-1}).[8] In the absence of oxygen, it has been established that $[Fe(bmi)_3]^{2+}$ undergoes very slow acid dissociation (k 2.8×10^{-6} s^{-1} at 333 K).

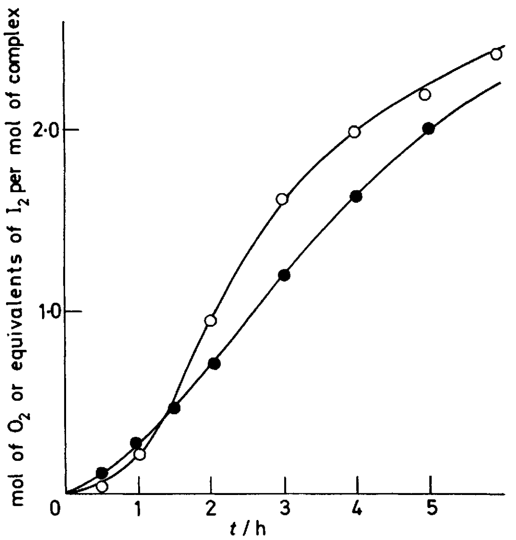

FIGURE 1 Autoxidation at 308.1 K in air of a solution of 1.00×10^{-3} mol dm^{-3} $[Fe(bmi)_3]^{2+}$ and 0.50 mol dm^{-3} H_2SO_4: (●) the uptake of oxygen; (○) the iodine liberated on titration of the oxidized solution with sodium iodide

Preliminary attempts to identify the oxidized products of the complex resulted in isolation of tarry polyiodides in 75% yield. Elementary analysis of these products revealed that the original Fe : N ratio of 1 : 6 is maintained, and thus suggests that autoxidation takes place at the ligands without cleavage of the metal–ligand bond.

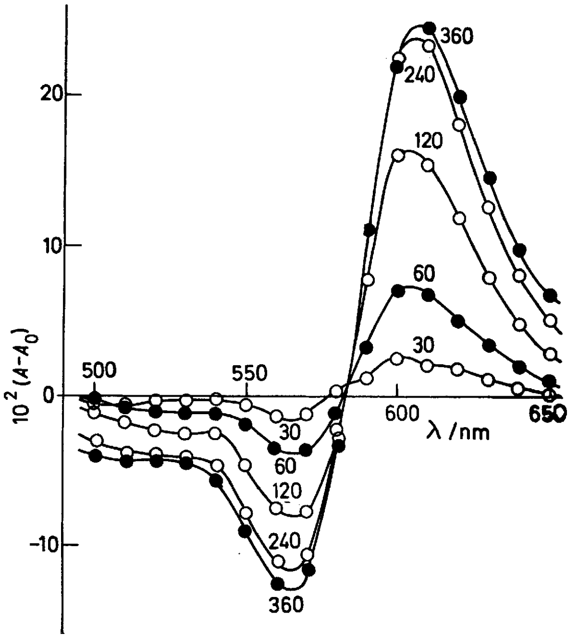

FIGURE 2 Differential-absorption spectra as a function of time (t/min) of an acidic solution of $[Fe(bmi)_3]^{2+}$ autoxidized in air at 313.1 K (A_0 represents the absorption of the original complex)

The course of the reaction was also followed by n.m.r. in D_2SO_4–D_2O solutions. The original complex displayed a peak at 2.66 p.p.m. downfield from the reference sodium 4,4-dimethyl-4-silapentanesulphonate due to the C-methyl groups, and another at 2.92 p.p.m. due to the N-methyl groups. This assignment was established by comparison with the spectrum of the complex $[Fe\{[^2H_6]bmi\}_3]^{2+}$ with fully deuteriated N-methyl groups. Whereas these two peaks decreased in intensity as a function of exposure time of the solution to oxygen, two new peaks at 3.14 and 5.25 p.p.m. increased correspondingly. The signal at 3.14 p.p.m. was absent in the spectrum of the oxidized solution of the deuteriated complex. After oxidation (6 h) at 308.1 K under conditions which correspond to the stoicheiometric uptake of 3 mol of O_2 per mol of complex, the n.m.r. intensities were in the ratio (starting downfield) of 2.0 : 3.0 : 3.2 : 3.0. These results indicate that the oxidation takes place initially on the C-methyl groups with formation of a CH_2 group either as a hydroperoxide or an alcohol. The former possibility is favoured by the results quoted below.

