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## Epoxidation of Olefins by Iodosylbenzene Catalyzed by Non-Porphyrin Metal Complexes

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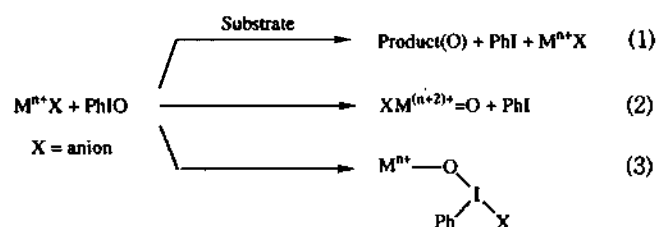
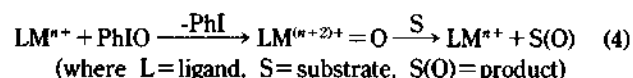
Epoxidation of olefins has been studied using iodosylbenzene (PhIO) as the terminal oxidant and binuclear and mononuclear complexes of Mn<sup>2+</sup>, Co<sup>2+</sup>, and Cu<sup>2+</sup> as catalysts. Epoxides were the predominant products with trace amounts of allylic oxidation products, and the metal complexes were found to be effective catalysts in the epoxidation reactions. The reactivity of binuclear copper complexes was greater than that of the mononuclear copper complexes, whereas the binuclear and mononuclear complexes of Mn<sup>2+</sup> and Co<sup>2+</sup> showed similar reactivities. The nature of the ligands bound to copper did not influence the reactivity of the binuclear copper complexes so long as copper ions were held in close proximity. A metal-iodosylbenzene complex, such as suggested previously for Lewis acidic metal complex-catalyzed epoxidation by iodosylbenzene, is proposed as the active epoxidizing species. Some mechanistic aspects are discussed as well.

### Introduction

Iodosylbenzene, PhIO, has been widely used as a source of oxygen atom in functionalization of hydrocarbons catalyzed by metal complexes, usually with the intention of understanding the mechanism of oxygen atom transfer reactions.<sup>1</sup> The general reactions by iodosylbenzene in the presence of metal complexes are shown in Scheme 1. Iodosylbenzene can transfer its oxygen to organic substrates in metal-catalyzed reactions (Eq. 1)<sup>2</sup> or to metal complexes to generate high-valent metal oxo species (Eq. 2).<sup>3</sup> Iodosylbenzene also reacts with

metal complexes to form metal-iodosylbenzene adducts (Eq. 3).<sup>4</sup>


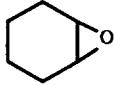

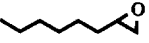





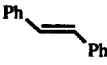
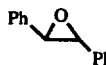
Since Groves and coworkers showed that high-valent iron oxo porphyrin cation radical, (TMP)<sup>+</sup>Fe<sup>IV</sup>=O, was generated in the reaction of Fe(TMP)Cl and iodosylbenzene,<sup>5</sup> it has generally been asserted that oxygen transfer from iodosylbenzene to organic substrates occurs *via* high-valent metal oxo intermediates in metal-catalyzed oxygen atom transfer reactions (Eq. 4).



Scheme 1.

In addition to the metalloporphyrin systems, it has been shown that simple metal salts are capable of transferring an oxygen atom from iodosylbenzene to organic substrates in catalytic epoxidation reactions.<sup>6</sup> Metal complexes containing non-porphyrin ligands have also been used in iodosylbenzene reactions in order to prove the intermediacy of high-valent metal oxo species and/or to make efficient catalysts.<sup>7</sup> The intermediacy of high-valent metal oxo complexes as rea-

**Table 1.** Epoxidation of Olefins by Iodosylbenzene Catalyzed by Binuclear and Mononuclear Copper(II) Complexes<sup>a</sup>

Substrate	Product	Yield, mM	
		1	2
		12.3	6.7
		4.1	0.5
		8.0	3.7
		0.3	0.2
		5.4	2.9
	PhCHO	3.5	1.7
		20	3.9
	PhCHO	7.0	1.1

