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Cobalt-Mediated Olefin Epoxidation and Oxidative DNA Cleavage with Potassium Monopersulfate

Wonwoo Nam^{1*}, Wonkoo Hwang², Jung Min Ahn¹,
Seh-Yoon Yi¹, and Gil-Ja Jhon^{1*}

¹Department of Chemistry, Ewha Womans University,
Seoul 120-750, Korea

²Department of Chemical Engineering,
Hong Ik University,
Seoul 121-791, Korea

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Elucidation of the mechanism of metal-mediated oxidations of organic substrates and oxidative cleavage of DNA has been a subject of recent studies in biological and bioinorganic chemistry.¹ In the studies, water-soluble potassium monopersulfate, KHSO₅, has been often used as an oxygen atom donor.² For example, Meunier and coworkers showed that metalloporphyrins³ and metallobleomycins⁴ are able to oxygenate organic substrates and cleave DNA with KHSO₅ in aqueous medium. They suggested that reactive intermediates responsible for the oxidation reactions are high-valent metal oxo complexes. In this communication, we report that a cobalt salt associated with KHSO₅ has the ability of epoxidizing olefins as well as cleaving DNA oxidatively in aqueous solution.

In a typical experiment, KHSO₅ (10 mM) was added to a reaction solution containing Co(NO₃)₂ (0.1 mM), CBZ (CBZ=carbamazepine, 1 mM, introduced as a 10 mM solution in methanol), and benzophenone (internal standard, 1 mM, introduced as a 10 mM solution in methanol) in 5 mL of water. The reaction mixture was stirred for 1 h at room temperature and analyzed by HPLC. We found that the conversion of CBZ was above 95%, and the yield of CBZ-oxide⁵ product was 75% under our reaction conditions (eq. 1). Formation of CBZ-oxide was not detected in the absence of either cobalt salt or KHSO₅.⁶ Other metal salts such as Mn²⁺, Fe²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ were inactive in the CBZ epoxidation reaction, and other oxidants such as H₂O₂, *t*-BuOOH, and PhIO did not give the epoxide product either.

We then studied oxidative cleavage of DNA using the M²⁺/KHSO₅ system. The cleavage of DNA was followed by monitoring the conversion of supercoiled pBR-322 DNA

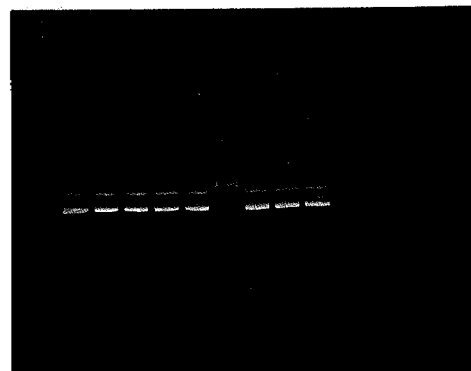
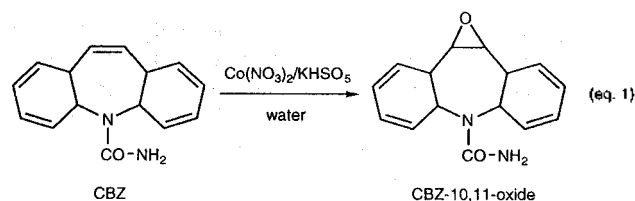
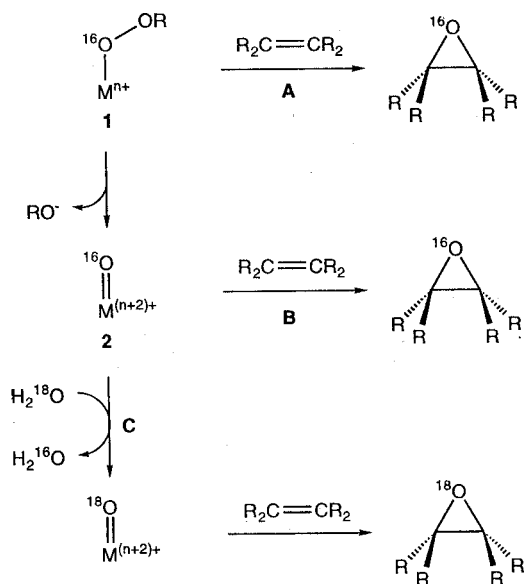


