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Oxidation of substituted alkynes catalyzed by a non-heme iron(III) bis benzimidazole diamide complex as catalyst under ambient conditions

Ruchi Bakshi, Ravinder Kumar & Pavan Mathur*
Department of Chemistry, University of Delhi, Delhi 110 007, India
Email: pavanmat@yahoo.co.in

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Bis-benzimidazole diamide ligand, N,N′- bis(2-methylbenzimidazolyl) hexanediamide [GBHA = L], and its Fe(III) complexes have been synthesized. The Fe(III) complexes have been analyzed for the composition $[Fe(L)X_3].nH_2O$ where X is an exogenous anionic ligand ($X=Cl^-$, NO_3^-) and characterized by IR, UV-visible, cyclic voltammetry and EPR spectroscopy. Low temperature EPR spectra have been obtained for the complexes that indicate rhombic geometry environment in solution state. Oxidation of substituted alkynes has been investigated using these Fe(III) complexes as catalyst with TBHP and H_2O_2 as an alternate source of oxygen. The isolated products have been characterized by GC-MS.

Keywords: Coordination chemistry, Oxidation, Iron, Alkynes, Benzimidazole diamides, Amides, Benzimidazoles,

Oxidation of organic substrates by synthetic non-heme iron complexes is of interest as chemical models of non-heme iron oxygenase[1-4]. Important examples are the stereoselective alkane hydroxylation and olefin epoxidation by iron complexes of tetradentate ligands[5-9]. Oxidation of alkynes has been attempted earlier, utilizing excess of oxidant, viz., chromium trioxide[10] or in the presence of up to seven equivalent of *tert*-butyl hydroperoxide and long reaction times[11]. More recently aerobic oxidation of alkynes has been reported with N-hydroxy phthalimide and $[Co(acac)_2]$[12] and with metal salts and *tert*-butyl hydroperoxide at 70 °C for 24 h under O_2[13]. Alkynes, unlike alkenes, cannot form stable products by a single, direct oxygen transfer[14]. Further it has been observed for Pd-catalysed oxidation that the reactivity of 1-aryl-2-alkyl ethynes is comparatively more sensitive to substitutions and experimental conditions than 1,2-diaryl ethynes[15]. This prompted us to study the oxidation of 1-aryl-2-alkyl ethyne and 1,2 diaryl ethyne utilizing an iron complex as catalyst in the presence of hydroperoxides. The purpose of this study is to investigate whether the oxidation occurs at the C-C triple bond or on an adjacent methylene group, and also whether it is affected by the nature of the iron catalyst or the oxidant. The present study reports the oxidation of substituted alkynes utilizing the new Fe(III) complexes as catalyst with low concentrations of the oxidant, tri-*tert*-butyl hydroperoxide and hydrogen peroxide.

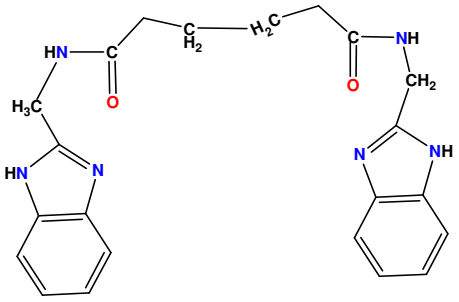
Materials and Methods

Glycine benzimidazole dihydrochloride was prepared following the procedure reported by Cescon and Day.[16] Freshly distilled solvents were employed for all synthesis work. Spectroscopic grade solvents were employed for spectral experiments. All other chemicals were of AR grade.

Elemental analyses of iron(III) complexes were obtained from CDRI, Lucknow, India. Electronic spectra were recorded on an Shimadzu 1601 spectrometer. IR spectra were recorded in the solid state as KBr pellets on a Perkin-Elmer FTIR-2000 spectrometer in the region of 400-4000 cm^{-1}. Cyclic voltammetric measurements were carried out on a BAS-CV 50W electrochemical analysis system. Cyclic voltammograms of all the complexes were recorded in DMSO with 0.1 *M* TBAP as a supporting electrolyte.