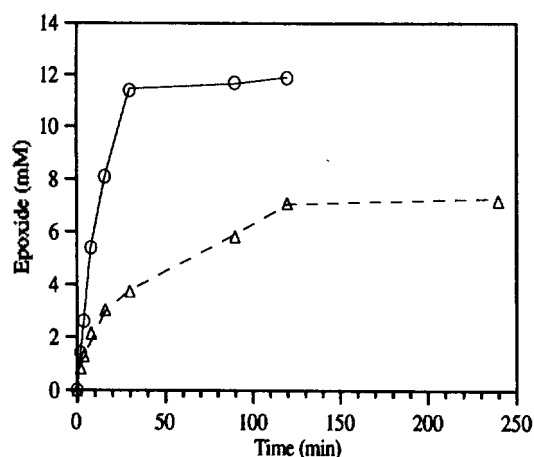
<sup>a</sup>See experimental section for detailed experimental procedures.

ctive intermediates has been assumed or asserted on the basis of studies of metalloporphyrin-catalyzed oxygenation reactions and on the basis of indirect evidence, such as, for example, the observation of <sup>18</sup>O incorporation into the oxygenated product when H<sub>2</sub><sup>18</sup>O is added to the reaction mixture of substrate, PhI<sup>16</sup>O, and catalyst,<sup>8</sup> since it has been shown in some instances that high-valent metal oxo complexes can exchange with water.<sup>3(a),9</sup> The latter has recently been proved to be insufficient proof of the presence of high-valent metal oxo complexes as intermediates in oxygenation reactions.<sup>8(a)</sup>

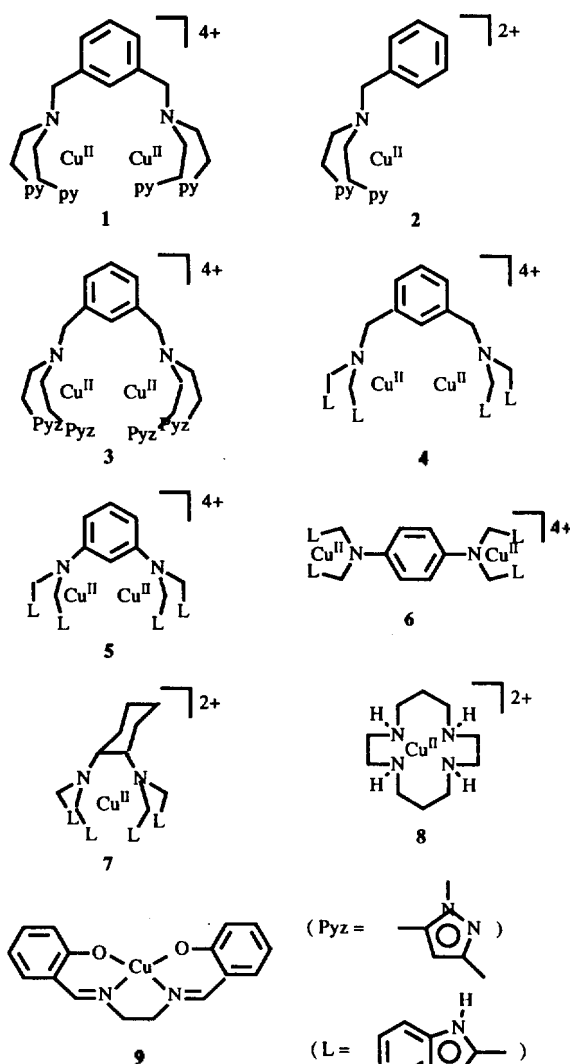
In this paper, we compare the reactivities of various binuclear and mononuclear copper, manganese, and cobalt complexes in the epoxidation of olefins by iodosylbenzene. We carried out the reactions by varying the structures of copper complex as well as by changing the metal from copper to cobalt to manganese in order to study the effect of ligands and metal ions. It became clear from these and other studies<sup>10</sup> that iodosylbenzene was not acting simply as an oxygen atom donor to a metal complex to generate a high valent metal oxo species. It is our conclusion that a metal-iodosylbenzene complex is a plausible intermediate for olefin epoxidations.