Figure 1. Cleavage of pBR 322 plasmid DNA (form I) by Co²⁺/KHSO₅. Reactions were initiated with the addition of KHSO₅ in 50 mM phosphate buffer at pH 6.0. Preincubation of DNA with metal salts was performed for 10 min at 25 °C. Digestion time with KHSO₅ was 1 min. Conversion of form I to form II DNA was detected by gel electrophoresis on 1% agarose with ethidium bromide staining. Lane 1, reaction control, DNA (22.7 μM in base pairs) alone; lane 2, reaction control, Co(NO₃)₂ (22.7 μM); lane 3, reaction control, KHSO₅ (113.5 μM); lane 4, cleavage reaction [Mn(CH₃CO₂)₂ (22.7 μM), KHSO₅ (113.5 μM)]; lane 5, cleavage reaction [Fe(ClO₄)₂ (22.7 μM), KHSO₅ (113.5 μM)]; lane 6, cleavage reaction [Co(NO₃)₂ (22.7 μM), KHSO₅ (113.5 μM)]; lane 7, cleavage reaction [Ni(NO₃)₂ (22.7 μM), KHSO₅ (113.5 μM)]; lane 8, cleavage reaction [Cu(CF₃SO₃)₂ (22.7 μM), KHSO₅ (113.5 μM)]; lane 9, cleavage reaction [Zn(CF₃SO₃)₂ (22.7 μM), KHSO₅ (113.5 μM)].



(form I) to an open circle (form II).⁷ As shown in Figure 1, among the tested metal salts, only the cobalt salt showed the activity of cleaving DNA efficiently. This reactivity pattern was the same as that observed in the CBZ epoxidation reaction, suggesting that there is close correlation between the olefin epoxidation and the DNA cleavage by metal salt and KHSO₅.

Cobalt-HSO₅ complex, **1**, and high-valent cobalt oxo complex, **2**, are proposed to be a possible intermediate for the oxidation of substrates (see Scheme 1). Since Meunier *et al.* reported that the reactive oxidizing agent generated in water-soluble manganese porphyrin-catalyzed CBZ epoxidation by KHSO₅ was high-valent manganese oxo complex and that the manganese oxo complex readily exchanged its oxygen atom with that of solvent water,^{3(b)} we attempted the CBZ epoxidation by Co²⁺/KHSO₅ in H₂O solution.⁸ When the origin of the oxygen atom incorporated into the CBZ-oxide product was analyzed,⁹ we found that the oxygen atom came from the oxidant, not from the solvent water, under our reaction conditions. This result is in sharp contrast to



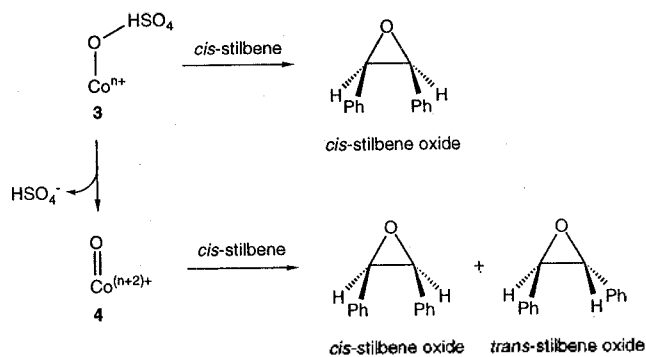
Scheme 1.