A three electrode configuration composed of Pt-disk working electrode, a Pt wire counter electrode and an $Ag/AgNO_3$ reference electrode was used. The reversible one-electron Fc/Fc^+ couple has an $E_{½}$ of 0.1 V versus an $Ag/AgNO_3$ electrode. Solution state EPR spectra were recorded on X-band on a Bruker-Spectrospin with a variable temperature liquid nitrogen cryostat at 120 K at IIT Kanpur, Kanpur. Mass spectra were obtained on a KC455 ESIMS spectrometer, while GC-MS data were obtained on a GCMS-QP2010(plus) Schimadzu instrument at AIRF, JNU, New Delhi.

The ligand, N,N′- bis(2-methylbenzimidazolyl)-hexanediamide [GBHA] (L), was prepared as follows[17]: To a solution of adipic acid (1.67 g, 11.4 mmol) in pyridine (20 ml) was added a solution of glycinebenzimidazole dihyrochloride (5.0 g, 22.8 mmol) in pyridine (30 ml). The reaction mixture was then heated slowly on a water bath at a temperature of 40 °C and to it was added triphenyl phosphate (7.08 ml, 22.8 mmol) dropwise over a period of 15 min. The clear solution was stirred for 1 h. at 75 °C. The white crystalline product so obtained was recrystallized with a EtOH-H_2O (1:2) mixture[17]. ^{1}H NMR (d_6-DMSO) δ ppm: 1.5 (s, 4H), 2.2 (s, 4H), 4.4 (d, 4H, J = 5.5Hz), 7.1-7.2 (m,4H), 7.4-7.5 (m,4H), 8.4 (t, 2$H_{amideNH}$, J = 5.1Hz), 12.1 (s, 2H).



(L)

The Fe(III) complexes, [Fe(L)X_3], where X = Cl^-, NO_3^-, were prepared as follows: A methanolic solution of ligand L (5 ml, 0.118 mmol) was added to a methanolic solution of FeX_3 (5 ml, 0.118 mmol). The yellow coloured solution was stirred for 5 h. To the resulting solution, dropwise addition of cold diethyl ether resulted in the formation of a dark red precipitate which was filtered, washed with a small amount of methanol and dried under vacuum over anhydrous $CaCl_2$. The compounds analysed for the following compositions:

[$FeC_{22}N_6O_2H_{24}Cl_3.2H_2O$]: Anal. (%) Found (Calc.): C, 44.1(43.8); H, 4.6(4.6); N, 14.2(13.9), Yield(%): 90 mg (68 %); IR (KBr pellets, cm^{-1}): 3396 (υ_{OH}), 3016 ($\upsilon_{NH\ amide}$), 2918 ($\upsilon_{NH\ benzim}$), 1653 ($\upsilon_{C=O\ amideI}$), 1527 ($\upsilon_{C-N\ amideII}$), 1458 ($\upsilon_{C=N-C=C-\ benzim}$), 765 ($\upsilon_{c=c}$ benzene ring vibration); λ_{max}, nm (log ε): 276 (4.4), 282 (4.2), 340 (3.55); $E_{½}$ = –332.0 mV, m/z = 602.

[$FeC_{22}N_6O_2H_{24}(NO_3)_3.H_2O$]: Anal. (%) Found (Calc.): C, 41.8(40.0); H, 4.7(4.0); N, 19.0(18.9), Yield (%) : 105 mg (72 %); IR (KBr pellets, cm^{-1}): 3415 (υ_{OH}), 3253 ($\upsilon_{NH\ amide}$), 2953 ($\upsilon_{NH\ benzim}$), 1655 ($\upsilon_{C=O\ amideI}$), 1527 ($\upsilon_{C-N\ amideII}$), 1458 ($\upsilon_{C=N-C=C-\ benzim}$), 765 ($\upsilon_{c=c}$ benzene ring vibration), 1384 ($\upsilon_{O-N-O\ (symm)}$), 826($\upsilon_{O-N-O\ (asymm)}$) ; λ_{max} , nm (log ε): 276(4.5), 282(4.3), 340(3.4); $E_{½}$ = -195.5 mV, m/z = 664.