## Results

**Epoxidation of Olefins by Iodosylbenzene Catalyzed by Copper(II) Complexes.** Epoxidation of olefins was carried out in CH<sub>3</sub>CN solution at room temperature. In order to have the same amounts of copper ions in the reaction mixture, 2 mM for binuclear copper complexes and 4 mM for mononuclear copper complexes were used. The results of olefin epoxidations were listed in Table 1. In all






**Figure 1.** Time course for cyclohexene epoxidation by iodosylbenzene catalyzed by copper complexes (solid line for binuclear copper complex 1 and dotted line for mononuclear copper complex 2).



**Figure 2.** Structures of various copper(II) complexes.

**Table 2.** Cyclohexene Epoxidation by PhIO Catalyzed Various Copper Complexes<sup>a</sup>

Catalyst	Products (mM)			PhI	Epoxide yield (%) <sup>b</sup>	turn-over <sup>c</sup>
						
1	12	0.6	1.9	73	17	6
2	6.7	0.2	0.4	57	12	1.7
3	13	0	0.5	74	17	6.5
4 <sup>d</sup>	16	0.4	0.8	70	23	8
5 <sup>d</sup>	14	1.3	0.4	73	19	7
6 <sup>d</sup>	8.1	0.84	0.3	60	14	4.1
7 <sup>d</sup>	0.3	0	0	5	6	0.2
8	0	0	0	3	0	0
9	0	0	0	3	0	0

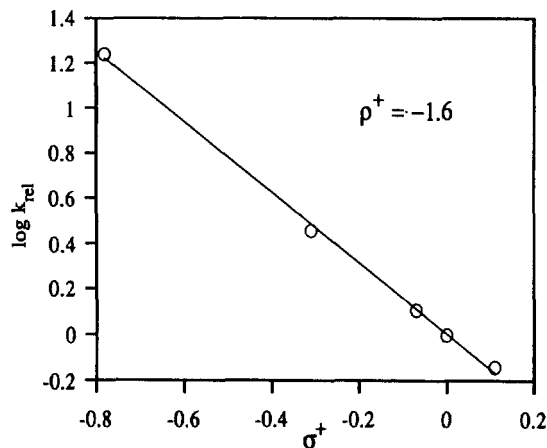
<sup>a</sup>Iodosylbenzene (0.4 mmol, 80 mM) was added to a reaction solution containing copper(II) complex (2 mM for binuclear copper complexes and 4 mM for mononuclear copper complexes) and cyclohexene (200 mM) in CH<sub>3</sub>CN (5 mL). <sup>b</sup>Percent yield epoxide based on PhI formed. <sup>c</sup>(Millimoles of epoxide)/(millimoles of metal complex). <sup>d</sup>Cupric triflate and corresponding ligands were stirred for 1 hr before the reaction was started.

**Table 3.** Relative Reactivities of *para*-Substituted Styrenes to Styrene in Epoxidation Catalyzed by Binuclear Copper Complex 1

Styrenes	$\sigma^+$	$\log(k_{\text{sub-styr}}/k_{\text{styr}})$
4-CH <sub>3</sub> O-styrene	-0.78	1.24
4-CH <sub>3</sub> -styrene	-0.31	0.46
4-F-styrene	-0.07	0.11
4-Cl-styrene	0.11	-0.14

of the reactions, epoxides were the predominant products with small amounts of allylic oxidation products, and *trans*-stilbene oxide was formed as a major product in the oxidation of *cis*-stilbene. The binuclear copper(II) complex 1 was considerably better catalyst than the mononuclear copper(II) complex 2 in terms of epoxide yields.<sup>11</sup> The reactivity differences between the binuclear and mononuclear copper(II) complexes were followed by the time course of the cyclohexene epoxidation. The time dependence study shown in Figure 1 demonstrates the enhanced yield of cyclohexene oxide as well as the fast formation of epoxide with the binuclear copper complex 1.

In order to evaluate the effect of ligand structure on the catalytic efficiency of copper(II) complexes, we studied various types of binuclear and mononuclear copper(II) complexes (Figure 2). The results shown in Table 2 indicate that the reactivities of the binuclear complexes 1, 3, 4, and 5 were all very similar and that higher yield of cyclohexene oxide was obtained with the binuclear copper complexes than with the mononuclear analogues 2 and 7. The binuclear copper complex 6, which has two copper ions far apart, showed a reactivity similar to that of the mononuclear copper complex

**Figure 3.** Hammett plot for relative rates of substituted styrenes in iodosylbenzene reaction catalyzed by binuclear copper complex 1.

