# Photolysis of oxygen saturated ethers in the presence of Sn(II) or Cu(II) salts

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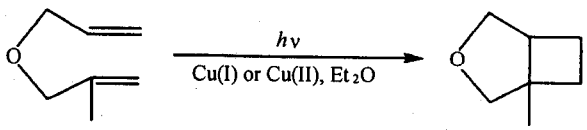
**Photolysis of diethyl ether-oxygen charge transfer complex in the presence of Sn(II) or Cu(II) salts gave higher yields of the oxidation products, ethyl acetate, acetaldehyde, ethanol, ethyl formate and methanol compared with those without the salts. In addition, the photolysis of an oxygen saturated tetrahydrofuran (THF) or dibutyl ether solution gave γ-butyrolactone or butanol and butyl butyrate as major products with small amounts of undetermined compounds, respectively. Their yields were also affected by the addition of Cu(II) or Sn(II) salts.**

**Keywords** Photolysis, Sn(II) salt, Cu(II) salt, ether, oxidation products

## Introduction

It has been reported that oxygen-saturated diethyl ether exhibits a charge transfer absorption band which upon irradiation gave ethyl acetate, acetaldehyde, ethanol, ethyl formate, and methanol as major products.[1a-d] The mechanism has been completely elucidated by Sonntag and his co-workers. Later, it was found that the similar photo-induced reaction could take place by irradiation of oxygen-saturated amines.[1e-h] The radical species has been detected by ESR spectroscopic analysis.[1e] Basically this is a reaction of excited CCT complex (contact charge transfer complex) derived from substrate with oxygen upon irradiation. Recently, in the course of study on the photo-induced [2 + 2] intramolecular cycloaddition reaction in diethyl ether in the presence of CuOTf or $Cu(OTf)_2$ (Scheme 1), it was found that ethyl acetate, ethyl formate, methanol and ethanol could also be detected by GC analysis if the oxygen was not completely purged off. Surprisingly, it was further confirmed that this interesting photo-induced oxidation reaction could be largely accelerated to give higher yields of ethyl acetate, ethyl formate, methanol and ethanol in the presence of a small amount of $Cu(OTf)_2$ or $Sn(OTf)_2$. Herein, we wish to report the full details of this oxidation process.

**Scheme 1**




## Results and discussion

The results are shown in Fig. 1 and Fig. 2. The data of the product yields indicated on the vertical axes are the amount of products (mmol) in 3 mL of ether solution. It can be seen from Fig. 1 and Fig. 2, nearly doubled yields of the oxidation products were obtained in the presence of Sn(II) or Cu(II) salt (0.5 mM) upon irradiation compared with those without the metal salts. The photolysis was carried out in a Pyrex tube (> 290 nm) with 3 mL of ether using a 300 W high pressure mercury lamp (Eikosha) fitted with a Vycor sleeve under

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the same conditions by means of a merry-go-round apparatus. The control experiment showed that no reaction could take place if the reaction solution was stirred in the presence of Sn(II) or Cu(II) salt without irradiation.

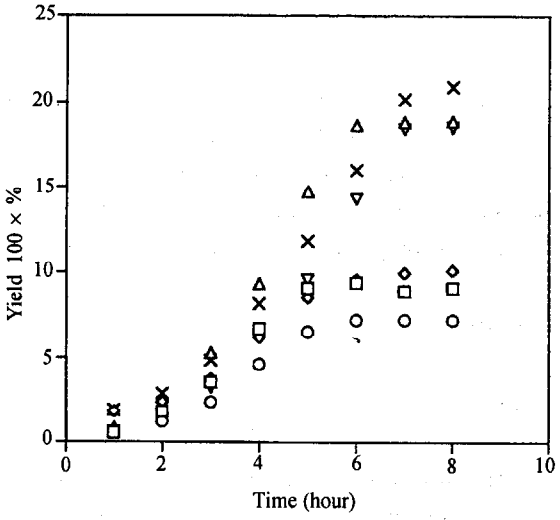



**Fig. 1** Yields of ethyl acetate, ethanol, and ethyl formate upon irradiation of oxygen saturated diethyl ether in the absence/presence of copper(II) triflate (0.5 mM, 3 mL) as a function of irradiation time: (○) ethyl formate; (◇) ethanol; (□) ethyl acetate, in the absence of Cu(II) triflate; (▽) ethyl formate; (×) ethanol; (△) ethyl acetate, in the presence of Cu(II) triflate.