The presence of peroxides in the product species was established by the yield of iodine obtained as a function of time on titration of the oxidized solution with sodium iodide [11] (Figure 1). These same experiments conducted with solutions eluted from an ion-exchange column failed to yield any iodine. This fact eliminates H_2O_2 as one of the main products and reinforces the idea that the peroxide groups are in the ligands. We can therefore conclude that

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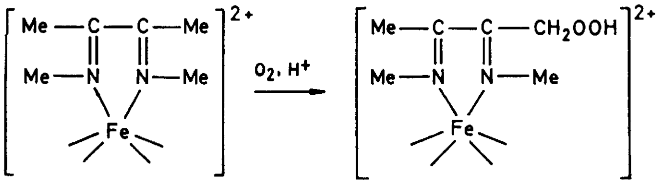
[9] P. E. Figgins and D. H. Busch, *J. Amer. Chem. Soc.*, 1960, **82**, 820.

[10] P. Krumholz, *Structure and Bonding*, 1971, **9**, 139.

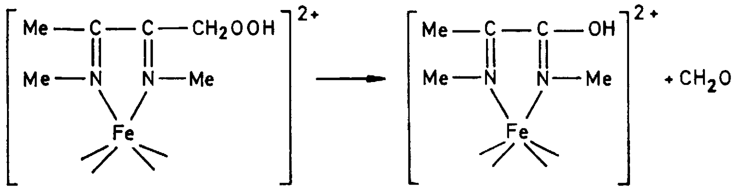
[11] R. D. Mair and R. T. Hall, 'Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1971, vol. 2, p. 535.

the initial process of the autoxidation is as shown in Scheme (1).



SCHEME 1

Attempts to isolate the product species of the autoxidation as a crystalline solid were unsuccessful. Tests to identify the products by dissociation of the oxidized complex, precipitation with 2,4-dinitrobenzaldehyde hydrazone, and analysis by t.l.c. on silica gel resulted in five to eight spots which were not reproducible. Likewise, attempts to isolate the oxidized complex by gel filtration were unsuccessful. These results are not unexpected for species containing hydroperoxide groups which can undergo further oxidation and decomposition. Further support for our hydroperoxide product comes from small quantities of formaldehyde [(4.0 ± 0.6) × 10^{-2} mol per mol of complex] and pyruvic acid [(8.0 ± 1.0) × 10^{-2} mol per mol of complex] which were determined[12,13] after reaction (6 h) at 308.1 K. Formaldehyde can be produced as in Scheme 2, while hydrolysis of the resulting complex would lead to pyruvic acid.



SCHEME 2

The continuous absorption of O_2 by the complex can be rationalized by further oxidation according to the well known process which converts hydroperoxides into carboxylic acids. Strong indication for this step was obtained by monitoring the evolution of CO_2 from the solution. This is typically observed only after a few hours of oxidation and obeys an approximately linear relation with time. At 313.1 K and after 9 h of reaction, a typical experiment yielded 0.021 mol of CO_2 per mol of oxygen absorbed.

Kinetics.—Experiments carried out at 308.1 K and 0.511 mol dm^{-3} in H_2SO_4 yielded equation (1) for the initial autoxidation of $[Fe(bmi)_3]^{2+}$. This rate equation is based

$$v = k_{obs.}'[Fe(bmi)_3{}^{2+}][O_2]^{0.5} \qquad (1)$$

on measurements of the initial rates of consumption of oxygen after the induction period (see Table 1). Variation of the acid concentration from 5.1 × 10^{-3} to 1.0 mol dm^{-3} H_2SO_4 showed that the rate is independent of the acid concentration above 0.25 mol dm^{-3} (Figure 3). Neglecting effects due to changes in activity coefficients, the acid behaviour of the reaction can be described by expression (2).

$$k_{obs.}' = \frac{k_\infty[H^+]}{k_c + [H^+]} \qquad (2)$$

Plots of $1/k_{obs.}'$ against $1/[H^+]$ yielded k_∞ = (1.00 ± 0.05) × 10^{-2} $dm^{\frac{3}{2}}$ $mol^{-\frac{1}{2}}$ s^{-1} and k_c = (1.03 ± 0.02) × 10^{-2} mol dm^{-3}.

