

Synergetic Effect in Benzyl Alcohol Oxidation

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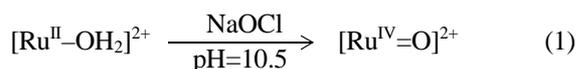
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High oxidation state oxo complexes have been known as the reactive intermediates in metalloporphyrin-catalyzed reaction.¹ Although many oxo complexes tend to be reactive oxidants, they are receiving continuous attention because of their usefulness as catalysts in different types of reaction.² Recently, ruthenium oxo forms are observed as effective complexes for the oxidation of the base functionality of guanosine 5'-monophosphate in DNA.³

It is well known that a phase transfer reagent is catalytically effective in different solubility of reactants.⁴ Because aquo complexes could be mostly produced from the oxidation reaction of substrate and oxidants, original oxo complexes have been regenerated electrochemically or by using co-oxidants.⁵ Therefore it is quite interesting to investigate oxidation reaction in the presence of metal complex, a phase transfer catalyst, and substrate in organic phase and co-oxidant in aqueous phase. This might be an interesting example where a combination of two catalysts provides a remarkable synergetic effect.

It has been pointed out that ethers and alcohols are readily oxidized by a ruthenium complex. Addition of stoichiometric amount of benzyl alcohol or phenol into $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ in acetonitrile leads to the formation of $[\text{Ru}^{\text{II}}-\text{OH}_2]^{2+}$ and corresponding oxidized organic product as found earlier.⁶ From the rate law and product analyses, the mechanism of benzyl alcohol oxidation involved the hydride transfer, on the other hand the oxidation of phenol appeared to be the electrophilic attack on the aromatic ring. For catalytic purpose, the electron transfer type oxidants such as porphyrin-based complexes with co-oxidants have been broadly used as described previously.⁷ In its reaction, the $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ system may be different from those oxidants and has a problem by requiring excessive amounts of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, thus limiting general use.

Here, the oxidation of benzyl alcohol by $[(\text{bpy})_2(\text{py})\text{Ru}^{\text{IV}}(\text{O})]^{2+}$ or $[(\text{bpy})_2(p\text{-tert-butylpy})\text{Ru}^{\text{IV}}(\text{O})]^{2+}$ or $[(\text{tpy})(\text{bpy})\text{Ru}^{\text{IV}}(\text{O})]^{2+}$ ($\text{bpy}=2,2'$ -bipyridine; $\text{py}=\text{pyridine}$; $p\text{-tert-butylpy}=\text{para-tertiary-butylpyridine}$; $\text{tpy}=2,2':6',2''$ -terpyridine) can be made catalytic with OCl^- as co-oxidant and by using the phase transfer condition. The resultant $[\text{Ru}^{\text{II}}-\text{OH}_2]^{2+}$ was readily re-oxidized to give $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ under OCl^- solution, which was confirmed from the disappearance of an MLCT band by UV/visible spectrophotometer (Eq. 1).



In a typical experiment, 0.02 mmol of either $[(\text{bpy})_2(\text{py})\text{Ru}(\text{OH}_2)](\text{ClO}_4)_2$ or $[(\text{bpy})_2(p\text{-tert-butylpy})\text{Ru}(\text{OH}_2)](\text{ClO}_4)_2$

or $[(\text{tpy})(\text{bpy})\text{Ru}(\text{OH}_2)](\text{ClO}_4)_2$ was dissolved in 10 mL of CH_2Cl_2 with a 100-fold excess of benzyl alcohol and 0.04 mmol of the phase transfer catalyst benzyldimethyltetradecylammonium chloride (abbreviated as BDTA^+Cl^-). 10 mL of an alkaline NaOCl solution (chlorine 5% minimum, Aldrich Chemical Co.) and 10 mL of a $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ phosphate buffer solution ($\text{pH}=10.5$) were layered over the reaction mixture in CH_2Cl_2 , which was stirred vigorously. Aliquots of the organic layer was monitored by G.C. every 10 or 15 min. After 3 h, the organic layer was dropped into ether to precipitate the metal complex. The product was collected and rotary evaporated under reduced pressure, and the remaining liquid was analyzed for aldehyde by spectroscopic techniques.

In blank experiments without added a ruthenium complex, the reaction of benzyl alcohol with NaOCl showed only small amounts of benzaldehyde. Adding a phase transfer catalyst, BDTA^+Cl^- , to benzyl alcohol in CH_2Cl_2 containing NaOCl solution gave a huge increase in overall yield. By employing BDTA^+Cl^- as a phase transfer catalyst with the $[(\text{bpy})_2(\text{py})\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$ catalyst we have found that the reaction was accelerated under catalytic condition where benzyl alcohol and NaOCl were used in larger amounts in Figure 1.