that reported in the manganese porphyrin-catalyzed CBZ epoxidation reaction in which half of the oxygen in the CBZ-oxide product came from the isotopically labeled water.^{3(b)} Although the incorporation of ^{18}O from $H_2^{18}O$ into oxygenated products has often been considered as sufficient evidence for the intermediacy of high-valent metal oxo species in catalytic oxygenation reactions (see Scheme 1),^{3(b),10} the absence of ^{18}O in the CBZ-oxide product formed in the CBZ epoxidation by Co^{2+} and $KHSO_5$ does not imply that high-valent cobalt oxo species can be ruled out as a potent oxidizing agent since, in some cases, the oxygen exchange between high-valent metal oxo complex and water (pathway C in Scheme 1) is slow relative to the rate of substrate oxidation (pathway B in Scheme 1).¹¹

Another mechanistic study that we carried out is the epoxidation of *cis*-stilbene by Co^{2+} and $KHSO_5$ since analysis of the product distributions (i.e. the ratio of *cis*-stilbene oxide to *trans*-stilbene oxide) may give us clues for understanding the nature of the reactive intermediate.¹² In the *cis*-stilbene oxidation, *cis*-stilbene was oxidized to *cis*-stilbene oxide predominantly with small amounts of *trans*-stilbene oxide and benzaldehyde products.¹³ The ratio of *cis*- to *trans*-stilbene oxide products was high in this reaction, whereas *trans*-stilbene oxide was usually produced as a major product in other cobalt-mediated *cis*-stilbene oxidation reactions.¹⁴ Although the yield of *trans*-stilbene oxide product was low, the observation of *trans*-stilbene oxide formation suggests that cobalt oxo complex, **4**, might be responsible for the epoxidation of *cis*-stilbene because we expect that the cobalt-HSO₅ complex, **3**, produces only the *cis*-stilbene oxide product (see Scheme 2).¹²

In our future studies, we hope to elucidate the exact nature of oxidizing agent as well as the mechanism of the oxidation reaction by $Co^{2+}/KHSO_5$ and to extend this system to site-specific DNA cleavage.

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Scheme 2.

N.), the Korea Science and Engineering Foundation (Grant No. 93-05-00-04) (W.N.), and the 95 Special Fund for University Research Institute, Korea Research Foundation (G.J.) is gratefully acknowledged.

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- CBZ-oxide was synthesized according to ref. 3(b) and used as an authentic sample for the determination of product yields.
- The oxidation of CBZ was inhibited in phosphate buffer solution at high pH values, i.e. above pH=5. A similar reactivity pattern was observed in iron porphyrin- and nickel complex-catalyzed oxidation reactions: (a) Labat, G.; Meunier, B. *J. Org. Chem.* **1989**, *54*, 5008-5011. (b) Labat, G.; Meunier, B. *New. J. Chem.* **1989**, *13*, 801-804. (c) Nam, W.; Hwang, W.; Jhon, G.-J., manuscript in preparation.
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- Labeled water experiment was performed in $H_2^{18}O$ (250 μ L, 95% ^{18}O enrichment) solution containing CBZ (1

- mM), $\text{Co}(\text{NO}_3)_2$ (0.2 mM), and KHSO_5 (10 mM). The reaction solution was analyzed by LC/MS.
- ^{16}O and ^{18}O compositions in CBZ-oxide product were determined by the relative abundances of mass peaks at $m/z=253$ for ^{16}O and $m/z=255$ for ^{18}O .
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 - A solvent mixture (5 mL) containing 50% H_2O , 40% CH_3CN , and 10% CH_3OH was used to make the reaction solution homogeneous. Reaction conditions were the same as for the CBZ epoxidation reaction except that $\text{Co}(\text{NO}_3)_2$ (0.2 mM) and *cis*-stilbene (10 mM) were used. *cis*-Stilbene oxide (0.9 mM), *trans*-stilbene oxide (0.11 mM), and benzaldehyde (0.08 mM) were found to be formed as products in this reaction.
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Optical Time-of-Flight Studies on the Laser Ablation of Boron Nitride