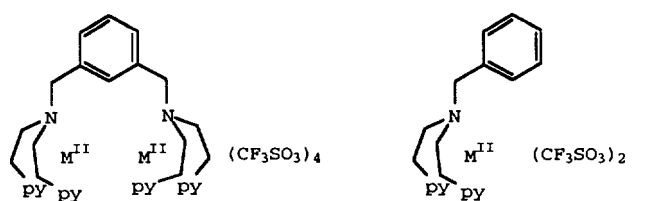
2. Other mononuclear copper complexes such as 7, 8 and 9 were inactive or nearly inactive as catalysts. These results demonstrated that copper complexes with two closely situated copper ions, a tetrahedral structure, and a vacant site for binding iodosylbenzene were good catalysts for the olefin epoxidations by iodosylbenzene.

**Relative Reactivities of *para*-Substituted Styrenes in Epoxidations Catalyzed by the Binuclear Copper Complex, 1.** Table 3 lists the results of relative reactivities of *para*-substituted styrenes to styrene.<sup>12</sup> A Hammett treatment of the relative reactivities against  $\sigma^+$  (Figure 3) gives the  $\rho^+$  value of -1.6 with a good correlation coefficients ( $\rho^2=0.998$ ). The large negative  $\rho^+$  value indicates the development of a positive charge on the  $\alpha$ -carbon atom of the styrene in transition state.<sup>12(b)</sup>

**Reaction of Iodosylbenzene with the Binuclear Copper(II) Complex, 1, in the Absence of Organic Substrate.** When the blue solution of the copper(II) complex 1 was treated with excess iodosylbenzene (10 equiv.) in CH<sub>3</sub>CN, the solution turned to dark green. Green solid was isolated and analyzed by elemental analysis, infrared spectrophotometer, and UV/vis spectrophotometer. Elemental analysis indicates that the green solid contained two equivalents of iodine per copper ion. This result was further confirmed by obtaining iodobenzene dimethoxide when the green solid was dissolved in methanol (Eq. 5).



The infrared spectrum of the green solid showed bands attributable to the C-H vibrations of the phenyl ring in iodobenzene. The UV/vis spectrum of the green solid showed a new band at 225 nm which might be from the phenyl  $\pi$ - $\pi^*$  transition. The *d-d* band shifted from 630 nm in the blue solution of the copper complex 1 to 660 nm in the green solution. There was no band attributable to phenolate to metal charge transfer, indicating that the hydroxylation of the ligand did not occur with iodosylbenzene.<sup>13</sup> After copper was demetallated from the green solid, a mass spectrum with a peak at  $m/z=557$  for the protonated starting ligand  $\text{MH}^+$  was obtained. This result further indicates that the ligand was not oxygenated. All of these results suggest that



10 for Co and 12 for Mn      11 for Co and 13 for Mn

Figure 4. Structures of cobalt and manganese complexes.

Table 4. Catalytic Epoxidations by Binuclear and Mononuclear Complexes of Cobalt and Manganese<sup>a</sup>

Substrate	Product	Yield, mM			
		10	11	12	13
		9.2	8.9	12	9.5
		1.8	1.2		
		8.0	8.3		
		4.2	6.2	9.8	9.4
		4.4	2.2	6.0	5.5
	PhCHO	2.4	2.6	5.8	6.5
		15	18		
	PhCHO	2.9	2.8		

the green solid formed in the reaction of the copper complex 1 with excess iodosylbenzene contained iodosylbenzene bound to the copper complex and that the ligand was not oxidized.

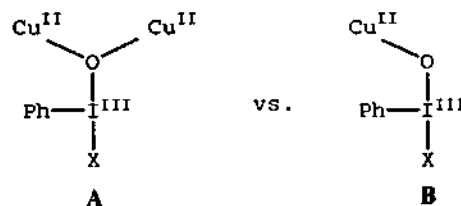
**Epoxidation of Olefins by Iodosylbenzene Catalyzed by Cobalt and Manganese Complexes.** Cobalt(II) and manganese(II) complexes containing the ligands of complexes 1 and 2 were used as catalysts in the epoxidation reactions by iodosylbenzene. The results listed in Table 4 demonstrate that the reactivities of the binuclear complexes of cobalt 10 and manganese 12 were similar to the mononuclear complexes of cobalt 11 and manganese 13 unlike in the case of copper complex-catalyzed reactions (see Figure 4 for structures). Olefins were converted to their epoxides with trace amounts of allylic oxidation products. Significant amount of *cis*-stilbene oxide was produced in the *cis*-stilbene epoxidations by the binuclear and mononuclear cobalt and manganese complexes. These results were different from the *cis*-stilbene epoxidations by copper complexes in which only a small amount of *cis*-stilbene oxide was produced.

