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Communications

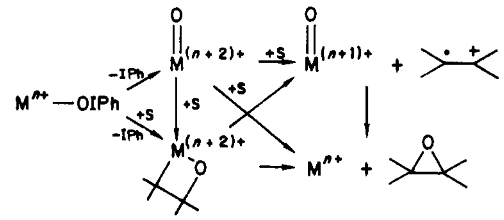
Oxygenation of Organic Substrates by Iodosylbenzene Catalyzed by Soluble Manganese, Iron, Cobalt, or Copper Salts in Acetonitrile

Sir:

The development of new oxygen atom-transfer reagents and elucidation of the mechanisms of their reactions with organic substrates have been the goals of a number of laboratories for some time.[1] Dramatic progress in reaching these goals has been achieved in recent years with iodosylbenzene, peroxyacids, amine oxides, or hypochlorite anion as oxygen atom sources and porphyrin complexes of iron, chromium, and manganese as catalysts.[1,2]

We recently reported that simple copper salts could also mediate the transfer of oxygen atoms from iodosylbenzene to olefins.[3] This discovery prompted us to investigate whether other non-porphyrin metal ions and complexes might show the same type of chemistry with iodosylbenzene. We report here that soluble metal ion salts of manganese, iron, and cobalt, in addition to copper, will catalyze epoxidation and hydroxylation of organic substrates by iodosylbenzene in acetonitrile and, moreover, that the catalytic properties of the iron and manganese salts with regard to stilbene epoxidation are remarkably similar to those of the iron and manganese porphyrins.

Scheme I



S = olefin

The reactions were carried out by addition of iodosylbenzene to a solution of the metal salt[4,6] plus organic substrate in acetonitrile[7] under an argon atmosphere.[8] The reactants, products, and conditions are given in Tables I and II. A number of conclusions can be drawn from these results. The most obvious point is that the metal ion catalysis of the reaction of iodosylbenzene with olefins or cumene does not require porphyrins or other similar ligands. It therefore appears likely that this reactivity will be found to occur for a wide variety of transition-metal ions and complexes. In addition to the metal salts listed in Table I, we have also attempted the reaction with (*E*)-stilbene using $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, or $AgNO_3$. None of these salts gave any reaction. We conclude that the Lewis acidity of the metal ions is not the only property required for this reaction to proceed. We suspect that the redox properties of the metal ions also play a significant role. It is important to note that we do not know the exact nature of the catalytic species in these reactions. The catalysts may well be high oxidation state species produced by iodosylbenzene oxidation of the metal ions initially added to the reaction, e.g. Mn(III) or higher rather than Mn(II).

One unexpected observation described in Table I is that certain of these metal salts in the presence of iodosylbenzene catalyze the isomerization of (*Z*)- to (*E*)-stilbene. Cobalt nitrate is a particularly good example of this (see Table I). We believe that a likely mechanism for this isomerization involves oxidation of (*Z*)-stilbene to its radical cation.[9] At this point we know relatively little about the mechanism of the epoxidation reaction and especially if it is related to the formation of the olefin radical cation.[10] In two cases, however, i.e. the epoxidation of (*Z*)-stilbene catalyzed by ferric and ferrous triflate, we can rule out the participation of an intermediate that can rotate freely about the carbon–carbon bond since those reactions give predominantly (*Z*)-stilbene

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(1) Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981.

(2) (a) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786–5891 and references therein. (b) Chang, C. K.; Kuo, M.-S. *Ibid.* **1979**, *101*, 3413–3415. (c) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *Ibid.* **1981**, *103*, 2884–2886. (d) Nee, M. W.; Bruice, T. C. *Ibid.* **1982**, *104*, 6123–6125. (e) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *Ibid.* **1983**, *105*, 3510–3515 and references therein. (f) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *Ibid.* **1980**, *102*, 6375–6377. (g) Groves, J. T.; Kruper, W. J., Jr. *Ibid.* **1979**, *101*, 7613–7615. (h) Guilmet, E.; Meunier, B. *Tetrahedron Lett.* **1980**, *21*, 4449–4450.

(3) Franklin, C. C.; VanAtta, R. B.; Tai, A. F.; Valentine, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 814–816.

(4) The metal salts we chose for this study were either nitrate salts or, for reasons of solubility, anhydrous trifluoromethanesulfonate (triflate), $CF_3SO_3^-$ (OTf^-), salts. Halides, X^-, and anions containing halides such as BF_4^- were avoided because of their possible reaction with OIPh to form X_2IPh.[3] Perchlorates were also avoided, both for reasons of safety and due to the possibility that ClO_4^- itself might act as an oxygen atom donor.[5]

(5) Taube, H. In "Mechanistic Aspects of Inorganic Reactions"; Rorabacher, D. B., Endicott, J. F., Eds.; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 198, pp 151–179.

