



Stabilization and electron spin resonance characterization of $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$ by radiolysis of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed on silica gel

Kaoru Matsuura^{a,1}, Larry Kevan^{b,*}

^a *Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-0494, Japan*

^b *Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA*

Received 1 November 2000; accepted 15 February 2001

Abstract

$\text{Ru}(\text{bpy})_3^{3+}$, which is important in artificial photosynthetic systems due to its high reduction potential, is stabilized together with its counter anion, $\text{Ru}(\text{bpy})_3^+$, by radiolysis of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed on silica gel at 77 K. Both species are characterized by electron spin resonance. © 2001 Elsevier Science Ltd. All rights reserved.

$\text{Ru}(\text{bpy})_3^{3+}$ (bpy is 2,2'-bipyridine), which is formed by oxidative quenching of $\text{Ru}(\text{bpy})_3^{2+}$, is a strong oxidizing agent and can thermodynamically oxidize water to oxygen. Therefore, photochemistry involving $\text{Ru}(\text{bpy})_3^{2+}$, and its use for solar energy conversion have been extensively studied (Gafney and Adamson, 1972; Balzani et al., 1978; Kalyanasundaram, 1982, 1987). However, $\text{Ru}(\text{bpy})_3^{3+}$, formed by photolysis has not been detected directly except for certain cases (Neumann-Spallart, 1980; Berkoff et al., 1980; Matsuura and Kevan, 1996), mainly because back-electron transfer is rapid and usually exothermic. Radiolysis is an excellent technique to generate such intermediates. $\text{Ru}(\text{bpy})_3^{3+}$ has been successfully generated at room temperature by radiolysis of acidic aqueous solution containing a high concentration of LiCl and the yield and stability of $\text{Ru}(\text{bpy})_3^{3+}$, depend on the concentrations of LiCl, $\text{Ru}(\text{bpy})_3^{2+}$ and HCl and on the kind of alkali metal (Mulazzani et al., 1986; Matsuura and Kevan, 1997).

Microporous silica gel is an attractive matrix to generate and stabilize unstable intermediates formed by radiolysis (Thomas, 1993; Werst et al., 1998; Edlund et al., 1967; Wong and Willard, 1968) because the constrained nanospace inside the pores provides an opportunity to control chemical reactions. Radical cations or anions of aromatic hydrocarbons are stabilized in silica gel by high-energy radiation (Edlund et al., 1967; Wong and Willard, 1968). However, less attention has been paid to one-electron oxidation or reduction of organic metal complexes in silica gel by radiolysis. Here, we have studied the radiolysis of $\text{Ru}(\text{bpy})_3^{2+}$ adsorbed on silica gel and found by electron spin resonance (ESR) that $\text{Ru}(\text{bpy})_3^{3+}$ is produced together with its counter anion, $\text{Ru}(\text{bpy})_3^+$, which is also an important intermediate which can reduce water to hydrogen because of its high oxidation potential.

$\text{Ru}(\text{bpy})_3^{2+}$ ions were adsorbed into silica gel as follows. Silica gel powders (2.0 g) were impregnated with 4 ml of 10 mM aqueous solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ for 1 day. The silica gel was filtered, washed with distilled water until the washings became colorless, and then dried in air at 313 K. Then, 0.15 g of the powder samples were filled into Suprasil quartz ESR (2 mm i.d. \times 3 mm o.d.) tubes and dehydrated at 473 K under vacuum for 1 day. Dehydration temperatures higher than 473 K caused damage to the sample. The loading of $\text{Ru}(\text{bpy})_3^{2+}$

*Corresponding author. Tel.: +1-713-743-3250; fax: +1-713-743-2709.

E-mail address: kevan@uh.edu (L. Kevan).

¹Present address: The Institute of Scientific and Industrial Research, Osaka University, Japan.

adsorbed on silica gel was measured optically and was $10 \mu\text{mol g}^{-1}$ of silica gel. For some $\text{Ru}(\text{bpy})_3^{2+}$ /silica gel samples, N_2O , CCl_4 or tetracyanoethylene (TCNE) was added as an electron scavenger. In the case of TCNE, 1.0 g $\text{Ru}(\text{bpy})_3^{2+}$ /silica gel powder was immersed in 4 ml of 60 mM benzene solution of TCNE for 1 day. Then the samples were filtered and dried in air. The amount of the electron scavengers was about 10 times as much as that of the $\text{Ru}(\text{bpy})_3^{2+}$ in all cases. The silica gel powders were γ -irradiated by a ^{60}Co source at 77 K to a total dose of 16 kGy at a dose rate of 16 kGy h^{-1} . ESR measurements were carried out on a JEOL TES-200 X-band spectrometer with 100 kHz magnetic field modulation.