Seung Min Park*, Keon Bae Shin, and Young Man Kim†

Department of Chemistry and
Research Institute for Basic Sciences,
Kyung Hee University, Seoul 130-701, Korea
†Advanced Analysis Center,
Korea Institute of Science and Technology,
Seoul 130-650, Korea

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The laser ablation of solid targets has been a research topic of interest since the invention of lasers. With developments of high power lasers in the ultraviolet region, deposition of thin films by laser ablation has been extensively studied aiming at the growth of high quality films of different types including superconductors, semiconductors, ferroelectrics, and dielectrics.¹ In particular, laser ablation technique has been proved to be especially powerful in the stoichiometric deposition of multi-element materials like YBCO superconductors.² Currently, deposition of thin films by laser reactive ablation is emerging, where laser ablation occurs under reactive gas environment. This technique has been applied to the deposition of refractory nitride materials such as boron nitride,^{3a} silicon nitride,^{3b} and carbon nitride.^{3c}

In this communication, we report experimental results on the optical time-of-flight (TOF) studies of laser ablation of

pyrolytic boron nitride (pBN, Union Carbide) in nitrogen. This is the first optical TOF study of BN laser ablation to our knowledge. The laser ablation of BN has been done by several groups with a goal to deposit epitaxial cubic boron nitride (cBN) thin films.⁴ cBN is one of the most promising materials with diverse applications in electronics, optics, and hard coatings.⁵ The efforts to deposit epitaxial cBN films by laser ablation, however, were not successful presumably due to the deficiency of detailed information on the laser ablation dynamics.

The quality and properties of films deposited by laser ablation are expected to be highly dependent on the characteristics of the plume generated in laser ablation process. The information on the formation and evolution of laser-induced plume from the target and the transport of the ablated species to the substrate will be of critical importance in understanding the dynamics involved in the pulsed laser deposition of materials. So far several methods including probe beam deflection,⁶ laser-induced fluorescence,⁷ time-of-flight,⁸ optical time-of-flight,⁹ resonance absorption,¹⁰ resonance ionization,¹¹ and ultrafast photography¹² have been employed to diagnose the plume in laser ablation. Among these methods, optical TOF technique has its unique features in that it can measure the dynamic properties of chemical species including both neutrals and ions with spectral resolution *in situ*, where the ambient pressure is often too high for a TOF or quadrupole mass spectrometer to be used.

In this work, we have adopted optical TOF technique to investigate the velocity and concentration of the species produced in the laser ablation of pBN. The laser ablation of pBN was done by the fourth harmonic of Nd:YAG laser (266 nm, Quanta-Ray GCR 150) with pulse duration of 5 ns operating at 10 Hz. The experimental setup is shown in Figure 1. Briefly, the Nd:YAG laser beam was focused onto the pBN target by a SIUV lens with focal length of 20 cm. Optical emission from the plume generated by the laser ablation was imaged into an optical fiber by a lens ($f=3.7$) and fed to a monochromator (SPEX 500M) equipped with a photomultiplier. The photomultiplier signal was averaged and stored in a digital storage oscilloscope (LeCroy 9304, 175 MHz). The emission spectrum was also obtained with the monochromator, where a boxcar averager (PAR 162) was employed for signal processing. Vibrational progressions from molecular BN transition ($A^3\Pi \rightarrow X^3\Pi$) as well as emissions from the excited B atoms and B^+ ions were also obser-

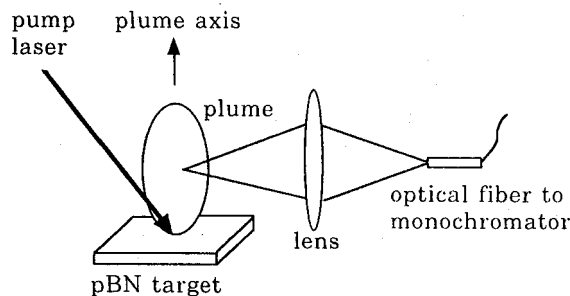


Figure 1. The experimental setup for optical TOF studies of laser ablation. The lens was mounted on a 3-dim. translational stage.