(6) Metal trifluoromethanesulfonate (triflate) salts were prepared by minor modifications of procedures found in: Hayes, J. S.; Sams, J. R.; Thompson, R. C. *Can. J. Chem.* **1981**, *59*, 669–678. Fujinaga, T.; Sakamoto, I. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *73*, 235–246.

(7) Acetonitrile was deaerated and then dried by passage through a column of Woelm Super I Grade alumina.

(8) See footnotes to Tables I and II for reaction conditions.

(9) (a) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155–278. (b) Tang, R.; Kochi, J. K. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3845–3856.

(10) We have confirmed that the epoxide oxygen is derived from iodosylbenzene using $^{18}OIPh$.

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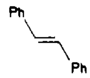
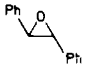
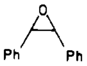
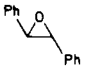
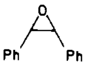
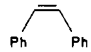
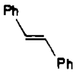
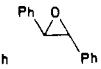
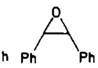
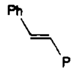
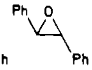
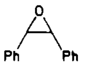
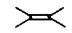
Table I. Metal Ion Catalyzed Reactions of Iodosylbenzene and Organic Substrates[a]

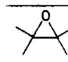
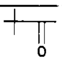
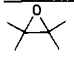
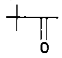
Substrate = (*E*)-Stilbene 

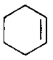
metal salt	products (yields,[b] %)			% substrate consumed	reaction time, min	metal salt	products (yields, %)			% substrate consumed	reaction time, min
			Ph-CHO						Ph-CHO		
$Cu(NO_3)_2\cdot 2.5H_2O$	76	0	10	68	120	$Co(OTf)_2$	26	0	11	69	30
$Cu(OTf)_2$[c]	52	0	26	8	60	$Mn(OTf)_2$	16	0	10	33	1-2
$Co(NO_3)_2\cdot 6H_2O$	76	0	14	68	30	$Fe(OTf)_2$[d]	86	0	0	64	20
						$Fe(OTf)_3$[d]	77	0	<2	62	15

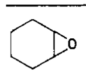
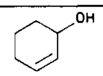
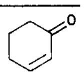
Substrate = (*Z*)-Stilbene 

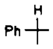
metal salt	products (yields, %)				% substrate consumed	reaction time, min	metal salt	products (yields, %)				% substrate consumed	reaction time, min
				Ph-CHO							Ph-CHO		
$Cu(NO_3)_2\cdot 2.5H_2O$	44	28	0	28	27	120	$Co(OTf)_2$	11	41	8	27	33	30
$Cu(OTf)_2$	24	50	3	24	17	60	$Mn(OTf)_2$[e]	23	20	14	10	20	2
$Co(NO_3)_2\cdot 6H_2O$	82	9	trace	trace	93	30	$Fe(OTf)_3$[d]	0	3	31	trace	61	30

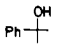
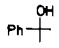
Substrate = 2,3-Dimethyl-2-butene 

metal salt	products (yields, %)		% substrate consumed	reaction time, min	metal salt	products (yields, %)		% substrate consumed	reaction time, min
									
$Cu(NO_3)_2\cdot 2.5H_2O$	28	*f*	92	120	$Co(OTf)_2$	37	6	36	1
$Cu(OTf)_2$	31	4	42	15	$Fe(OTf)_3$	26	8	90	1
$Co(NO_3)_2\cdot 6H_2O$	36	*f*	12	30					

Substrate = Cyclohexene 

metal salt	products (yields, %)			% substrate consumed	reaction time, min
					
$Cu(NO_3)_2\cdot 2.5H_2O$	28	1.8	2.6	26	120

Substrate = Cumene 

metal salt		% substrate consumed	reaction time, min	metal salt		% substrate consumed	reaction time, min
$Cu(OTf)_2$	2	16	60	$Mn(OTf)_2$	23	6	5
$Co(OTf)_2$	34	1	30	$Fe(OTf)_3$	9	5	1