The presence of water molecules was determined by IR and TGA data.

Results and Discussion

Spectral charaterisation

The electronic spectra of iron(III) complexes were recorded in HPLC grade dimethyl sulphoxide (DMSO) solvent. Two peaks in the range 270-285 nm are observed for all the complexes which have been assigned to intraligand π–π* transition of benzimidazole moiety in their respective ligand[18]. The bands show enhanced absorption relative to the respective ligands as indicated by their extinction coefficients. Both the complexes exhibit a broad shoulder in the region 300-400 nm, characteristic of a charge transfer transition. The band at 340 nm in the above complexes are predominantly assigned to charge transfer transition from $p\pi$ orbital of chloride or oxygen of nitrate to half filled $d\pi^*$ orbital of the Fe^{III} metal centre[19-24] i. e., $Cl^- \rightarrow Fe^{III}$ / $NO_3^- \rightarrow Fe^{III}$.

In the IR spectra, shift in amide I band due to C=O group and increase/decrease in amide II band due to C-N group in the ligand are indicative of the coordination of the amide through carbonyl oxygen in the complexes[24-29]. In the complexes, the $\upsilon_{C=O\ amide1}$ band increases and $\upsilon_{C-N\ amideII}$ band decreases as compared to the ligand L by 15-25 cm^{-1}. In all the complexes, IR bands due to benzimidazole NH and amide NH are shifted, indicating hydrogen bonding either with the solvent molecules or with the exogenous anionic ligand in the complexes[24,25]. A broad band in the 3300-3500 cm^{-1} region is due to υ(O-H), indicating the presence of water molecule. The nitrate complex shows bands at 1384 and 826 cm^{-1} due to υ_{O-N-O} (symm) and υ_{O-N-O} (antisymm) stretching of the coordinated nitrate group[30].

Both the complexes display a quasi-reversible redox wave (Fig. 1) due to Fe^{III}/Fe^{II} redox couple. The $E_{1/2}$ values observed for the iron complex with chloride as an exogenous anion are cathodic. In the analogous complex with nitrate as an exogenous anion, the $E_{1/2}$ values are more anodic than the corresponding chloride counterpart. This suggests that the bound nitrate ion affects the relative destabilization of iron(III).

X-band EPR spectra of the iron(III) complexes were recorded as frozen DMSO solution at liquid nitrogen temperature (Fig. 2, Table 1). The present series of Fe(III) complexes bound with chloride ion show signals at g ~ 4.3, with transitions at low field (g ~ 5.5 and g ~ 7.2) and in the case of nitrates, an additional signal at g = 3.2 was also observed. Since in the present series of iron(III) complexes, multiple signals are observed, distortion towards axial geometry appears to be strong enough to allow transitions from the other Kramer's doublet in S = 5/2 multiplet[31]. The complex, $[Fe(L)(NO_3)_3]$ seems to have iron(III) in a coordination environment that is distorted even more towards axial geometry. This is borne out by the width of the central g ~ 4.3 signal that is atleast two/three times larger than the relatively sharp signal found for the chloride complex. The nitrate complex also exhibits a high field transition at g ~ 3.0, which is absent in the analogous compound. The large width of the central signal may be the signature of a large departure from purely rhombic geometry.