Catalysis and Inhibition.—The presence of iron(III) ions in concentrations of the order of 10^{-3} mol dm^{-3} accelerated the reaction such that the induction period was shortened appreciably (Figure 4). Table 2 lists values of the phenomenological rate constant [equation (3)] for this case. The order of reaction with respect to $[Fe^{3+}]$ was 0.2 and the

TABLE 1

Initial velocity of the autoxidation of $[Fe(bmi)_3]^{2+}$ at 308.1 K and 0.511 mol dm^{-3} H_2SO_4

$10^7 v$ [a]	$10^3[Fe(bmi)_3{}^{2+}]$	$10^3[O_2]$ [b]	$10^2 k'_{obs.}$ [c]
mol dm^{-3} s^{-1}	mol dm^{-3}		$dm^{\frac{3}{2}}$ $mol^{-\frac{1}{2}}$ s^{-1}
1.50	0.50	0.88	1.00
2.10	0.75	0.88	0.95
2.83	1.00	0.88	0.95
4.12	1.50	0.88	0.92
5.50	2.00	0.88	0.93
1.33	1.00	0.18	0.98

[a] ±0.02 × 10^{-7} mol dm^{-3} s^{-1}. [b] ±0.01 × 10^{-3} mol dm^{-3}. [c] Typically, ±0.03 × 10^{-2} $dm^{\frac{3}{2}}$ $mol^{-\frac{1}{2}}$ s^{-1}.

$$v_{Fe^{3+}} = k_{cat.}[M(bmi)_3{}^{2+}][O_2]^{0.5} \qquad (3)$$

reaction was independent of acid concentration in the range 0.50 × 10^{-2}—0.50 mol dm^{-3} H_2SO_4. For this catalyzed reaction the plot in Figure 4 can be resolved into two curves. While the adjustment of the two curves is somewhat arbitrary, the first curve (*b*) could be identified with the first step, while curve (*c*) could be associated with the second step of the oxidation. In this approximation, curve (*c*) is first order with respect to the complex concentration and zeroth order with respect to the concentration of oxygen.

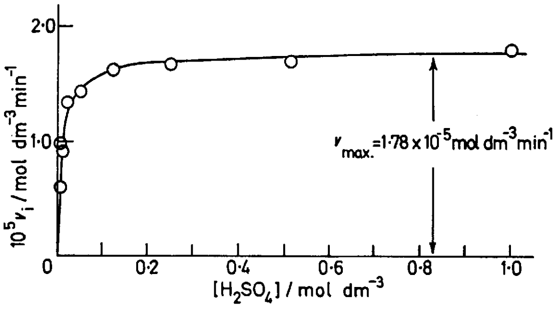


FIGURE 3 Initial velocity of autoxidation as a function of the concentration of H_2SO_4. Reactions were carried out under pure oxygen at 308.1 K for 1.00 × 10^{-3} mol dm^{-3} $[Fe(bmi)_3]^{2+}$

The reaction was inhibited by the presence of Fe^{2+} ions for several hours, after which the reaction suddenly acceler-

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[12] T. Nash, *Biochem. J.*, 1953, **55**, 416.

[13] G. D. Lu, *Biochem. J.*, 1939, **39**, 249; H. Katsuki, T. Yoshida, C. Tanegashima, and S. Tanaka, *Analyt. Biochem.*, 1971, **43**, 349.

ated to a rate equal to that induced by an equivalent amount of iron(III) ions. This was verified by simply displacing in time the curve for oxygen uptake. Ethylenediaminetetra-acetic acid (H_4edta) (10^{-3} mol dm^{-3}) caused the initial velocity of the reaction to decrease by *ca.* 30%, while in the iron(III)-catalyzed process the inhibition reached 98%.