[a] In a typical reaction, 0.1 mmol of the metal salt was weighed into a Schlenk tube. Acetonitrile, 5 mL, was added by syringe. Substrate, 0.5 mmol, was added and the solution stirred for 5-30 min. A sample was removed for analysis after which time 0.4-0.8 mmol of OIPh was added all at once. Aliquots were taken for analysis at timed intervals. All operations were carried out at room temperature under an inert atmosphere. Aliquots removed were passed through a 0.45-μm filter; 100 μL of the sample was then diluted with 2 mL of methanol and analyzed by HPLC, or the undiluted sample was passed through a 1-cm alumina column to remove any metals and analyzed by GLC. Reaction times for each system were chosen to give the highest yield of epoxide based on the amount of substrate consumed. [b] Yields are based on substrate consumed. [c] OTf^- is $CF_3SO_3^-$, trifluoromethanesulfonate or "triflate". [d] These reactions were run with lower concentrations of metal ion salts (0.01 mmol), and the iodosylbenzene was added in small portions over the reaction time. [e] Deoxybenzoin (5%) was also detected. [f] Not determined.

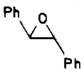
oxide. Some possible pathways for formation both of the epoxide and also the radical cation are described in Scheme I.

The nature of the anion also influences this reaction, as can be seen from the differences in reactivity between the nitrate and triflate salts. In general, the triflate salts show a higher degree of reactivity than the nitrate salts. However, we do find that the product epoxides themselves react slowly under the reaction conditions and long reaction times significantly decrease the apparent yields of such products.

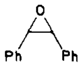
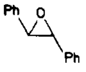
The data presented in Table II demonstrate that the reactivities of the iron and manganese salts are comparable to those of the iron and manganese porphyrins. Thus far we have no evidence suggesting that the mechanisms are similar for the metalloporphyrins and metal triflate salts. It is interesting to note, however, that the manganese porphyrin and manganese triflate are similar in that they both react with (*Z*)-stilbene to give substantial amounts of (*E*)-stilbene oxide in addition to the *Z* oxide. The iron porphyrin and iron triflate are also similar in that the porphyrin yields only *Z* oxide and the triflate gives primarily *Z* oxide. One pronounced difference in the relative reactivities of the porphyrins and triflates is the higher rates of reaction of the porphyrin complexes with (*Z*)- as compared to (*E*)-stilbene. This behavior has been attributed

Table II. Relative Reactivities of Metal Triflate Salts and Metalloporphyrins in Reactions of (*Z*)- and (*E*)-Stilbene[a]

(*E*)-Stilbene

catalyst	products, mmol × 10^2 	products, mmol × 10^2 PhCHO
$Fe(OTf)_3$	19.5	trace
Fe(TPP)Cl[b]	9.5	0
$Mn(OTf)_2$	3.8	5.1
Mn(TPP)Cl	trace	0

(*Z*)-Stilbene

catalyst	products, mmol × 10^2 		PhCHO
$Fe(OTf)_3$	11.7	1.3	trace
Fe(TPP)Cl	17.0	0	0
$Mn(OTf)_2$	1.3	1.8	3.6
Mn(TPP)Cl[c]	13.5	7.1	0

[a] These reactions were carried out under conditions such that we could obtain a qualitative comparison of the relative reactivities of the metal triflates and the comparable metalloporphyrins. The reaction conditions are therefore not optimized for any particular system. For these studies, 10^{-2} mmol of the metal salt or metalloporphyrin and 0.5 mmol of (*Z*)- or (*E*)-stilbene was dissolved in 5 mL of acetonitrile (metal triflate) or dichloromethane (metalloporphyrin). Iodosylbenzene, 0.35 mmol, was added slowly over a period of 20 min. The solution was stirred for an additional 10 min. At this point, a 100-μL aliquot was removed, diluted with 2 mL of methanol, and analyzed by HPLC. The metal triflate reactions were carried out in acetonitrile while the metalloporphyrin reactions were carried out in dichloromethane for reasons of solubility. [b] TPP is tetraphenylporphinato. [c] Deoxybenzoin (3.0×10^{-2} mmol) was also detected.

to unfavorable steric interactions between the *E* olefin and the porphyrin.[2] A number of other epoxidation reagents have also been observed to react faster with *Z* olefins.[11] Our preliminary evidence indicates that (*E*)-stilbene is reacting faster than (*Z*)-stilbene in the case of the metal ions. Further mechanistic studies are required in order to explain the preference for (*E*)-stilbene in the metal salt-catalyzed reactions. Nevertheless, we can conclude at this point that the rate of oxygen atom transfer in the metal ion catalyzed reactions is considerably less sensitive to the disposition of the phenyl rings in (*Z*)- and (*E*)-stilbene than are the rates of the iron and manganese porphyrin-catalyzed reactions.

