

## Transition Metal Ion Catalysed Autoxidation of Dimethylformamide

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Dimethylformamide is autoxidized in the presence of certain transition metal complexes giving carbon dioxide and dimethylamine.

Dimethylformamide (DMF), which is used as a solvent for diverse reactions, including transition metal ion catalysed autoxidation of phenols,<sup>1a</sup> is seen to be autoxidized at room temperature in the presence of catalytic quantities of several bipyridine and 1,10-phenanthroline complexes of transition metal ions. This appears to be the first example of metal ion catalysed autoxidation of an amide.

No autoxidation of dimethylacetamide was observed under these conditions, although autoxidation of several amides, caused by ultraviolet radiation, photosensitizers, or heat has been documented.<sup>2</sup> These reactions occurred *via* homolysis of an alkyl C-H bond, adjacent to the amide nitrogen, followed by oxidation of the generated radical by O<sub>2</sub>. Products, such as acylamides, were produced from the oxidation of the alkyl

**Table 1.** Products of the autoxidation of DMF<sup>†</sup> catalysed by metal ions.

Catalyst <sup>a</sup>	Absorption of O <sub>2</sub> <sup>c</sup> O <sub>2</sub> /M <sup>n+</sup> (mol/mol)	Evolution of CO <sub>2</sub> CO <sub>2</sub> /M <sup>n+</sup> (mol/mol)	Evolution of NHMe <sub>2</sub> NHMe <sub>2</sub> /M <sup>n+</sup> (mol/mol)
[Fe(bipy) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>	16(M), 19(P)	7	2.0
[Fe(bipy) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O <sup>c</sup>	9(M), 12(P)	9	2.0
[Fe <sub>2</sub> O(bipy) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]- (ClO <sub>4</sub> ) <sub>4</sub> ·0.5 bipy <sup>b</sup>	12(P)	8	2.5
[Co(bipy) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>	<sup>f</sup>	13	4.0 ± 0.2
[Co(bipy) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O <sup>d</sup>	7 ± 0.5(P)	18 ± 2	7
[Cu(bipy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O <sup>d</sup>	40 ± 10(P)	30 ± 3	12.0 ± 2

<sup>a</sup> bipy = bipyridine. <sup>b</sup> Time lag between absorption of O<sub>2</sub> and evolution of CO<sub>2</sub> 5–10 min; <sup>c</sup> ca. 1 h; <sup>d</sup> ca. 2½ h. <sup>e</sup> P polarography, M manometry. <sup>f</sup> Showed instantaneous absorption of the dissolved O<sub>2</sub> in contrast to the slower rate of uptake observed in the presence of the other catalysts. Further absorption on resaturation with air took place slowly as with the others.

centre. The metal ion catalysed autoxidation of DMF,† on the other hand, led to evolution of CO<sub>2</sub> and NHMe<sub>2</sub> as gaseous products, indicating that the alkyl group remains unaffected. The data are summarized in Table 1.

Polarographic estimates of O<sub>2</sub> were obtained by measuring the decay of the O<sub>2</sub> reduction current at a fixed potential of -0.85 V (vs. saturated calomel electrode) as a function of time in air saturated solutions of the catalysts (ca. 10<sup>-4</sup> M). As the current decayed to a minimum owing to gradual absorption of the dissolved O<sub>2</sub> from the solvent, it was resaturated with air and the decay of the current monitored again. The step was repeated several times until no further decay of the O<sub>2</sub> current occurred on resaturation. The amount of O<sub>2</sub> absorbed was calculated from the total loss of O<sub>2</sub> current in the preceding steps. The O<sub>2</sub> uptake was also measured by the Warburg (manometric) technique for the Fe–bipy complexes (ca. 2 × 10<sup>-4</sup> M), using air as the equilibrating gas. The O<sub>2</sub> uptake lasted for 3–6 h, depending upon the catalyst and its concentration. Evolution of CO<sub>2</sub> and NHMe<sub>2</sub> was measured by bubbling O<sub>2</sub> through the solution of the catalysts in DMF for ca. 36 h and trapping the exit gas in dilute HCl and saturated Ba(OH)<sub>2</sub> successively. Evolution of CO<sub>2</sub> and NHMe<sub>2</sub> lagged behind the uptake of O<sub>2</sub> by several minutes to several hours (Table 1), depending upon the catalyst, and continued after cessation of the O<sub>2</sub> uptake.

No catalytic effect was observed for the bipyridine complexes of Mn<sup>II</sup>, Ni<sup>II</sup>, or Zn<sup>II</sup>, or free bipyridine. Similarly, a solution of Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O in DMF showed no O<sub>2</sub> uptake until bipyridine was added to the solution. The reaction is inhibited by 2,6-di-*t*-butyl-4-methylphenol, a peroxy radical

inhibitor,<sup>1b</sup> indicating a radical mechanism. The reaction is also subject to a marked concentration inhibition by the Cu<sup>II</sup> complex. Thus while a normal pattern of O<sub>2</sub> uptake was observed in the presence of 1.2 × 10<sup>-4</sup> M Cu(bipy)<sub>2</sub><sup>2+</sup>, virtually no absorption took place when the concentration was increased to 6 × 10<sup>-4</sup> M. This effect is probably caused by the ready oxidation of the chain propagating radical by Cu<sup>II</sup>.<sup>1c</sup>

Uptake of O<sub>2</sub> could also be initiated by addition of *t*-butyl hydroperoxide in the absence of a metal ion catalyst. However no evolution of CO<sub>2</sub> or dimethylamine was observed.

It is not possible to offer a mechanism on the basis of the available data. However, the observations seem to indicate that the O<sub>2</sub> uptake is initiated by homolysis of the carbonyl C–H bond of DMF through a redox reaction with the metal centre, and that further involvement of the metal ion is necessary for the production of CO<sub>2</sub> and dimethylamine following the uptake of O<sub>2</sub>. In this respect there appears to be some similarity with the metal ion catalysed autoxidation of aldehydes,<sup>1d</sup> although the simple model fails to explain all the observations adequately. An alternative mechanism involving formation of a metal–dioxygen complex also appears to be unlikely particularly for the Fe<sup>III</sup>, Co<sup>III</sup>, and Cu<sup>II</sup> systems in view of the lack of any substantiative data on such complexes with these ions. A preliminary examination of the e.s.r. spectrum of Fe(bipy)<sub>3</sub><sup>3+</sup> in DMF showed no change in the multiplet on saturation with O<sub>2</sub>.

Received, 20th July 1983; Com. 976

## References

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† Reagent grade DMF (J. T. Baker) was distilled and stored over molecular sieves before use.