84 *Bull. Korean Chem. Soc., Vol. 9, No. 2, 1988*

Yong Tae Park et al.

decreasing the concentration of conduction electron by eq.(1) and (2). If O_2 adsorption is rate determining then total reaction order must be 0.5. But this order is not agree with kinetic data. Therefore we conclude that the adsorption of oxygen should be only the reaction initiation step, and eq.7 should be the rate determining step. From eq.7 production rate of CO_2 is

$$d[CO_2]/dt = k[CO][O^{2-}(ads)] \qquad (8)$$

and by eq.(6)

$$d[CO_2]/dt = k''[CO][O_2]^{1/2} \qquad (9)$$

From this proposed rate law, we could get the partial orders of CO and O_2 that are first and 0.5, respectively, consistent with experimentally observed rate law.

References

1. Astumin, R. D., and Schelly, Z. A., *J. Am. Chem. Soc*, **103**, 304 (1984).
2. Kim, K. H., Han, H. S., and Choi, J. S., *J. Phys. Chem.*, **83**, 1286 (1979).
3. Kim, K. H., Kim, D., and Choi, J. S., *J. Catal*, **86**, 219 (1984).
4. Lee, S. H., Kim, Y. R., Kim, K. H., and Choi, J. S., *J. Kor. Chem. Soc.*, **29**, 111 (1985).
5. Morrison, S. R. "The Chemical Physics of Surface", Chapter 2, Plenum Press, New York, 1978.
6. Van Oeffelen, D. A. G., Von Hooff, J. H. C., and Schuit, G. C. A., *J. Catal.*, **95**, 84 (1985).
7. Choi, J.S., and Kim, B.W., *Bull. Chem. Soc. Jpn.*, **46**, 21 (1973).
8. Choi, J. S., Kim, K. H., and Choi, S. R., *Inter. J. Chem. Kinetics*, **9**, 489 (1977).
9. Inoue, Y., Sato, K., and Suzuki, S., *J. Phy. Chem.*, **89**, 2827 (1985).
10. Kim, K. H., Jun, J. H., and Choi, J. S., *Bull. Kor. Chem. Soc.*, **5**, 41 (1984).
11. Benjelloun, D., Bonnet, J., Dordor, P., Launay, J., Onillon, M., and Hagenmuller, P., Revue de Chimie Mineralf, **21**, 721 (1984).
12. Reymond, J. P., Meriaudeau, P., and Teichner S. J., *J. Catalysis* **75**, 39 (1982).
13. G. Bate, "Ferromagnetic Materials", vol 2, chapter 7, E. P. Wohlfarth ED., North-Holland Pub. Co., N. Y., 1980.
14. Lee, S. H., Heo, K., Kim, K. H., and Choi, J. S., *Inter. J. Chem. Kinetics* **19**, 1 (1987).
15. Yoon, K. H., and Choi, J. S., *J. Phys. Chem.*, **74**, 1095 (1969).
16. Iwamoto, M., Yoda, Y., Yamazoe, N., and Seyomu, T., *J. Phys. Chem.*, **82**, 2564 (1978).
17. Kim, Y. Y., Master Thesis, Yonsei University, 1986.

Transient Absorption Spectra of Phenothiazine Derivative in the Vesicle System Containing Ru²⁺ Complex as a Sensitizer

Yong-Tae Park and Young-Doo Kim

Kyungpook National University, Department of Chemistry, Taegu 702-701

Richard D. Burkhart and Norris J. Caldwell

University of Nevada, Department of Chemistry, Reno, Nevada 89557, U.S.A.

The Photophysical and photochemical properties of Ruthenium bipyridine with two long hydrocarbon chains, [Ru(bipy)₂ (dhbipy)]²⁺ and transient phenothiazine derivative cation radical (PTD⁺) in the cationic vesicle were studied. Transient absorption spectra of cation radical of phenothiazine derivative in the vesicle system containing the Ru²⁺ complex, [(Ru(bipy)₂ (dhbipy)]²⁺, (1) as sensitizer and phenothiazine derivative as electron donor was observed by XeCl excimer laser photolysis system. Thus the excited ruthenium complex would be quenched by phenothiazine derivative(PTD) reductively in the vesicle system. The quenching rate constant(K_Q) of Ru²⁺ with two long hydrocarbon chains in the vesicle by PTD was 9.6 × 10⁸M⁻¹ S⁻¹. The absorption decay kinetics showed that lifetime of phenothiazine derivative cation radical is a value in the 4-8m sec range.