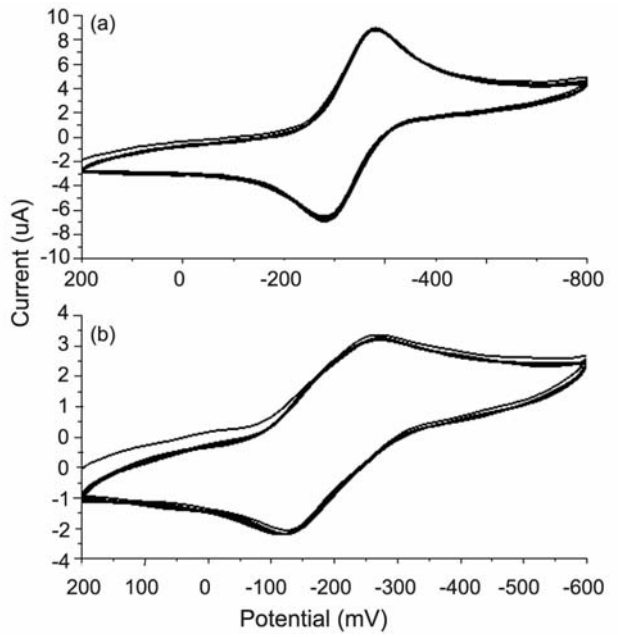


Fig. 1—Cyclic voltamograms of the Fe(III) complexes at a scan rate of 100 mV/s in DMSO. [(a) $[Fe(L)Cl_3]$; (b) $[Fe(L)(NO_3)_3]$].

Oxidation of substituted alkynes

Oxidation of substituted alkynes was studied using $[Fe(L)X_3]$ complex and *tert.*-butyl hydroperoxide (TBHP) and hydrogen peroxide (H_2O_2) as oxidants. A solution of substituted alkynes (0.664 mmol) in 5 ml methanol was prepared. A suspension of the $[Fe(L)X_3]$ complex (0.033 mmol) in methanol was added to the above solution followed by addition of tri-*tert*- butyl hydroperoxide (0.664 mmol) or hydrogen peroxide (H_2O_2) as oxidant. The reaction mixture was stirred for 4-5 h on a water bath at a temperature of 45 °C and was monitored continuously using TLC. A single spot was visualized at R_f = 0.46 in UV, and the course of reaction followed by using 2,4-DNP reagent. After 5 h, the reaction mixture was worked-up on a short column and eluted with 10 % ethyl acetate:hexane. The product was isolated, dissolved in EtOH and a DNP derivative was prepared. This was further characterized by ^{1}H NMR and mass spectroscopy.

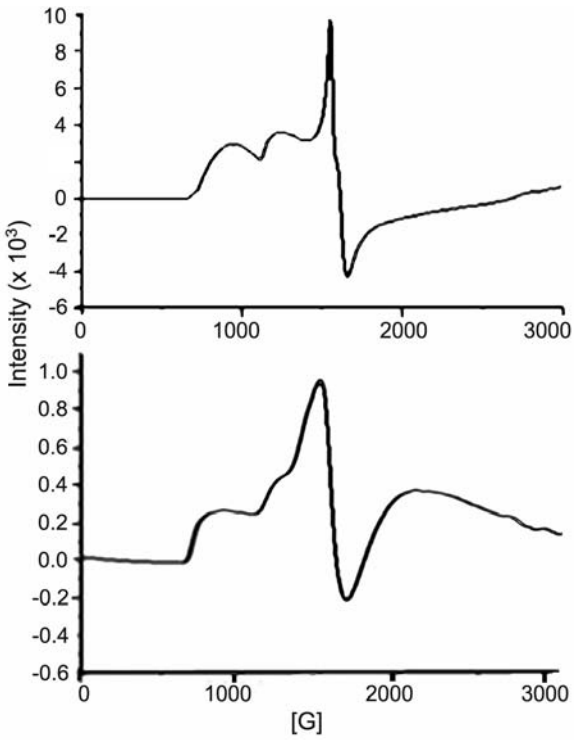


Fig. 2—X-band EPR spectra of the Fe(III) complexes in DMSO at liquid nitrogen temperature. [(a) $[Fe(L)Cl_3]$; (b) $[Fe(L)(NO_3)_3$; microwave power = 10 mW, microwave frequency = 9.4 GHz, receiver gain = 1×10^3].

