Excellent Stability of Ruthenium(II) Complex Photosensitizers during Photo-Oxidation of 1,3-Cyclopentadiene

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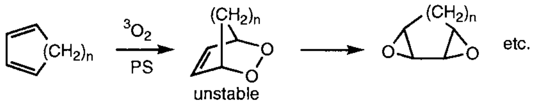
Tris(2,2'-bipyridine)ruthenium(II) and partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes have excellent stability during the photo-oxidation of 1,3-cyclopentadiene and can be sufficiently and repeatedly used as photosensitizers.

The photo-oxidation of organic and inorganic compounds by activated oxygen such as singlet oxygen and the superoxide anion generated by various photosensitizers is of considerable interest. Generally, rose bengal, methylene blue, chlorophyll, porphyrins and phthalocyanines, which have a strong absorption in the visible region, have been used as the photosensitizers for the photo-oxidation of sulfides,[1,2] thiols,[3,4] phenols[5-7] and other organic compounds.[8-11] One of the most reactive substrates for the endoperoxide formed by the photo-oxidation reaction is 1,3-cycloalkadiene, and many studies have been reported using various photosensitizers.[12-19]

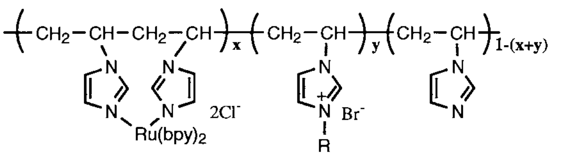
Scheme 1.



PS: photosensitizers (rose bengal, methylene blue and eosin)
n = 1, 2, 3 and 4

Although such systems frequently demonstrate high reaction activity, their investigations rarely focused on the stability of the photosensitizers. On the other hand, the tris(2,2'-bipyridine)ruthenium(II) complex [Ru(bpy)$_3^{2+}$] is a very famous photosensitizer for water oxidation and photo-reduction reactions.[20-22] Furthermore, we have reported the photo-reduction reaction using partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes (RuQPIms) as photosensitizers.[23-25] Though the ruthenium(II) complexes have a high quantum yield of the singlet oxygen formation, particularly Ru(bpy)$_3^{2+}$,[26] these ruthenium(II) complexes have little been applied to photo-oxidation reactions. We now describe the photo-oxidation of 1,3-cyclopentadiene (CP) using Ru(bpy)$_3^{2+}$ and RuQPIms in ethanol as the photosensitizers and their excellent stability during the reaction.

RuQPIms and Ru(bpy)$_3^{2+}$ were prepared according to the literature.[23,27] The photo-oxidation experiments were carried out at 25 °C in a 50 ml ethanol saturated by oxygen. The sample solutions were adjusted to 5.0 x 10^{-5} M photosensitizer and 2.5 x 10^{-2} M CP.[28] The light irradiation used visible light at 180 mW cm^{-2} (halogen lamp, 250 W). The reactions were monitored by the change in the oxygen consumption during visible light irradiation.



		x	y
C_6RuQPIm	R = C_6H_{13}	0.004	0.2297
C_{12}RuQPIm	R = $C_{12}H_{25}$	0.004	0.2235
C_{16}RuQPIm	R = $C_{16}H_{33}$	0.004	0.2233

Figure 1. Chemical structure of polymer-bound Ru(II) complexes.

When an oxygen saturated ethanol solution containing photosensitizer and CP was irradiated by visible light, the oxygen in the reaction cell was consumed. Since the oxygen was not consumed in the absence of the photosensitizer and the quenching reaction of the photoexcited photosensitizers with CP did not take place under an argon atmosphere, the CP would be oxidized by singlet oxygen generated by energy transfer from the photoexcited photosensitizer to the triplet molecular oxygen. Furthermore, the saturated oxygen consumption was about 25.5 ml, indicating that most of CP reacted with the singlet oxygen at 1:1 according to Scheme 1. Figure 2 shows the change in the oxygen consumption during visible light irradiation for the Ru(bpy)$_3^{2+}$ and C_{12}RuQPIm systems.[29] The Ru(bpy)$_3^{2+}$ photosensitizer demonstrated excellent stability for the repeated experiments; in addition, it was confirmed by absorption spectrum measurements that the Ru(bpy)$_3^{2+}$ photosensitizer was not decomposed during the repeated experiments. On the other hand, the reaction activity of the polymer-bound ruthenium(II) complex photosensitizers gradually decreased with repeated reactions. When the irradiation time was changed from 20 min to 30 min for the 10th and 11th runs, however, the reaction activity was similar to that of the 1st and 2nd runs. During the reaction, the absorption maximum of the polymer-bound ruthenium(II) complexes changed from 490 nm to 510 nm, indicating that these ruthenium(II) complexes changed to Ru(Cl)QPIm complexes in which one imidazolyl ligand was substituted by a chloride ion.[31] Therefore, the decrease in reaction activity is caused by the formation of new polymer

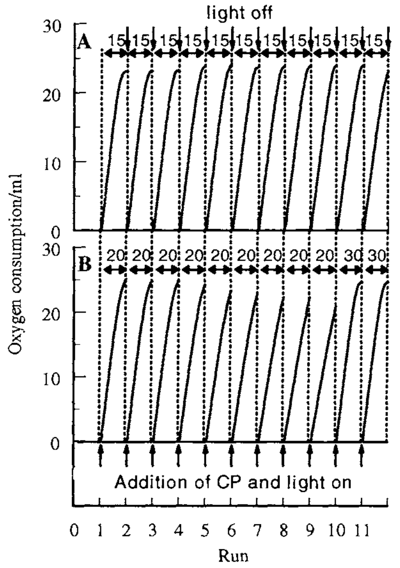


Figure 2. Repeated experiments of photo-oxidation reaction of CP using (A) Ru(bpy)$_3^{2+}$ and (B) C$_{12}$RuQPIm as photosensitizers at [Ru(II)] = 5.0 x 10^{-5} M and [CP] = 2.5 x 10^{-2} M x runs in ethanol. Irradiation time of one cycle is 15 min for Ru(bpy)$_3^{2+}$ system and 20 min in 1st to 9th cycles and 30 min for 10th and 11th cycles for C$_{12}$RuQPIm system.

ruthenium(II) complexes. Although the Ru(Cl)QPIm photosensitizers have a low reaction activity comparable to the original complexes (RuQPIms), however, they demonstrate the same maximum oxygen consumption when changing the irradiation time to 30 min and have an excellent stability for the photo-oxidation reaction.

In summary, we find that Ru(bpy)$_3^{2+}$ and polymer-bound ruthenium(II) complexes can be sufficiently used as photosensitizers for the photo-oxidation of 1,3-cyclopentadiene. Furthermore, these ruthenium(II) complexes, which have excellent stability for the photo-oxidation reaction, can be repeatedly used. We have now confirmed that these ruthenium(II) complex photosensitizers barely lose the reaction activity after 50 cycles. Further studies on the detailed reaction mechanism and application of these photosensitizers to the photo-oxidation reactions of other substrates are now in progress in our laboratory.

References and Notes

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28 CP used in the present experiments was obtained by heating dicyclopentadiene at 170 °C just before use.

29 For all the polymer systems, the same results were obtained. Therefore, only one result, which was the C$_{12}$RuQPIm system, was described.

30 During the repeated experiments, absorption band around 510 nm, corresponding to the [Ru(Cl)QPIm] complex, increased and that at 490 nm decreased during the repeated experiments. Furthermore, Ru(Cl)QPIm was very stable, and a further ligand substitution reaction did not occur even when repeated experiments were continued.