Introduction

Within recent years, substantial research effort has been extended in photochemical conversion of solar energy. In a solar energy storage study, a vesicle system of Calvin(1978)[1] Tunuli (1981)[2] and Fendler (1985)[3] is of interest. The attachment of Ru catalyst on the well of a vesicle containing sensitizer, electron donor and electron acceptor was devised

by Park (1983).[4] Hydrogen was produced when the vesicle solution containing phenothiazine derivative and Ru²⁺ bipyridine complex with two long tails was irradiated with blue light. However, the reaction mechanism of the vesicle system was not clear. In a study of the vesicle system containing [Ru(bipy)₂ (dhbipy)]²⁺ the transient absorption of phenothiazine derivative in the sysem was observed. The absorption decay kinetics was also studied.
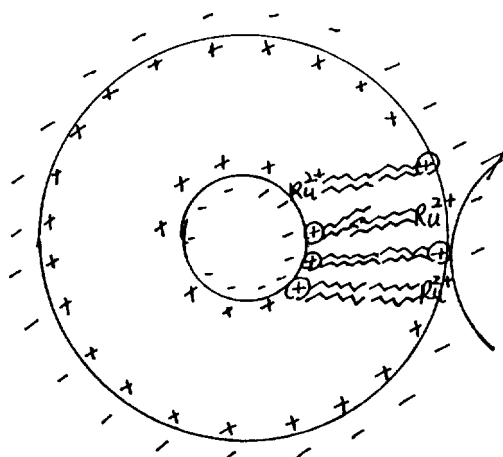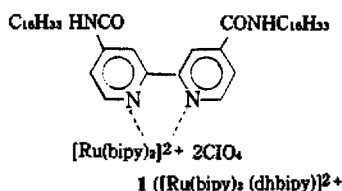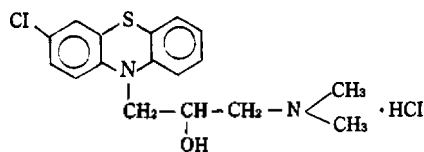
Figure 1. Vesicle system containing [Ru (bipy)$_2$ (dhbipy)]$^{2+}$ and PTD. (prepared with didodecyl dimethyl ammonium bromide).

[Ru(bipy)$_3$]$^{2+}$ 2ClO$_4$

1 ([Ru(bipy)$_3$ (dhbipy)]$^{2+}$

N,N-di (1-hexadecyl)-2,2-bipyridinium-4,4-dicarboxamide)-bis(2,2-bipyridine) ruthenium perchlorate

10-Phenothiazineethanol, 2-chloro-α-(dimethylaminomethyl), hydrochloride, PTD

Materials and Methods

Didodecyl dimethyl ammonium bromide was obtained from Eastman. 10-phenothiazine ethanol, 2-chloro- α -(dimethylaminomethyl)hydrochloride was obtained from Upjohn. N,N'-di-(1-hexadecyl)-2,2'-bipyridinium-4-4'-dicarboxamide -bis(2,2'-bipyridine) ruthenium perchlorate [Ru(bipy)$_2$ (dhbipy)]$^{2+}$ was provided by Dr. W. Ford, (Univeristy of California, Berkeley, U.S.A.). Triple distilled water was used in this experiment. Vesicles were prepared with Ru^{2+} complex, (**1**) (0.2mg, 1.6 × 10^{-8} moles), didodecyldimethyl ammonium bromide (12.6 mg, 2.7 × 10^{-5}moles) and water (5m*l*). (see Fig. 1). The ruthenium complex was not dissolved in water. The mixture was placed in a test tube, Vortex-stirred and then heated to boiling until the ruthenium complex dissolved.

Luminescence spectra of Ru(bip)$_2$ (dhbipy)$^{2+}$ in the vesicle. The solution-like vesicles (3m*l*) were placed in a quartz rectangular cuvette (10mm) and then deaerated with Ar gas. The 10mm cuvette was irradiated with 308 nm radiation from XeCl excimer laser. Luminescence was detected at right angle to the path of excitation beam. The luminescence was focussed onto the slit of a spex double monochromator. In this experiment, the photocurrent from a Thorn EMI 9789 QB photomultiplier was applied directly to a Nicolet LAS 12/70 Signal Averager (0.1 sec/ch). It was possible to digitize and observe the "tail-end" of the transient luminescence
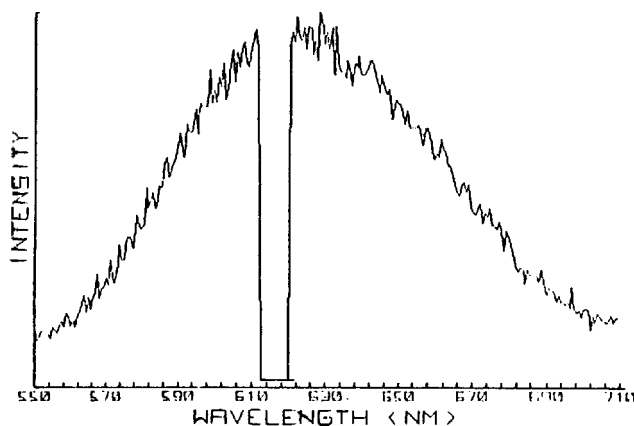
Figure 2. The luminescence spectra of [Ru(bipy)$_2$ (dhbipy)]$^{2+}$.