#### Attempted Olefin Epoxidation by Iodosylbenzene

**Catalyzed by Nickel(II) Complexes.** Binuclear and mononuclear nickel complexes containing ligands of complexes 1 and 2 were tested in the epoxidation of cyclohexene by iodosylbenzene. Formation of epoxide was not observed, but only a small amount of iodobenzene was formed. Kochi and Burrows showed independently that nickel(II) cyclam complex is a competent catalyst for olefin epoxidation by iodosylbenzene.<sup>8(c),12(c),14</sup> These results suggest that, whereas nickel complexes with a square planar structure such as nickel cyclam complex are adequate catalysts for iodosylbenzene reactions, nickel complexes with tetrahedral structures are not.

## Discussion

It has been shown previously that binuclear and mononuclear copper complexes are competent catalysts and that the binuclear copper complexes are better catalysts than the mononuclear copper complexes in olefin epoxidations by iodosylbenzene.<sup>11</sup> The time dependence study shown in Figure 1 further indicates that not only the yield of epoxide is higher but also the formation of epoxide is faster with the binuclear copper complex than with the analogous mononuclear copper complex. The fast formation of epoxide is probably due to the fact that the binuclear copper complex is a better Lewis acid and dissolves the polymeric iodosylbenzene and forms metal-iodosylbenzene complexes at a faster rate. The enhanced yield of epoxide product with the binuclear copper complex may be due to an enhanced reactivity of the  $I^{III}$  center in a binuclear complex A as opposed to a mononuclear complex B toward olefinic substrates.



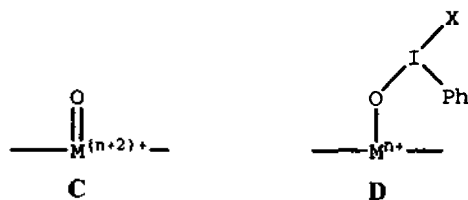
Significant anion effects in the copper and manganese complex-catalyzed epoxidation of olefins by iodosylbenzene further support this explanation for the reactivity differences between the binuclear and mononuclear copper complexes. The yield of epoxides was influenced by the types of anions in the starting metal complexes. Triflate ( $CF_3SO_3^-$ ) and perchlorate ( $ClO_4^-$ ) anions gave higher yield of epoxides than nitrate ( $NO_3^-$ ), tetrafluoroborate ( $BF_4^-$ ), and acetate ( $CH_3COO^-$ ).<sup>11(b)</sup> This result can be rationalized by the fact that these anions, *i.e.* triflate and perchlorate, dissolve polymeric iodosylbenzene fast and accelerate the formation of the metal-iodosylbenzene complex and that these anions also have a high leaving group ability because triflate and perchlorate anions are poor ligands and weak nucleophiles; therefore, metal complexes with these anions tend to form metal-iodosylbenzene complexes easily and to give high yields of epoxide products.

The reactivities of the binuclear copper complexes 1, 3, 4, and 5 shown in Figure 2 are all very similar in terms of epoxide yields, indicating that the change of ligand structure bound to copper ions does not greatly influence the reactivity of the copper complexes. This result is in sharp

contrast to the observation that the ligand oxygenation of binuclear copper complexes with dioxygen depends strongly on the nature of the ligands bound to copper ions.<sup>13</sup> Moreover, externally added substrates such as cyclohexene are not oxidized by other oxidants such as hydrogen peroxide or MCPBA (*m*-chloroperbenzoic acid). An (acylperoxo)-copper(II) complex and a (hydroperoxo)-copper(II) complex, which are generated by the reaction of a copper complex with MCPBA or H<sub>2</sub>O<sub>2</sub>, oxidize PPh<sub>3</sub> to O=PPh<sub>3</sub>, but those complexes do not react with cyclohexene to produce cyclohexene oxide.<sup>15</sup> In the iodosylbenzene reactions, the ligand oxygenation of the copper complexes does not occur, but externally added olefins are oxidized to the corresponding epoxides. These contradictory results obtained from iodosylbenzene and other oxygen atom donors such as MCPBA and H<sub>2</sub>O<sub>2</sub> suggest that oxygen atom transfer from iodosylbenzene to olefins may not proceed *via* a high-valent copper oxide intermediate.

