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PHOTO-OXIDATION OF ARYL ETHERS IN THE PRESENCE OF FERRIC CHLORIDE

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Photo-oxidation of aryl ethers in the presence of ferric chloride in aqueous acetonitrile afforded alcohols, aldehydes (or ketones), and N-alkylacetamides. One electron-transfer mechanism from the ether to Fe(III) was suggested for this photo-oxidation.

Recently much attention has been paid to the transition metal catalyzed photo-reaction from both synthetic and mechanistic viewpoints. It has been suggested that a ketyl radical and/or an alkoxy radical are involved as the intermediates in the photo-oxidation of alcohols to ketones or aldehydes with Fe^{3+}, Ag^{+}, or Cu^{2+} [1], and that the photo-reaction of olefins with Fe^{3+} under the oxygen atmosphere occurs through a long range electron-transfer to give α-chloro ketones.[2]

We describe here a new photochemical oxidation of aryl ethers in the presence of ferric chloride in 40% aqueous acetonitrile. The typical procedure for the dibenzyl ether(1) is as follows. An aqueous acetonitrile solution containing 0.8 mmol of (1) and 1.2 mmol of ferric chloride hexahydrate was irradiated with a high-pressure mercury lamp through a Pyrex filter for about 180 h in air.[3] The solution, which changed from yellow to colorless by irradiation (white precipitates were sometimes observed), was washed with water and extracted with a mixture of benzene and acetonitrile. Products were analyzed by Glc. The results are summarized in Table.

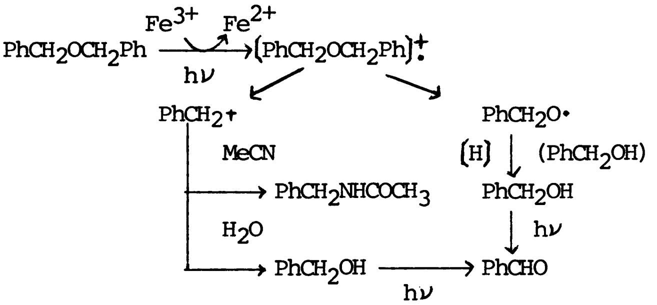
Aryl ethers decomposed oxidatively with ether linkage scission and afforded exclusively alcohols and aldehydes (or ketones), together with N-alkylacetamides as minor products corresponding to the ethers used. Phenyl benzyl ether, however, was almost inert to this decomposition reaction. No reactions occurred in the dark under the same conditions.

In order to elucidate these interesting photo-reactions, quantitative analyses of Fe(III), Fe(II), and organic products were performed in course of irradiation time. As shown in Figure, the oxidative photo-decomposition of ethers proceeds depending upon the extent of the reduction of Fe(III) to Fe(II). No charge transfer complex of a substrate with ferric ion was observed for the

Table Yield of Photo-Products from Aryl Ethers

Substrates(R-O-R') R	R'	Irradiation Time(h)	Products(%)
$PhCH_2$-	$PhCH_2$-	172	$PhCH_2OH$(17.9), PhCHO(66.1), $PhCH_2NHCOCH_3$(trace)
$PhCH_2$-	$PhCH(CH_3)$-	106	$PhCH_2OH$(5.0), $PhCH(CH_3)OH$(15.7), PhCHO(12.6), $PhCOCH_3$(15.7), $PhCH_2NHCOCH_3$(2.1), $PhCH(CH_3)NHCOCH_3$(3.0)
$PhCH(CH_3)$-	$PhCH(CH_3)$-	172	$PhCH(CH_3)OH$(15.7), $PhCOCH_3$(29.2), $PhCH(CH_3)NHCOCH_3$(4.5)
$PhCH_2$-	Ph-	174	PhCHO(2.5), PhOH(1.1)
$PhCH_2$-	n-Bu-	125	$PhCH_2OH$(35.5), PhCHO(23.6), $BuNHCOCH_3$(2.7)

present systems, although the photo-oxidation of alcohols by ferric perchlorate involves excitation of a charge transfer band.[1c] These observation indicates that the photo-reaction was initiated by one electron-transfer from a substrate to Fe(III) excited at about 360 nm.[4,5] An unstable cation radical produced by the electron-transfer must undergo cleavage to a carbocation and an alkoxy radical, as suggested for the oxidation of p-methoxybenzyl phenyl sulfide by Co(III).[6] Thus the oxidative products in Table should be derived from the following scheme, taking into account that the primary process in the photo-oxidation by Fe(III) involves the cation radical formation (the scheme illustrates the reaction of (**1**)).[7] Particularly, detection of a small amount of N-alkylacetamide obtained by the Ritter addition of the carbocation to acetonitrile followed hydration might support this reaction scheme. As an additional proof for the cation radical formation, we carried out the reaction of (**1**) with ceric ammonium nitrate in aqueous acetonitrile which has been regarded as proceeding through the electron-transfer mechanism.[8] The reaction products were benzaldehyde(57.7%), benzyl alcohol(4.2%), and N-benzylacetamide(0.5%). These product distributions were similar to those of the photo-oxidation.



Scheme

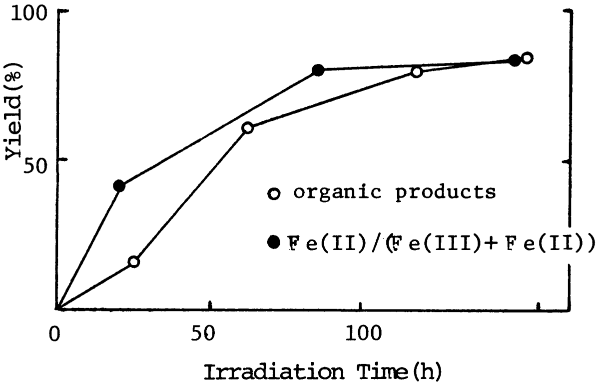


Figure Quantitative analyses of iron and organic products.

A similar photo-oxidation was performed by using dibenzyl sulfide, which was expected to generate a more inert thiyl radical according to the scheme described above. As a result, dibenzyl disulfide as a radical coupling product was obtained in 28.8% yield as expected, together with benzaldehyde(34.4%). This observation may provide the indirect evidence of the alkoxy radical formation.

Further studies on the electron-transfer reaction from the excited metal ion are now in progress in our larboratory.

References

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3) The irradiation under a stream of nitrogen exhibited no appreciable effect on the product yield.
4) Absorption spectra of Fe(III) solution in aqueous acetonitrile exhibited a strong band at 360 nm depending upon the concentration of acetonitrile, which was attributed to the acetonitrile to Fe(III) charge transfer complex.
5) The fact that two diastereomers of diphenetyl ether showed different photo-reactivities may suggest a complex formation between the excited Fe(III) and ethers : K.Seguchi and S.Hirota, Unpublished results.
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