Table 1. Lifetime of Ru(bipy)$_2$ (dhbipy)$^{2+}$ Luminescence in the Cationic Vesicle[a]

Channel Number (time, t)	Channel Number (Intensity, I)	Ln I
0	2.7	0.99
1	1.9	0.64
2	1.3	0.26
3	0.9	−0.11
4	0.5	−0.69
5	0.4	−0.92

(a) 200ns/channel, 0.05μs delay.

signal from the sample. Digital values from several signal averager channels were averaged for each wavelength at which observation were made. The use of a computer graphics program to plot these results vs. wavelength afforded pictorial representation of the spectrum. (see Fig. 2).

Lifetime measurement of [Ru(bipy)$_2$ (dhbipy)]$^{2+}$ in the vesicle. The optical arrangement is identical to that for luminescence spectra experiment. However, for this experiment the photomultiplier current was applied to a 50 Ω load. The voltage across the load was monitored with a Tektronix 2465 oscilloscope. Values for the amplitude of the decaying signal were visually estimated at various values of the oscilloscope time-base(see table 1). A log plot of these results and subsequent least squares analysis yielded the lifetime of the excited Ru(bipy)$_2$ (dh bipy).$^{2+}$

Transient absorption spectra of Phenothiazine derivative in the vesicle system. To get the transient absorption spectra of PTD in the vesicles the following experiment has been done. The mixture containing ruthenium complex with two long hydrocarbon chains, [Ru (bipy)$_2$ (dhbipy)]$^{2+}$ (0.6 mg), PTD (2.5mg), dodecy dimethyl ammonium bromide (13.4mg), and water (5m*l*) was stirred with Vortex mixer and then heated to boiling for 2 sec. For this experiment, excitation of the vesicle was provided by the 308 nm radiation from an excimer laser. Probing of the optical absorption of intermediate produced by excitation was provided by a D.C. powered tungsten lamp. The beam of the tungsten lamp was focussed on the slit of monochromator and the resulting photocurrent applied to a Nicolet 12/70 Signal Averager, after being passed through a preamplifier. Probe and excitation beams propagated through the sample cell at right angle. The signal averager is used to observe the relaxation of the probe beam to its initial intensity as the transient absorbing
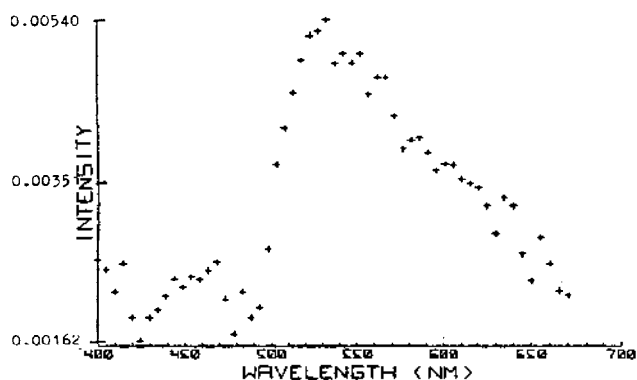
86 *Bull. Korean Chem. Soc., Vol. 9, No. 2, 1988*

Yong Tae Park et al.

Figure 3. Transient absorption spectrum of phenothiazine derivative. (PTD) in the vesicles.
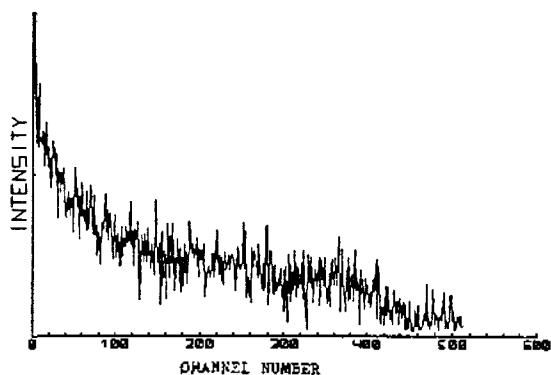