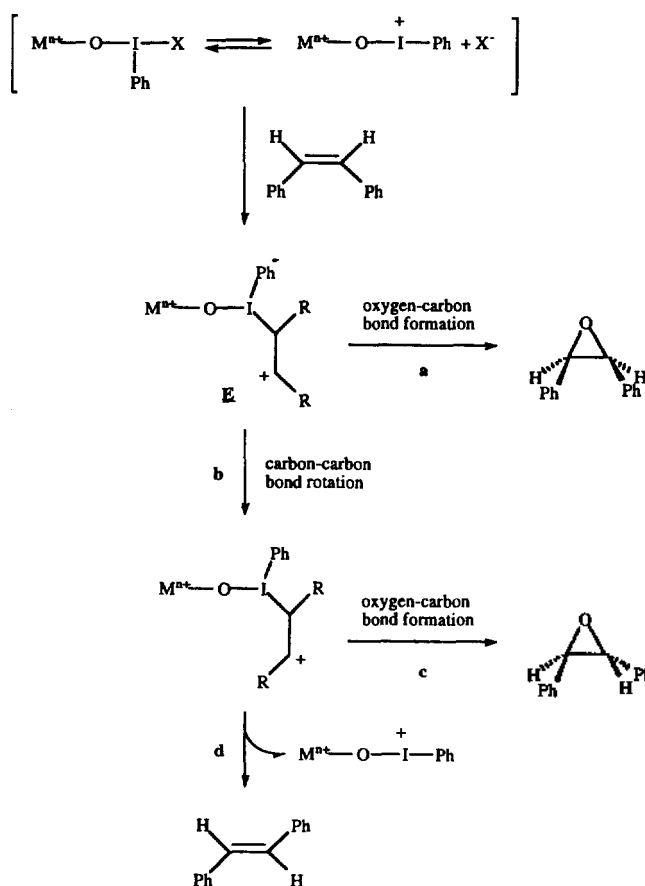
The reactivity of other binuclear metal complexes such as cobalt and manganese is found to be very similar to that of the copper complexes. In another study, we showed that binuclear zinc complex, which cannot form a high-valent zinc oxo complex, is a good catalyst for olefin epoxidations by iodosylbenzene.<sup>10(c)</sup> Since non-redox metal complexes or salts such as Zn(II) and Al(III) have been shown to be good catalysts in olefin epoxidation by iodosylbenzene,<sup>10</sup> a metal-iodosylbenzene complex has been suggested as an active intermediate and a new mechanism that involves electrophilic attack of I<sup>III</sup> on olefin double bond was proposed.<sup>10(c)</sup> Similar reactivity patterns observed in the reactions of various metal complexes such as copper, cobalt, manganese, and zinc suggest that the oxygen transfer reaction may occur *via* the same intermediate.

Two possible species such as a high-valent metal oxo complex C and a metal-iodosylbenzene complex D are postulated as oxygenating intermediates.



The high-valent metal oxo complexes C has been well accepted as a reactive intermediate in metalloporphyrin systems, whereas the metal-iodosylbenzene complex D was recently proposed as an epoxidizing intermediate in non-redox Lewis acidic metal-catalyzed epoxidation reactions.<sup>10</sup> From the results discussed above, we conclude that the metal-iodosylbenzene complex D is a plausible intermediate for olefin epoxidations in the iodosylbenzene reactions catalyzed by binuclear and mononuclear metal complexes based on the following observations: (1) that the reactivities of binuclear copper complexes do not depend greatly on the nature of ligands, (2) that binuclear metal complexes including non-redox zinc complex have similar reactivities, and (3) that the iodosylbenzene reaction catalyzed by metal complexes is significantly influenced by the nature of the anions of the metal complexes.