Table 1—X-band EPR data of iron(III)-L complexes at 120 K

Complex	H (gauss)				g_{av}			
	$H1$	$H2$	$H3$	$H4$	$g1$	$g2$	$g3$	$g4$
$Fe(L)Cl_3$	–	1575	1230	930	–	4.28	5.49	7.26
$Fe(L)(NO_3)_3$	2100	1560	1280	850	3.21	4.37	5.25	7.94

The product isolated was found to be 1-(4-phenylbut-3-yn-2-one)-2-(2,4-dinitrophenyl)-hydrazine (yield: 42 mg). ^{1}H-NMR ($CDCl_3$) δ(ppm): 2.36 (s,3H), 7.46 (s, 2H), 7.70-7.73 (d, 2H), 7.41 (s, 1H), 8.00 (d,1H), 8.29 (d, 1H), 9.15 (d,1H), 12.00 (s, 1H); *m/z* = 339

The benzene ring protons were observed between 7.4-7.7 ppm (H_f, H_j singlet at 7.4 ppm; H_g, H_h doublet of doublet at 7.70-7.73 ppm (J_{ortho} = 5.1 Hz for H_{ab} and J_{meta} = 1.5 Hz for H_{ac}) and H_i singlet at 7.4 ppm, while three methyl protons appeared at 2.3 ppm as singlet (Fig. 3).

A similar product was obtained using $[Fe(L)(NO_3)_3]$. However there was a relative increase in turnover no. and % yield, (yield: 53 mg) (Table 2). A large turnover in the case of phenylbutyne may be due to the relative easy conversion of Fe(III) to Fe(II) as reflected in the anodic half wave potential for the $[Fe(L)NO_3)_3]$ complex, relative to the chloride bound complex.

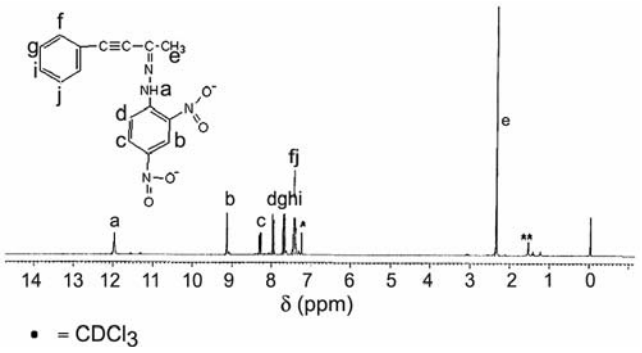
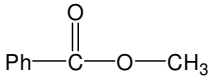
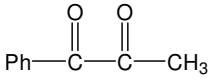
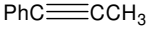
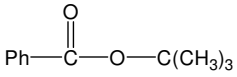
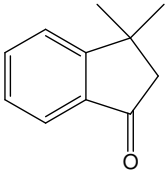
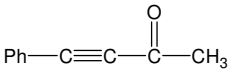
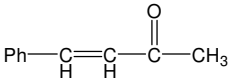
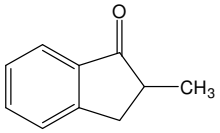
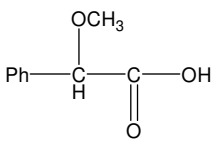


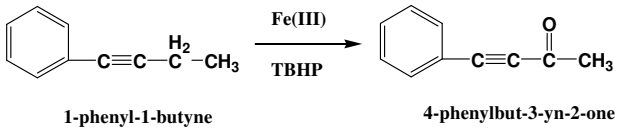
Fig. 3—^{1}H NMR spectra of the 2, 4-DNP derivative of the oxidation product of 1-phenyl-1-butyne in $CDCl_3$.