Figure 4. Decay curve measured at 525 nm for PTD cation radical in the vesicle. 1 channel = 200 usec from channel 0 to channel 400. 1 channel = 5m sec from channel 400 to 512.
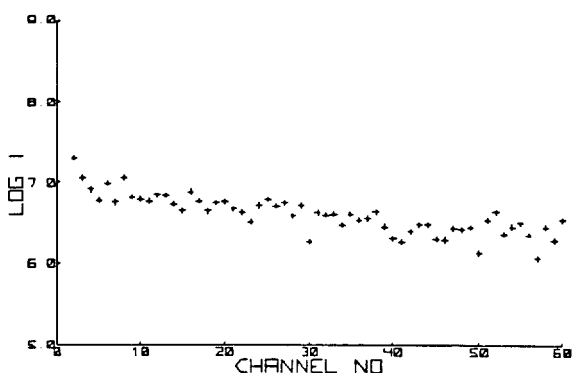

Figure 5. Log plot of the decay curves shown in Figure 4 for the early portion of the curves. 1 channel = $200\,\mu$sec.

species decay. An observation of probe beam intensity at some time after excitation and for a long time after excitation where all absorption has decayed allows computation of the transient optical absorption. When these absorption are plotted vs. wavelength, a transient absorption spectrum results (Fig. 3).

Absorption decay kinetics of PTD cation radical.
The method of the absorption decay kinetics of PTD cation redical in the cationic vesicle was similar to the transient absorption experiment. Now, we tried to accurately obtain decay of the absorption signal at 525 nm. The dual time-base feature of the LAS 12/70 averager was used to accurately digitize the relatively quickly decaying early portion of the

signal while being able to capture the late part of the signal where I(t) approaches I_0. The memory size used was 512 channels. From channel 0 to channel 400 was 200 usec/channel, 5 msec/channel up to channel 511. The electronic filter was 2 KHZ. A delay of 50usec (after laser pulse) was set by the +B gate of the oscilloscope used to trigger the signal averager. 200 scans of the decay were averaged (maximum absorbance turned out to be only about 10^{-3} absorbance units). The data were transferred through an interface to a CYBER 830 computer. The scale of the $\pm$ 0.25V data was corrected for the offset current by using a computer program to add a number corresponding to the offset current to the digital voltage values; i.e., the data were corrected in such a way that the value for channels at the end, near ch. 512, was near the digitally encoded value corresponding to 4.00V. A plot of absorbance vs. channel number was prepared. Also, the absorbance decay was examined for logarithmic decay. Since $A_0 C_T$, C_T is a transient concentration, if C_T has a 1st order decay, then A α e^{-kt}. A computer program that optimizes the value of k (actually $\tau = 1/k$) by a least squares routine was used to "fit" the data. see Fig. 4 and 5.

Results and Discussion

The luminescence of $[Ru(bipy)_2 (dhbipy)]^{2+}$ in the vesicles is shown in Fig. 2. The maximum luminescence of the spectra is 620 nm(E_T = 46 Kcal/mole). The doubling line of laser light (308nm) was eliminated in the spectra. The emission maximum of $(Ru(bipy)_3)^{2+}2Cl^-$ was reported to vary from 605 nm in water to 625 nm in aquous micellar sodium dodecyl sulfate by Infelta *et al* (1980)[5] (see Table 2). The luminescence spectra of $Ru(bipy)_2 (dhbipy)^{2-}$ in the vesicles is similar to that $Ru(bipy)_3^{2+}$ in the micelles. This indicates that the environment of $Ru(bipy)_2 (dhbipy)^{2+}$ in the vesicle was obviously hydrophobic. The life time of the luminescence of the complex with two long hydrocarbon chains in the vesicle solution was 502 ns. This is a quite similar value to that of $(Ru(bipy)^{2+}$ (0.6 us) measured by Lytle *et al.*[6] Lifetime of the ruthenium complex with and/or without quencher, phenothiazine derivative in the vesicle was also observed by oscilloscope. When 100u*l* of PTD, 10-phenothiazineethanol, 2-chloro-α-(dimethylaminomethyl) hydrochloride solution (11 mg of PTD was dissolved in 1m*l* of water) was introduced in 3m*l* of the vesicles, the lifetime was 371ns. Thus the quenching constant by Stern Volmer equation is 9.6 $\times$ 10^8 M^{-1}S.$^{-1}$ The transient absorption spectrum of vesicle system containing ruthenium bipyridine with two long hydrocarbon chain and phenothiazine derivative was shown in Fig. 3. The spectra mainly consists of two bands with maxima located 450 nm and 530 nm. Kiwi and Gräetzel (1978)[7] reported that methylphenothiazine cation radical absorbs at 515 nm band light and the triplet state of methylphenothiazine absorbs 460 nm band in microemulsion