Fig. 1 shows the ESR spectrum observed at 77 K for $\text{Ru}(\text{bpy})_3^{2+}$ /silica gel after γ -irradiation at 77 K. Before irradiation no ESR absorption was observed. The broad ESR absorption observed at $g_{\perp} \sim 2.63$ is assigned to $\text{Ru}(\text{bpy})_3^{3+}$. This g_{\perp} value is in good agreement with reported values (DeSimone and Drago, 1970; Quayle and Lunsford, 1982). The g_{\parallel} component was reported at $g_{\parallel} \sim 1.24$ (Quayle and Lunsford, 1982) but could not be observed in this work, apparently because of its weak intensity. When the sample was annealed at room temperature, the ESR absorption due to $\text{Ru}(\text{bpy})_3^{3+}$ decayed to half its intensity in about 10 min. A sharp doublet with a hyperfine coupling of about 50 mT is also observed and is due to hydrogen atoms.

The central part of the spectrum in Fig. 1 is shown in Fig. 2a. A very broad absorption with a g value less than 2.0023 is observed. For comparison, the ESR spectrum was measured at 77 K for deuterated silica gel after γ -irradiation at 77 K and is shown in Fig. 2b. It is clear that the radical arises from $\text{Ru}(\text{bpy})_3^{2+}$ and not from the silica gel matrix because its intensity depends on the loading of $\text{Ru}(\text{bpy})_3^{2+}$. This radical is assigned to the reduction product of $\text{Ru}(\text{bpy})_3^{3+}$, $\text{Ru}(\text{bpy})_3^+$. This assignment is supported by the lack of this signal when

N_2O , TCNE or CCl_4 were added as electron scavengers although $\text{Ru}(\text{bpy})_3^{3+}$ is still formed. The broad signals due to $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$ survive for 1 day at room temperature.

The spectral features at room temperature are essentially the same as those at 77 K. The g value and the linewidths of $\text{Ru}(\text{bpy})_3^+$ are 1.996 and about 2.5 mT at both 77 K and room temperature. The electrochemical one-electron reduction product of $\text{Ru}(\text{bpy})_3^{2+}$ [i.e. $\text{Ru}(\text{bpy})_3^+$] in acetonitrile has been reported to give a singlet ESR signal at $g = 1.997$ in solution at room temperature and in a frozen solution at 173 K (Motten et al., 1981). The g factor also supports our assignment of $\text{Ru}(\text{bpy})_3^+$.

Motten et al., observed a temperature dependence of the ESR linewidth (9.0 mT at room temperature and 2.6 mT at 173 K) and concluded that the unpaired electron is predominantly in a ligand π^* orbital rather than in a metal d orbital and that the unpaired electron is localized on a single bipyridine ligand at 173 K with the smaller linewidth and hops among the three bipyridine ligands at room temperature with a larger linewidth (Motten et al., 1981). The linewidth of $\text{Ru}(\text{bpy})_3^+$ observed in silica gel is about 2.5 mT at both 77 K and room temperature and does not depend on temperature. By comparison with Motten's work, this linewidth indicates that the electron is localized on one bipyridine ligand at both room temperature and 77 K in silica gel since this is a solid state system.