Apparently, Sn(II) or Cu(II) must have a catalytic effect on this photoinduced oxidation reaction although the turnover number could not be determined since this photoinduced oxidation could also take place even without metal salt.[1] The UV spectrum of oxygen saturated diethyl ether with $Cu(OTf)_2$ showed no additional absorption band compared with that of the degassed diethyl ether. Meanwhile, the charge transfer absorption band of oxygen saturated diethyl ether[1] overlapped with the UV spectrum of $Cu(OTf)_2$ or $Sn(OTf)_2$ in degassed diethyl ether solution. Thus, no insight information could be obtained from UV spectrum. Due to the charge transfer complex of diethyl ether and oxygen the UV absorption broadened in the oxygen saturated-ether solution than in the degassed one. But it is very clear that in the Pyrex-transparent region > 300 nm the optical densities (OD) are very similar. At present we do not understand the exact reason for the metal salt to affect this photoinduced oxidation. Recently some interesting papers and reviews on transition metal catalyzed radical reaction including photoinduced oxidation have been reported.[2,3] But it is very difficult to determine the exact role of metal salt in this photoinduced oxidation reaction. The metal salt may only play an important role in the radical chain reaction or may involve the excited state under irradiation.

In addition, the irradiation of an oxygen saturated THF solution gave γ-butyrolactone as a major product with trace amounts of undetermined compounds (Scheme 2). The addition of $Sn(OTf)_2$ or $Cu(OTf)_2$ also increased the yield of γ-butyrolactone (Fig. 3). On the other hand, irradiation of an oxygen saturated dibutyl ether, which was carefully purified by passing through an activated alumina column to remove the peroxide and followed by distillation from $CaH_2$ under reduced pressure, gave the corresponding butanol and butyl butyrate as major products with trace amounts of undetermined compounds (Scheme 3, Fig. 4). The result is very similar to that of diethyl ether. The formation of γ-butyrolactone, butanol and butyl butyrate was confirmed by comparison of their $^1H$ NMR spectral data, GC retention time and GC mass spectral data with those of the authentic samples, respectively.

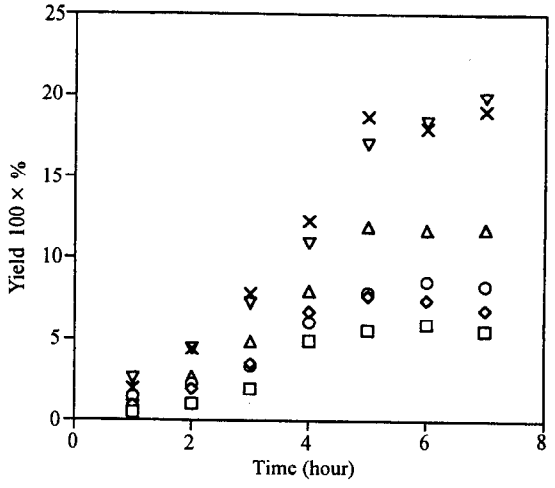
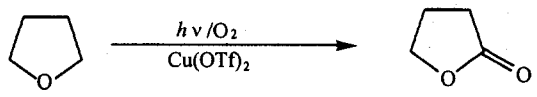



**Fig. 2** Yields of ethyl acetate, ethanol, and ethyl formate upon irradiation of oxygen saturated diethyl ether in the absence/presence of tin(II) triflate (0.5 mM, 3 mL) as a function of irradiation time: (□) ethyl formate; (◇) ethanol; (○) ethyl acetate, in the absence of Sn(II) triflate; (◇) ethyl formate; (▽) ethanol; (×) ethyl acetate, in the presence of Sn(II) triflate.

**Scheme 2**



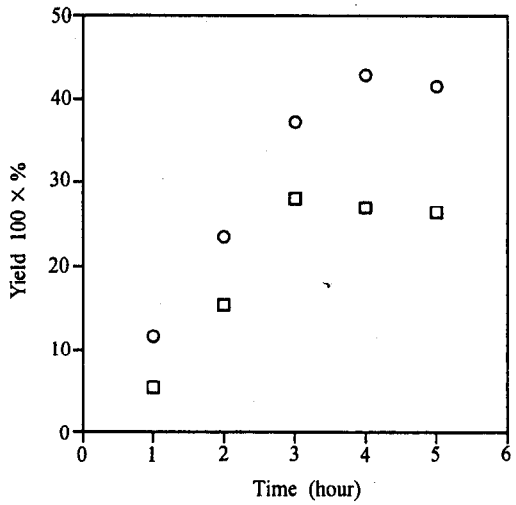




**Fig. 3** Yield of γ-butyrolactone upon irradiation of oxygen saturated THF in the absence/presence of copper(II) triflate (0.5 mM, 3 mL) as a function of irradiation time: (□) γ-butyrolactone, in the absence of Cu(II) triflate; (○) γ-butyrolactone, in the presence of Cu(II) triflate.