In our future studies we hope to elucidate the mechanisms of these reactions and to extend our studies to other metal ions and complexes and to other oxygen atom donors.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

Registry No. $Cu(NO_3)_2$, 3251-23-8; $Cu(OTf)_2$, 34946-82-2; $Co(NO_3)_2$, 10141-05-6; $Co(OTf)_2$, 58164-61-7; $Mn(OTf)_2$, 55120-76-8; $Fe(OTf)_2$, 59163-91-6; $Fe(OTf)_3$, 63295-48-7; iodosylbenzene, 536-80-1; (*E*)-stilbene, 103-30-0; (*Z*)-stilbene, 645-49-8; 2,3-dimethyl-2-butene, 563-79-1; cyclohexene, 110-83-8; cumene, 98-82-8.

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(11) Miyaura, N.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 2368-2378 and references therein.

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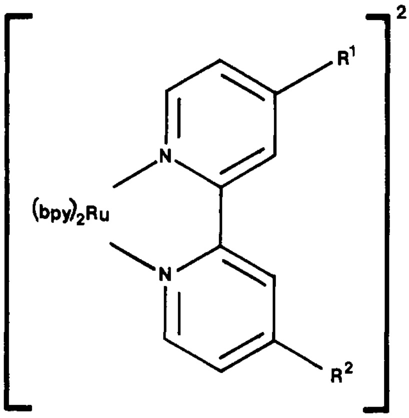
Catherine C. Franklin
Joan Selverstone Valentine*

Received June 7, 1984

Proton Transfer in the Excited State of Carboxylic Acid Derivatives of Tris(2,2'-bipyridine-*N*,*N*')ruthenium(II)

Sir:

Interest in the bis(2,2'-bipyridine-*N*,*N*')(2,2'-bipyridine-4,4'-dicarboxylic acid-*N*,*N*')ruthenium(II) ion (I) initially arose because it was the first transition-metal complex in which proton transfer was observed in its excited state.[1] We have found that I has two pK_a values (pK_{a1}* = 3.6, pK_{a2}* = 4.5) separated by ~1 pK_a unit. A similar separation has been found for the ground-state pK_a values,[2] where the protons are much more acidic.



Ia: $R^1 = R^2 = CO_2H$
b: $R^1 = CO_2H$, $R^2 = CO_2^-$
c: $R^1 = R^2 = CO_2^-$
IIa: $R^1 = CO_2H$, $R^2 = CH_3$
b: $R^1 = CO_2^-$, $R^2 = CH_3$

The differences in acidities of ground and excited states result in the transfer of none, one, or two protons to the excited state (by control of pH). The results reported here differ greatly from photophysical properties reported previously[1,3] where only one ground-state and one excited-state pK_a value were observed.[1]

Our interest in the dicarboxylic acid complex I arose from the possibility of using the excited state of the neutral, doubly deprotonated species Ic as a sensitizer in the cobalt cage complex mediated photoreduction of water[4-10] (in the hope of reducing the electrostatic work terms involved in excited-state quenching). However, preliminary work on this sensitizer revealed quite different properties[2] to those reported previously.[1] The reported syntheses of the diacid complex[3,11-15] lead

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(1) Giordano, P. J.; Bock, C. R.; Wrighton, M. S.; Interrante, L. V.; Williams, R. F. X. *J. Am. Chem. Soc.* **1977**, *99*, 3187-3189.
(2) Ferguson, J.; Mau, A. W. H.; Sasse, W. H. F. *Chem. Phys. Lett.* **1979**, *68*, 21-24.
(3) Cherry, W. R.; Henderson, L. J., Jr. *Inorg. Chem.* **1984**, *23*, 983-986.
(4) Launikonis, A.; Lay, P. A.; Mau, A. W.-H.; Sasse, W. H. F.; Sargeson, A. M., to be submitted for publication in *Aust. J. Chem.*
(5) Lay, P. A.; Mau, A. W. H.; Sasse, W. H. F.; Creaser, I. I.; Gahan, L. R.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2347-2349.
(6) Creaser, I. I.; Gahan, L. R.; Geue, R. J.; Launikonis, A.; Lay, P. A.; Lydon, J. D.; McCarthy, M. G.; Mau, A. W.-H.; Sargeson, A. M.; Sasse, W. H. F., submitted for publication in *J. Am. Chem. Soc.*
(7) Launikonis, A.; Lay, P. A.; Sargeson, A. M.; Sasse, W. H. F., to be submitted for publication in *Inorg. Chem.*
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