***cis*-Stilbene Epoxidation Reaction.** *cis*-Stilbene has been used as a mechanistic probe in metalloporphyrin-cata-



Scheme 2.

lyzed epoxidation studies, in which *cis*-stilbene oxide as well as other products such as *trans*-stilbene and *trans*-stilbene oxide was formed.<sup>16</sup> The formation of *trans*-stilbene and *trans*-stilbene oxide was explained by the C-C bond rotation after the formation of carbon radical by the reaction of a high-valent metal oxo complex and olefin double bond.

We found that a significant amount of *trans*-stilbene oxide was formed in the non-porphyrin metal complex-catalyzed epoxidation of *cis*-stilbene by iodosylbenzene. In another study, Valentine and coworkers reported the isomerization of *cis*-stilbene to *trans*-stilbene and the formation of *trans*-stilbene oxide in the iodosylbenzene reactions catalyzed by simple metal salts. The formation of *trans*-stilbene and *trans*-stilbene oxide can be explained by the mechanism that involves a metal-iodosylbenzene complex D as an epoxidizing agent. The proposed mechanism outlined in Scheme 2 provides explanations for the isomerization of *cis*-stilbene to *trans*-stilbene as well as the formation of *cis*- and *trans*-stilbene oxide products.<sup>6(e)</sup> After E is formed *via* electrophilic addition of iodine(III) to *cis*-stilbene, then we observe the formation of *cis*-stilbene oxide if the oxygen-carbon bond formation is faster than the carbon-carbon bond rotation (pathway a). If the carbon-carbon bond rotation is fast enough (pathway b), then either *trans*-stilbene oxide by the oxygen-carbon bond formation (pathway c) or *trans*-stilbene by the formation of carbon-carbon bond (pathway d) is obtained.

In summary, we have shown that olefins are epoxidized by iodosylbenzene catalyzed by the binuclear and mononuclear metal complexes of non-porphyrin ligands. A metal-iodo-

dosylbenzene complex is proposed as an active epoxidizing species in the iodosylbenzene reaction, as suggested in the non-redox metal-catalyzed epoxidation by iodosylbenzene that the epoxidation reaction by the metal-iodosylbenzene complex is occurring *via* an electrophilic attack of iodine(III) on double bond of olefins.<sup>6(c)-(e)</sup>

## Experimental Section

**Materials.** Acetonitrile was refluxed over CaH<sub>2</sub> and distilled under argon, and further dried by passing through a column of Woelm activity grade Super I alumina in a dry box. Acetonitrile for HPLC was purchased from Fisher Scientific Co. (HPLC grade) and filtered before use. HPLC water was triply deionized. The following chemicals were purchased from Aldrich Chemical Co. and used without further purification unless otherwise indicated: cyclohexene, cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, 1-octene, 1,2-epoxyoctane, styrene, styrene oxide, 4-CH<sub>3</sub>O-styrene, 4-CH<sub>3</sub>-styrene, 4-F-styrene, 4-Cl-styrene, *cis*-stilbene, *cis*-stilbene oxide, *trans*-stilbene, *trans*-stilbene oxide, benzaldehyde, decane, nonane, iodobenzene diacetate, Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, cyclam (1,4,8,11-tetraazacyclotetradecane), and *N,N'*-bis-(salicylidene)-ethylenediamine. Co(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and Mn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> were prepared by refluxing metal carbonate salts and vacuum distilled trifluoromethanesulfonic acid.<sup>17</sup> *cis*-Stilbene was distilled or passed through a short alumina column and *trans*-stilbene was sublimed before use. Iodosylbenzene was prepared from iodobenzene diacetate by a literature method.<sup>18</sup> Ligands for the complexes 1 and 2 were prepared by a literature method.<sup>13(a)</sup> Ligands<sup>19</sup> for the complexes 3, 4, 5 and 7 were the gift from Professor Christopher A. Reed.