system containing N-methylphenothiazine and methyl viologen. The transient absorption at 530 nm probably is a composite of the absorption due to PTD cation radical and Ru(bipy)₂ (dhbipy),⁺ and that at 450 nm probably is due to PTD triplet state.[5] No such absorption was observed without PTD or Ru(bipy)₂ (dhbipy)²⁺ in the vesicle. Thus the excited state of ruthenium complex with two long hydrocarbon chains was quenched reductively by PTD in the vesicle system. The PTD cation radical is involved in the hydrogen generation vesicle system. The data of absorption decay kinetics were too poor to give consistent fits, but using different portions of the data, estimates for life time could be obtained. That indicates a value in the 4-8 msec range. (see Figure 4 and Figure 5) Also, we saw what appeared to be very weak slow component in the logarithmic plot of the decay. An estimate of the life time of this decay might be of order 20-40 msec. Probably the life of the PTD cation radical is longer in aquous portion than hydrophobic portion. The oxidized PTD cation radical escapes into aquous portion of the

References

1. M. Calvin, *Accts. Chem. Res.*, **11**, 369-374 (1978).
2. M. S. Tunuli, and J. H. Fendler J. *Amer. Chem. Soc.*, **103**, 2507 (1981).
3. J. H. Fendler, *J. Phys. Chem.*, **89**, 2730 (1985).
4. Y.-T. Park, *Bull. Korean Chem. Soc.*, **4**, 149 (1983).
5. P. P. Infelta, M. Gratzel, and J. H. Fendler, *J. Amer. Chem. Soc.*, **102**, 1479 (1980).
6. F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, **91**, 253 (1969).
7. Kiwi J. and M. Gratzel *J. Amer. Chem. Soc.*, **100**, 6314 (1978).

# Substitution Reaction of Fe(CO)₅ by Ethylene

Jaejung Ko

Department of Chemical Education, Korea National University of Education,
Choongbuk 363-890. Received November 9, 1987

The substitution reaction of Fe(CO)₅ by ethylene has been studied for plausible intermediates by means of extended Huckel calculations. Among various reaction mechanisms the favorable reaction pathway is via a dissociative mechanism in which ethylene approaches to Fe(CO)₄ unit. For Fe(CO)₄ fragment, the square planar conformation is found to be the most stable form by the extended Huckel calculations. Our calculations show that ethylene attacks square planar intermediate formed by removing one carbonyl from Fe(CO)₅ and then the unstable species thus formed is distored to the most stable trigonal bipyramid with the ethylene lying in the equatorial plane.

Introduction

Process in which complexes undergo ligand substitution reaction is the most important step in organometallic mechanisms. A delineation of the mechanisms by which these processes occur is vital to a full understanding of the chemistry of complexes.[1] The majority of proposed mechanisms require at least one ligand substitution steps via D, I_d, I_a, or A mechanism.[2] It is well documented[3] that 18 electron ML₆ and 16 electron ML₄ complexes in the organometallic ligand substitution reactions proceed with a dissociative (D or I_d) and an associative mechanism (A or Ia), respectively, albeit considerable ambiguity. Recent reports[4] on the ligand substitution reaction indicate that while 18 electron ML₅, and ML₄ complexes proceed with a dissociative mechanism via a 16 electron intermediate, there still be considerable conflict. Therefore, we chose the system which treats the reaction of Fe(CO)₅ with C₂H₄ because first, we are interested in mechanistic studies on 18 electron ML₅ complexes in order to check whether the system proceeds with a dissociative or associative mechanism, and secondly, little theoretical work has been brought to bear on this subject, and finally, complexes of type Fe(CO)₄ (η²-hydrocarbon) are easily accessible.[5]

The principal substitution process is the replacement of CO by C₂H₂ to form the stable monoethylene complex:

$$Fe(CO)_5 + C_2H_4 \rightarrow Fe(CO)_4(C_2H_4) + CO$$
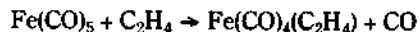
As likely mechanisms for this overall reactions, five mechanisms can be proposed as shown below (1a-e). The first three mechanism is the transient intermediate of reduced coordination number, giving rise to a D mechanism. The last two (1d-e) mechanism is a fully formed intermediate complex, so-called A mechanism. Therefore, computational calculations on each intermediate will help clarify the energetics of this reaction type as well as provide data for transition