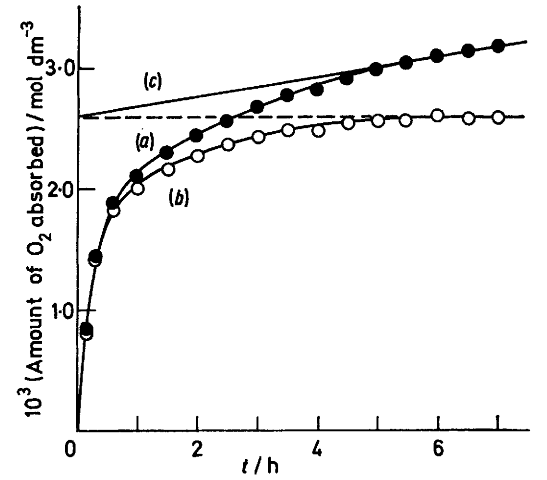

FIGURE 4 Autoxidation at 308.1 K under pure oxygen of a solution of 1.00×10^{-3} mol dm^{-3} $[Fe(bmi)_3]^{2+}$, 0.051 mol dm^{-3} H_2SO_4, and 1.02×10^{-4} mol dm^{-3} Fe^{3+}. The experimental curve (*a*) has been resolved into (*b*) which represents the initial oxidation of the ligands to hydroperoxide groups, and (*c*) which represents a second stage of the oxidation

TABLE 2

Rate constants for the autoxidation of $[Fe(bmi)_3]^{2+}$ catalyzed by Fe^{3+} at 308.1 K and 0.0511 mol dm^{-3} H_2SO_4

10^6v [a] / mol dm^{-3} s^{-1}	$10^3[Fe(bmi)_3]^{2+}$ / mol dm^{-3}	$10^3[O_2]$ / mol dm^{-3}	$10^4[Fe^{3+}]$ / mol dm^{-3}	$10^2k_{cat.}$ [b] / dm$^{3/2}$ mol$^{-1/2}$ s^{-1}
0.72	0.50	0.98	1.02	4.7
1.33	0.75	0.98	1.02	5.7
1.58	1.00	0.98	1.02	5.0
2.63	1.50	0.98	1.02	5.5
3.58	2.00	0.98	1.02	5.7
0.82	1.00	0.21	1.02	5.7
1.00	1.00	0.98	0.102	3.2
1.10	1.00	0.98	0.306	3.5
1.76	1.00	0.98	2.00	5.6
1.86	1.00	0.98	3.04	5.9

[a] $\pm 0.02 \times 10^{-6}$ mol dm^{-3} s^{-1}. [b] $\pm 0.2 \times 10^{-2}$ dm$^{3/2}$ mol$^{-1/2}$ s^{-1}.

In our earlier communication [6] evidence was advanced to show that the autoxidation of $[Fe(bmi)_3]^{2+}$ is a free-radical process. Further experiments using specific substrates to trap hydroxyl radical [14] inhibited the reaction (Table 3). Finally, no differences were detected in the rate of the reaction for processes carried out in the dark or under normal laboratory conditions.

Autoxidation of Other Di-imine Complexes.—The following di-imine complexes, $[Fe\{CR^1(\text{:NMe})\cdot CR^2(\text{:NMe})\}_3]^{2+}$, were also studied: $[Fe(gmi)_3]^{2+}$, $R^1 = R^2 = H$; $[Fe(pmi)_3]^{2+}$, $R^1 = H$, $R^2 = Me$; $[Fe(ptmi)_3]^{2+}$, $R^1 = Me$, $R^2 = Et$; $[Fe(chxmi)_3]^{2+}$, $R^1R^2 = H_2C[CH_2]_2CH_2$; $[Fe(pgmi)_3]^{2+}$, $R^1 = H$, $R^2 = Ph$; $[Fe(ppmi)_3]^{2+}$, $R^1 = Me$, $R^2 = Ph$. Manometric experiments as well as absorption spectra showed that the gmi, pmi, and pgmi complexes do not undergo autoxidation under the same conditions as bmi, while the other three complexes suffer comparable oxidation. It is clear that the oxidation takes place only when methyl or methylene groups are attached to carbon. It is also interesting that the ability to undergo autoxidation follows the redox potentials of these complexes.[15]