Table 2—Oxidation of various alkynes by non-heme iron catalysts and oxidant (TBHP/H_2O_2)

Substrate	Products		Yield with $[Fe(L)Cl_3]$[a] (%)		Yield with $[Fe(L)(NO_3)_3]$[a] (%)	
			TBHP	H_2O_2	TBHP	H_2O_2
		**(1)**	7	4	8	6
		**(2)**	8	7	6	4
		**(3)**	7	-	4	-
		**(4)**	15	-	16	-
Total yield of products (total turnover)			37(30)	11(9)	34(28)	10(8)
		**(5)**	15.3[b]	12	20.3[b]	18
		**(6)**	-	4	-	5
		**(7)**	-	5	-	5
Total yield of products (total turnover)			15.3[b](7)	21(10)	20.3 [b] (10)	28(13)
		**(8)**	12	-	-	-
Total yield of products (total turnover)			12(18)			

[a]Yield (%) obtained by GC-MS analysis; [b]Products were separated bycolumn chromatography.

Upon replacing the oxidant *tert*-butyl hydroperoxide (TBHP), by H_2O_2, it is found that the major product is still 4-phenylbut-3-yn-2-one with a slightly lower yield. However, as the product analysis in this case was obtained by GC-MS, two minor products were also obtained (Scheme 1, Table 2).



Scheme 1

Oxidation of 1-phenyl-1-propyne was also explored using both the oxidants. The GC-MS results show the formation of four oxidized product with a cyclised ketonic product as the major compound for the oxidant *tert*-butyl hydroperoxide, while with H_2O_2 only two oxidized products are obtained in low yield (Table 2). The oxidation of diphenylacetylene results in the formation of a single product which is an acid (Table 2). When the same reactions are performed without any complex, no oxidized product could be obtained during the same time period implying that the complex catalyses the oxidation of alkynes in the presence of TBHP and H_2O_2 (Scheme 1).

We have demonstrated here that the non-heme iron complexes are capable of catalyzing the oxidation of alkynes in the presence of oxidant (TBHP/H_2O_2). In the case of 1-phenyl-1-propyne, four products are formed as shown in Table 2; out of which three products (**1**, **3** and **4**, Table 2) are expected to be formed by carbon-carbon bond cleavage, while for 1-phenyl-1-butyne, three products are formed of which only one product (**7**, Table 2) is expected to be formed by carbon-carbon bond cleavage. In the case of diphenylacetylene, carbon-carbon bond cleavage does not appear to take place in the formation of the oxidized product. Interestingly, benzil was not detected as a component[14]. The products profiles obtained are indicative of a free radical mediated oxidation reaction. Such a radical mechanism with concomitant change in the oxidation state of the metal ion has been reported by us earlier also[25].

Earlier work has also reported the formation of α,β-acetylenic ketone by using silica supported iron^{II}-phalocyanine complex as a heterogenous catalyst[32]. The percentage conversion are higher than that found in the present study using a homogenous catalyst. However, in the earlier study a loading of catalyst to oxidant (1:200) was used, which is much higher than that used in the present work (1:20). A diketonic product along with the acetylenic ketone is formed by using iron(II) catalysts bound to tetradentate ligands in a homogenous catalytic study. The percentage yields of the earlier study when compared to the present study are lower since they have been calculated on the basis of oxidant rather than on the amount of substrate[14].

Conclusions

In summary, this study has demonstrated that a methanolic solution of Fe(III) complex acts as an efficient catalyst for the oxidation of substituted alkynes in presence of an oxidant as an external source of oxygen. This investigation reveals that for 1-phenyl-1-butyne the oxidation reaction does not affect the C-C triple bond and oxidation of the adjacent methyl group gives the ketonic product, while in the other substituted alkynes, the C-C triple bond is affected to a large extent.

Acknowledgement

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