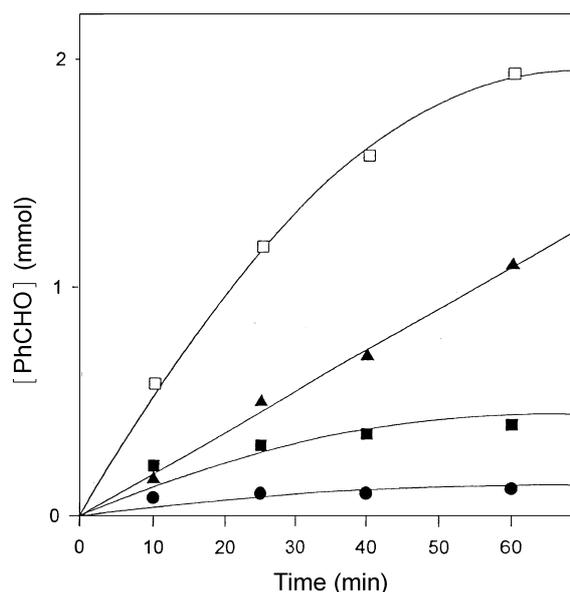
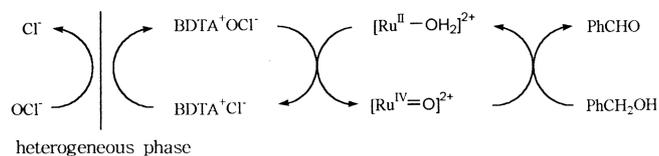


Figure 1. Plot of Time (min) vs. Conversion (mmol) Obtained for the Representative Catalytic Oxidation of Benzyl Alcohol (\bullet = benzyl alcohol + NaOCl ; \blacktriangle = benzyl alcohol + NaOCl + BDTA^+Cl^- ; \blacksquare = benzyl alcohol + NaOCl + $[(\text{bpy})_2(\text{py})\text{Ru}(\text{OH}_2)](\text{ClO}_4)_2$; \square = benzyl alcohol + NaOCl + $[(\text{bpy})_2(\text{py})\text{Ru}(\text{OH}_2)](\text{ClO}_4)_2$ + BDTA^+Cl^-).

Although there showed a decrease of overall yield in the oxidation reaction without using a phase transfer reagent, the combination of two catalysts was effective in the oxidative reaction as well as the phase transfer reaction. As mentioned, a ruthenium aquo complex changed to a ruthenium oxo intermediate very quickly in the presence of a phase transfer reagent and NaOCl, from which the oxidation by $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ complex could take place. The mechanism of this process could be similar to that proposed by the previous works.^{6a} The reaction would be described as following scheme.



Similar conditions except the use of different ruthenium complex were employed in the catalytic oxidation of benzyl alcohol. Contrary to the reaction of benzyl alcohol and NaOCl with $[(\text{bpy})_2(\text{py})\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$ complex, the direct oxidation of benzyl alcohol and NaOCl with $[(\text{tpy})(\text{bpy})\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$ or $[(\text{bpy})_2(p\text{-tert-butylpy})\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$ complex was considerably accelerated as shown in Table 1 (condition 3).

Although a catalytic reaction has occurred with a phase transfer reagent and a ruthenium complex (condition 4), examination of Table 1 reveals that the results are variable. As seen in the formerly reported results of the rate increase of the $[(\text{tpy})(\text{bpy})\text{Ru}^{\text{IV}}(\text{O})]^{2+}$ complex relative to $[(\text{bpy})_2(\text{py})\text{Ru}^{\text{IV}}(\text{O})]^{2+}$ complex toward PPh_3 ,^{2g} it is not surprising that the presence of both a ruthenium complex and a phase transfer catalyst causes an increase in the rate. The $[(\text{bpy})_2(p\text{-tert-butylpy})\text{Ru}^{\text{IV}}(\text{O})]^{2+}$ complex is not an efficient catalyst in the

Table 1. Turnover Number^a for the Oxidation of Benzyl Alcohol^b; condition 1, benzyl alcohol + NaOCl; condition 2, benzyl alcohol + NaOCl + BDTA⁺Cl⁻; condition 3, benzyl alcohol + NaOCl + ruthenium complex; condition 4, benzyl alcohol + NaOCl + ruthenium complex + BDTA⁺Cl⁻

Ru Complex Used	Time (min)	10	25	40	60
	Condition #				
$[(\text{bpy})_2(\text{py})\text{Ru}(\text{OH}_2)]^{2+}$	1	4	5	5	6
	2	8	25	35	55
	3	11	16	18	20
	4	29	59	79	96
$[(\text{bpy})_2(p\text{-tert-butylpy})\text{Ru}(\text{OH}_2)]^{2+}$	3	14	36	51	65
	4	66	74	81	72
$[(\text{tpy})(\text{bpy})\text{Ru}(\text{OH}_2)]^{2+}$	3	30	50	66	83
	4	67	87	93	95

^aTurnover number = no. of mol of benzaldehyde/no. of mol of Ru complex. ^bRu complex (0.02 mmol), BDTA⁺Cl⁻ (0.04 mmol), benzyl alcohol (2 mmol), and NaOCl (10 mL) in $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$ (10 mL/10 mL).

oxidation of benzyl alcohol and NaOCl with a phase transfer catalyst. Taking into consideration of the previous data of the huge rate decrease of $[(\text{bpy})_2(p\text{-tert-butylpy})\text{Ru}^{\text{IV}}(\text{O})]^{2+}$ in comparison with $[(\text{bpy})_2(\text{py})\text{Ru}^{\text{IV}}(\text{O})]^{2+}$,^{2g} it is not an unexpected result. Interesting to note is that $[(\text{bpy})_2(p\text{-tert-butylpy})\text{Ru}^{\text{IV}}(\text{O})]^{2+}$ complex is more unstable than $[(\text{bpy})_2(\text{py})\text{Ru}(\text{O})]^{2+}$ complex in basic solution in longer period of time, because *p-tert-butylpy* ligand is more susceptible to be oxidized than *py* in ligand oxidation reaction.⁸ In conclusion, this method provides a convenient and an efficient synthesis of benzaldehyde as electrocatalytic oxidation.⁹

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