TABLE 3

Inhibition by hydroxyl radical scavengers. Oxidations were carried out under pure oxygen at 308.1 K for solutions of 1.00×10^{-3} mol dm^{-3} $[Fe(bmi)_3]^{2+}$ and and 0.50 mol dm^{-3} H_2SO_4

Scavenger	Concentration mol dm^{-3}	Percentage inhibition
Pyrocatechol	1.0×10^{-4}	77.8
Ethanol	6.2×10^{-2}	24.6
D-Glucose	1.0×10^{-2}	15.3
D-Mannitol	1.0×10^{-2}	11.0
Benzoate	4.9×10^{-3}	14.4

Attempts were also made to study the influence of the metal ion in these processes. Experiments with $[Co(bmi)_3]^{2+}$ and $[Ni(bmi)_3]^{2+}$ revealed that these complexes undergo, dissociation without oxidation of the ligands under conditions similar to those used for $[Fe(bmi)_3]^{2+}$.

DISCUSSION

The results indicate that autoxidation of $[Fe(bmi)_3]^{2+}$ leads primarily to the formation of hydroperoxides in the methyl groups attached to carbon. The n.m.r. experiments also suggest that this reaction proceeds until at least three out of the six methyl groups are oxidized. After long exposure to oxygen it is also possible to infer further oxidation of the ligands to carboxylic acids.

Because of the difficulties involved in the isolation of the products of the reaction, it is not possible to establish the full stoicheiometry. Thus, minor secondary reactions cannot be dismissed in the present case, as shown by the experiments which measured the liberation of iodine; these resulted in more equivalents of oxidizing groups than can be accounted for simply by hydroperoxide groups.

The apparent relation between the ability to undergo autoxidation and the redox potential of the complex suggests that the iron(III) form is probably involved in the mechanism. The iron(III) complex would then undergo an intramolecular electron transfer similar to that postulated by Krumholz [16] in the oxidation of di-imine complexes by Ce^{IV} in 10 mol dm^{-3} H_2SO_4.

The kinetic order with respect to the oxygen concentration points to the participation of O_2 in the initiation process of a typical radical-chain mechanism. The fact that the induction period is not reproducible for similar samples suggests that the initiation may actually be a heterogeneous process, or be due to trace amounts of metal ions. The small decrease in the initial rate of the uncatalyzed reaction on addition of H_4edta makes it unlikely that

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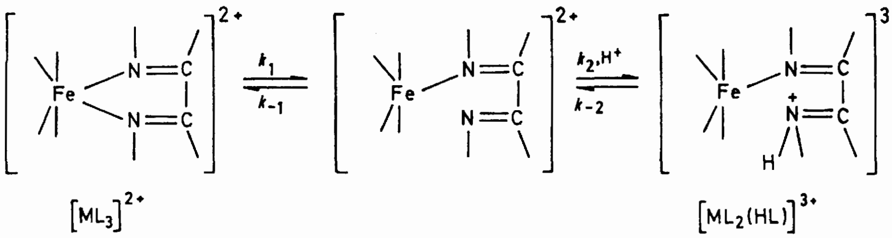
[14] C. Beauchamp and I. Fridrovich, *J. Biol. Chem.*, 1970, **245**, 4641; G. Cohen and R. E. Heikkila, *ibid.*, 1974, **249**, 2447.

[15] P. Krumholz, M. A. De Paoli, H. L. Chum, and E. J. S. Vichi, *Abs.* 18*th Internat. Conf. Co-ordination Chem.*, Dublin, 1974, 2.32b.