The metal complexes 1, 2, 8, 10, 11, 12, and 13 were prepared by reacting metal salts with ligands in acetonitrile. The solvent was evaporated and the product solid was washed with either Et<sub>2</sub>O or petroleum ether several times followed by drying *in vacuo*. The copper(II)-Schiff base complex 9 was prepared by reacting Cu(OAc)<sub>2</sub> and Salen ligand in ethanolic solution.<sup>20</sup>

**Instrumentation.** Infrared spectra were recorded on a Beckman 4260 infrared spectrophotometer, UV/vis on a Beckman UV 5270 spectrophotometer. Product analyses were performed on either a Hewlett Packard 5890A Gas Chromatograph coupled with a Hewlett Packard Model 5970B Mass Selective detector or Beckman 344 High Performance Liquid Chromatography equipped with a variable wavelength detector and with a Hewlett Packard 3390A integrator. Elemental analyses were performed by Galbraith Laboratories, Inc.

**General Epoxidation Reactions.** All reactions were carried out in a Vacuum Atmospheres glove box. In a typical experiment, iodosylbenzene (0.4 mmol) was added to a reaction solution containing metal catalyst (0.01 mmol for binuclear metal complexes and 0.02 mmol for mononuclear metal complexes), olefin (1 mmol), and an appropriate amount of an internal standard in CH<sub>3</sub>CN (5 mL). Aliquots (100  $\mu$ L) were periodically removed and diluted with 1 mL of CH<sub>3</sub>CN. The resulting solution was filtered through a 0.45  $\mu$ m filter and analyzed by either GC/MS or HPLC.

For the time course study, aliquots were taken at selected time intervals for analyses using GC/MS after iodosylben-

zene was added to the reaction solution containing copper catalyst (0.01 mmol for binuclear copper complex and 0.02 mmol for mononuclear copper complex), cyclohexene (1 mmol), and decane (internal standard) in CH<sub>3</sub>CN (5 mL).

**Relative Reactivities of Substituted Styrenes in Epoxidation by Iodosylbenzene Catalyzed by Binuclear Copper Complex.** The competitive reaction between substituted styrenes and styrene was carried out as follows: a stock solution containing styrene (0.45 mmol), substituted styrene (0.45 mmol), chlorobenzene (0.45 mmol, internal standard), and copper complex 1 (0.03 mmol) in CH<sub>3</sub>CN (15 mL) was prepared. Iodosylbenzene (0.08 mmol) was added to a reaction solution (5 mL) obtained from the stock solution and the reaction mixture was stirred for 1 hr. Aliquots taken before the addition of iodosylbenzene and after stirring 1 hr with iodosylbenzene added were analyzed by GC/MS. Data represent values averaged from three independent reactions.

**Reaction of Copper(II) Complex, 1, with Excess Iodosylbenzene in the Absence of Organic Substrates.** The copper complex ( $7.8 \times 10^{-2}$  mmol) in 5 mL of CH<sub>3</sub>CN was reacted with iodosylbenzene ( $7.8 \times 10^{-1}$  mmol). After the reaction mixture was stirred for 3 hr and filtered, Et<sub>2</sub>O (45 mL) was added to crush out green solid. The UV/vis spectrum of this complex in CH<sub>3</sub>CN showed bands at 225 nm and 660 nm. The infrared spectrum of the green solid showed bands attributable to the copper complex 1 and new bands at 1470, 735, and 680 cm<sup>-1</sup>. Elemental Analysis: C, 32.15; H, 2.99; N, 4.82; F, 13.00; I, 11.71; Cu, 6.609.

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## Chemistry of Carbonate-Sulfur Flux

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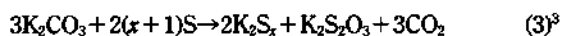
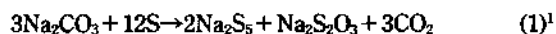
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Reactions of alkaline metal carbonates with sulfur are investigated in detail. The evolution of CO and a trace of SO<sub>2</sub> were observed in the course of reaction with major component of polysulfides. Some evidences that the reaction proceeds with breaking of terminal sulfur-sulfur bond in the sulfur polymer, and forming CO, SO<sub>2</sub> and polysulfide are presented. Polysulfides have the role of keeping free sulfur and allow it to react with other chemicals to rather high temperatures.

### Introduction

The reaction of alkaline metal carbonate and sulfur has been known to produce alkaline metal polysulfides.



(the reaction of Na<sub>2</sub>CO<sub>3</sub> with S begins at 275-280 °C; that

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