Fig. 3 shows the ESR spectrum at 77 K for $\text{Ru}(\text{bpy})_3^{2+}$ /silica gel with TCNE after irradiation at

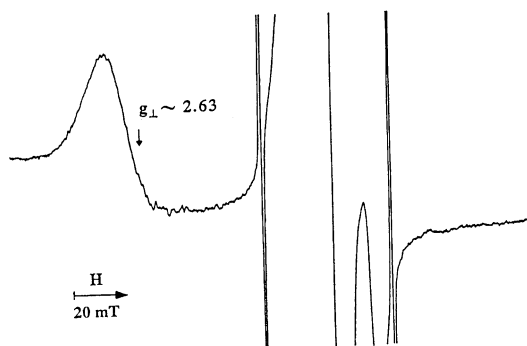


Fig. 1. ESR spectrum at 77 K of $\text{Ru}(\text{bpy})_3^{2+}$ on silica gel after γ -irradiation of $\text{Ru}(\text{bpy})_3^{2+}$ /silica gel at 77 K. The loading of $\text{Ru}(\text{bpy})_3^{2+}$ ions is $10 \mu\text{mol}$ per g of silica gel. The microwave power is 1 mW.

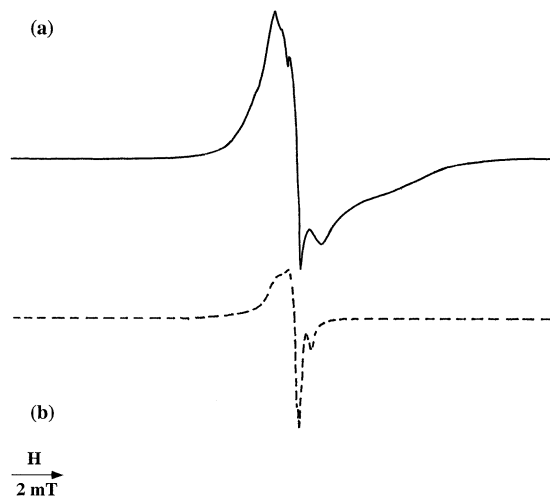


Fig. 2. (a) ESR spectrum at 77 K of $\text{Ru}(\text{bpy})_3^{2+}$ on silica gel after γ -irradiation of $\text{Ru}(\text{bpy})_3^{2+}$ /silica gel at 77 K (the expanded central portion of the spectrum in Fig. 1). The microwave power is $100 \mu\text{W}$. (b) ESR spectrum at 77 K of $\text{Ru}(\text{bpy})_3^{2+}$ on deuterated silica gel after γ -irradiation of $\text{Ru}(\text{bpy})_3^{2+}$ /silica gel at 77 K.

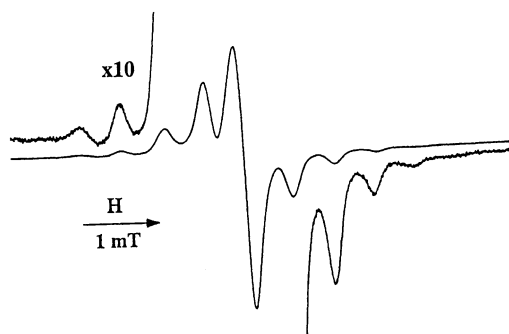


Fig. 3. ESR spectrum at 77 K of TCNE^- on silica gel after γ -irradiation of $\text{Ru}(\text{bpy})_3^{2+}/\text{TCNE}/\text{silica gel}$ at 77 K. The microwave power is $6 \mu\text{W}$. The loadings of $\text{Ru}(\text{bpy})_3^{2+}$ and TCNE are 10 and $100 \mu\text{mol g}^{-1}$ of silica gel.

77 K. Only the central portion of the spectrum is shown. In addition to $\text{Ru}(\text{bpy})_3^{3+}$ (not shown), a strong nine-line signal is observed and is assigned to TCNE^- (Gendell et al., 1964; Flockhart et al., 1969; Wong and Allen, 1969). $\text{Ru}(\text{bpy})_3^+$ was not generated in the presence of TCNE.

In summary, silica gel provides stabilization of ionic radicals of adsorbed organic molecules by radiolysis. We have applied this useful matrix for the production of radical ions of transition metal complexes. Radiolysis of $\text{Ru}(\text{bpy})_3^{2+}$ in silica gel successfully stabilizes the oxidation product $\text{Ru}(\text{bpy})_3^{3+}$ together with the reduction product $\text{Ru}(\text{bpy})_3^+$. Charge separation has also been achieved for $\text{Ru}(\text{bpy})_3^{2+}/\text{silica gel}$ with tetracyanoethylene (TCNE) to form $\text{Ru}(\text{bpy})_3^{3+}$ and TCNE^- .