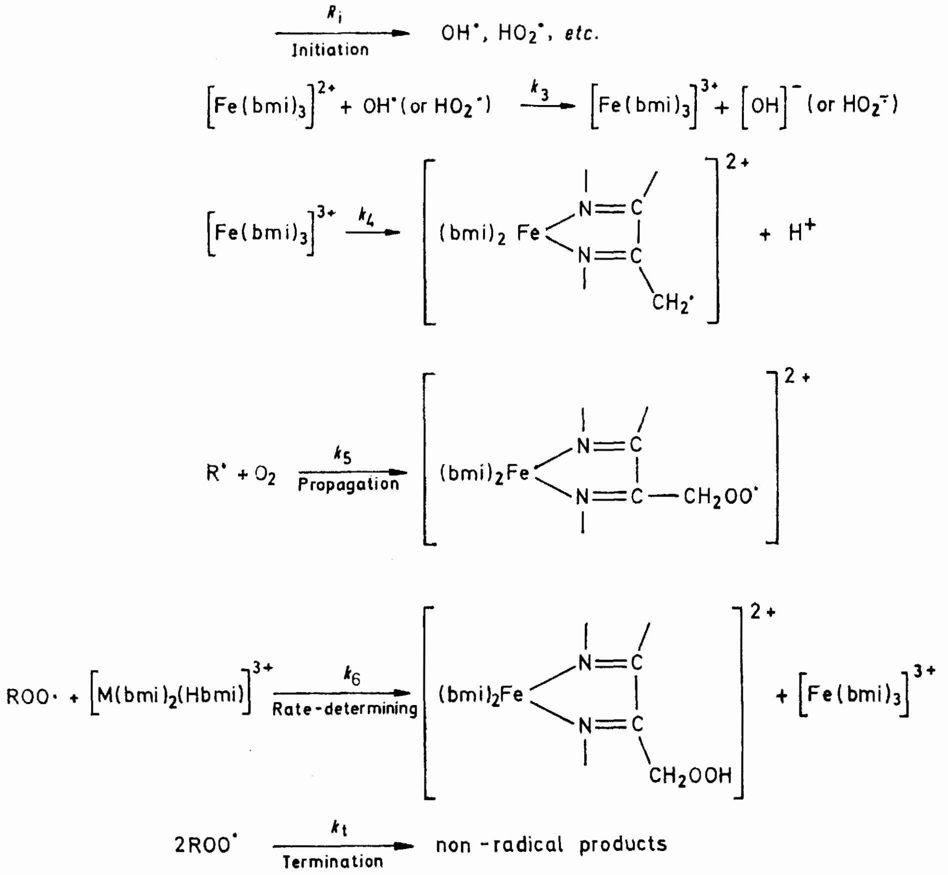
[16] P. Krumholz, *Abs.* 7*th Internat. Conf. Co-ordination Chem.*, Stockholm, 1962, p. 280; P. Krumholz and H. L. Chum, *Inorg. Chem.*, 1974, **13**, 514, 519.

free Fe^{3+} ions are the only metallic species responsible for the initiation of the reaction.

The acid dependence of the reaction is consistent with the participation of a protonated species in the rate-determining step. This behaviour is reminiscent of that observed in the acid dissociation of di-imine complexes.[10] The following equilibria can be postulated leading to very small quantities of the protonated complex (Scheme 3).



SCHEME 3



SCHEME 4

The above observations lead us to propose the mechanism in Scheme 4 for the formation of hydroperoxide groups in the ligands. This scheme establishes equation (4) for the initial velocity of the reaction. Applying

$$v = k_5[ROO^\bullet][M(bmi)_2(Hbmi)^{3+}] \qquad (4)$$

steady-state conditions to all the radical species, and assuming that $k_{-2}[M(bmi)_2(Hbmi)^{3+}] \ll k_1[M(bmi)_3{}^{2+}]$, expression (5) can be obtained. This mechanism, which involves attack of a peroxide radical on a protonated complex, would explain the selectivity observed in the oxidation of the methyl groups on carbon and not of those on nitrogen. The catalytic action of Fe^{3+} ions is

$$v = \frac{k_5}{k_{-2}} \cdot \left[\frac{2R_i}{k_6}\right]^{\frac{1}{2}} \cdot \frac{k_2 k_1[M(bmi)_3{}^{2+}][H^+]}{k_{-1} + k_2[H^+]} \qquad (5)$$

likely to take place primarily in the initiation step. The quenching of the reaction in the presence of H_4edta for this case, and the relative independence of the acidity, suggests that a somewhat different mechanism is operating in this system.

It should be stressed that, although the proposed mechanism is an attempt to explain the more important features of the reaction, further studies will be necessary to elucidate the participation of the different oxidizing species in these systems.

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