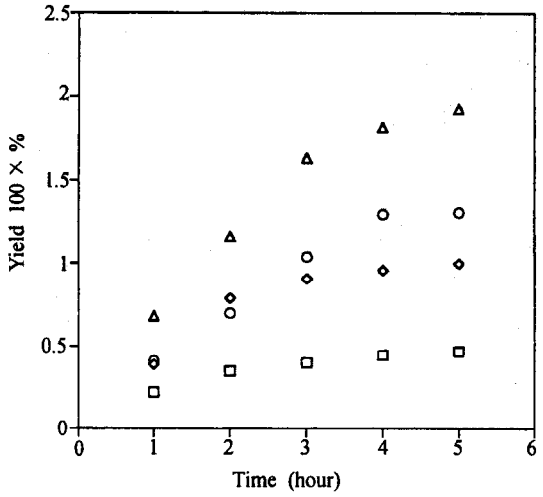
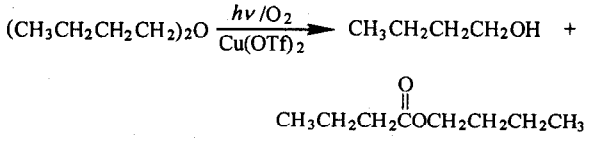



**Fig. 4** Yields of butanol and butyl butyrate upon irradiation of oxygen saturated dibutyl ether in the absence/presence of copper(II) triflate (0.5 mM, 3 mL) as a function of irradiation time: (□) butanol; (◇) butyl butyrate, in the absence of Cu(II) triflate; (○) butanol; (△) butyl butyrate, in the presence of Cu(II) triflate.

**Scheme 3**




Although the catalytic activity of this photochemical system is not sufficiently high and the reaction mechanism has not been clarified, this reaction may present a good example for the combination of photolysis and metal salt for oxidation reaction under oxygen atmosphere.

## Experimental

*General*

$^1$H NMR spectra were determined for solutions in $CDCl_3$ containing tetramethylsilane as an internal standard on a JEOL JNM-EX400 spectrometer. Mass spectra were recorded with a JEOL JMS D-300 instrument. Combustion analyses were performed on a Perkin-Elmer Model 240 analyzer.

Diethyl ether and THF were purchased from Aldrich and further purified by distilling over sodium under argon and stored under argon. Dibutyl ether was carefully purified by passing through an activated alumina column to remove the peroxide and then distilled from $CaH_2$ under reduced pressure. $Cu(OTf)_2$ and $Sn(OTf)_2$ were of commercial grade and used without further purification.

Gas chromatographic analyses of the formed ethyl acetate, ethyl formate, methanol and ethanol in photolyzed diethyl ether solution were performed on a 50-m capillary column (Shimadzu CBP20) at 65℃ on a Shimadzu 14A instrument using cyclooctane as an external standard. Gas chromatographic analyses of the formed butanol, butyl butyrate and γ-butyrolactone in photolyzed dibutylether or THF solution were also performed on a 50 m capillary column (Shimadzu CBP20) from 100℃ to 170℃ with a gradient 10℃/min on a Shimadzu 14A instrument using nonadecane as an external standard.

*Photolysis of oxygen saturated diethyl ether, dibutyl ether and* THF *in the presence/absence of* Sn(II) *or*

Cu(II) *salts*

All irradiations were carried out in a Pyrex tube ( > 290 nm) with a water bath at 25℃ using a 300 W high pressure mercury lamp (Eikosha) fitted with a Vycor sleeve. Dried oxygen gas was bubbled into two Pyrex tubes filled with 3 mL of diethyl ether, dibutyl ether or THF at 0℃ for 5 minutes and one Pyrex tube contained 0.5 mM of $Cu(OTf)_2$ or $Sn(OTf)_2$. The two oxygen saturated solutions were irradiated under the same conditions using a merry-go-round apparatus. After every 1 hour, 10 μL of photolyzed solution was taken out and 10 μL of diethyl ether solution of cyclooctane or nonadecane (5 mM) was added as an external standard. Then the combined solution was analyzed by GC.

In the case of photoirradiation of oxygen saturated THF and dibutyl ether, the oxidation products, γ-butyrolactone, butyl butyrate, and butanol were isolated from the reaction mixture by TLC plates 20 × 20 × 20 mm (eluent: hexane/ethyl acetate = 1/6). Their spectroscopic data were compared with those of authentic samples.

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