This work was supported by the REIMEI Research Resources of the Japan Atomic Energy Research Institute, Science and Technology Agency of Japan and by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

References

- Balzani, V., Bolletta, F., Gandolfi, M.T., Maestri, M., 1978. Bimolecular electron transfer reactions of the excited states of transition metal complexes. *Topics Curr. Chem.* 75, 1–64.
- Berkoff, R., Krist, K., Gafney, H.D., 1980. Measurement of the rates of the electron-transfer reactions between $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Co}(\text{phen})_3^{2+}$ or $\text{Co}(\text{bpy})_3^{2+}$ by flash photolysis techniques. *Inorg. Chem.* 19, 1–7.
- DeSimone, R.E., Drago, R.S., 1970. Magnetic resonance studies of some low-spin d_5 trisdiimine complexes. *J. Am. Chem. Soc.* 92, 2343–2352.
- Edlund, O., Kinell, P.-O., Lund, A., Shimizu, A., 1967. Electron spin resonance spectra of monomeric and dimeric cations of benzene. *J. Chem. Phys.* 46, 3679–3680.
- Flockhart, B.D., Leith, I.R., Pink, R.C., 1969. Electron transfer at alumina surfaces II. Electron donor properties of aluminas. *Trans. Faraday Soc.* 65, 542–551.
- Gafney, H.D., Adamson, A.W., 1972. Excited state of $\text{Ru}(\text{bpy})_3^{2+}$ as an electron-transfer reductant. *J. Am. Chem. Soc.* 94, 8328–8329.
- Gendell, J., Freed, J.H., Fraenkel, G.K., 1964. Lineshapes in electron spin resonance spectra. *J. Chem. Phys.* 41, 949–959.
- Kalyanasundaram, K., 1982. Photophysics, photochemistry and solar energy conversion with tris(bipyridyl)ruthenium(II) and its analogs. *Coord. Chem. Rev.* 46, 159–244.
- Kalyanasundaram, K., 1987. Photochemistry in Microporous Systems. Academic, Orlando, FL.
- Matsuura, K., Kevan, L., 1996. Stabilization and electron spin resonance characterization of $\text{Ru}(\text{bpy})_3^{3+}$ in silica gel by chemical oxidation and photoinduced electron transfer. *J. Phys. Chem.* 100, 10652–10657.
- Matsuura, K., Kevan, L., 1997. Stabilization and electron spin resonance characterization of $\text{Ru}(\text{bpy})_3^{3+}$ formed by radiolysis in concentrated alkalimetal halide solutions. *J. Chem. Soc. Faraday Trans.* 93, 1763–1768.
- Motten, A.G., Hanck, K., DeArmond, M.K., 1981. ESR of the reduction products of $\text{Fe}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$. *Chem. Phys. Lett.* 79, 541–546.
- Mulazzani, Q.G., Venturi, M., Bolletta, F., Balzani, V., 1986. Radiolytically induced outer-sphere oxidation of tris(bipyridine)ruthenium(II) ion in lithium chloride-water solutions. *Inorg. Chim. Acta.* 113, L1–L2.
- Neumann-Spallart, M., Kalyanasundaram, K., Graetzel, C., Graetzel, M., 1980. Ruthenium dioxide electrodes as suitable anodes for water photolysis. *Helv. Chim. Acta.* 63, 1111–1118.
- Quayle, W.H., Lunsford, J.H., 1982. Tris (2,2'-bipyridine)ruthenium(III) in zeolite Y: characterization and reduction on exposure to water. *Inorg. Chem.* 21, 97–103.
- Thomas, J.K., 1993. Physical aspects of the photochemistry and radiation chemistry of molecules adsorbed on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, zeolites and clays. *Chem. Rev.* 93, 301–320.
- Werst, D.W., Han, P., Trifunac, A.D., 1998. Radiation chemical studies in zeolites: radical cations and zeolite catalysis. *Radiat. Phys. Chem.* 51, 255–262.
- Wong, P.K., Allen, A.O., 1969. Charge transfer to molecules on the surface or irradiated porous glass. *J. Phys. Chem.* 74, 774–778.
- Wong, P.K., Willard, J.E., 1968. Evidence for electron migration during γ -irradiation of silica gels: reactions of adsorbed electron scavengers. *J. Phys. Chem.* 72, 2623–2627.