

Charge transfer photochemistry of $\text{Ru}(\text{bpz})_3^{2+}$ with carboxylic acids and carboxylate ions

P. Thanasekaran^a, S. Rajagopal^{a,*}, C. Srinivasan^b

^aSchool of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

^bDepartment of Materials Science, Madurai Kamaraj University, Madurai 625 021, India

Received 23 June 1998; received in revised form 25 September 1998; accepted 23 October 1998

Abstract

$\text{Ru}(\text{bpz})_3^{2+}$ (bpz = 2,2'-bipyrazine) has six peripheral uncoordinated nitrogen atoms potentially available for protonation in presence of acids. The emission from $^*\text{Ru}(\text{bpz})_3^{2+}$ is efficiently quenched by organic acids and the observed quenching rate constants are explained in terms of proton transfer from acids to $^*\text{Ru}(\text{bpz})_3^{2+}$. The absorption and emission intensity of $\text{Ru}(\text{bpz})_3^{2+}$ increases with increasing concentration of carboxylate ion suggesting the complex formation between the two reactants in the ground state. From these studies, the formation constant (K_f) have been evaluated by Benesi–Hildebrand method. The K_f values indicate that generally the ion pair association constants estimated from absorption and emission techniques are comparable and these values are sensitive to the structure of the carboxylate ions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: $\text{Ru}(\text{bpz})_3^{2+}$; Carboxylic acids; Proton transfer quenching; Carboxylate ions; Ion pair formation

1. Introduction

Ruthenium(II)-polypyridyl complexes play an important role in the development of efficient photosensitizers to use them in many applications [1–8]. The ground and excited state properties of these complexes can be tuned by judicious choice of ligands [7,8]. The photoinduced electron transfer (ET) reactions between ruthenium(II) complexes and various organic substrates have been extensively studied with special reference to chemical conversion and storage of light energy [9,10]. $\text{Ru}(\text{bpz})_3^{2+}$ (bpz = 2,2'-bipyrazine) has been shown to be an excellent photocatalyst and has six peripheral non-coordinated nitrogen atoms potentially available for protonation in presence of acids [11–17] and therefore, the excited-state acid–base properties of $\text{Ru}(\text{bpz})_3^{2+}$ have been extensively studied [16,17]. On the other hand, the oxalate ion undergoes electron transfer reaction with this complex [18,19]. Thus, $^*\text{Ru}(\text{bpz})_3^{2+}$ is quenched by either ET or proton transfer process depending on the nature of the quencher. Therefore to understand the behaviour of different carboxylic acids towards this metal ion the authors studied the reactions of $^*\text{Ru}(\text{bpz})_3^{2+}$ with several carboxylic acids and their anions in acetonitrile and aqueous media, respectively, and the results are presented in this report.

2. Experimental details

$\text{Ru}(\text{bpz})_3^{2+}$ was synthesized as its chloride salt and purified by column chromatography [20]. All organic acids used in the present study were purified by vacuum distillation or by recrystallization before use. The carboxylate ions were prepared by mixing stoichiometric amounts of corresponding acids and NaOH. The absorption and emission spectral measurements were performed using JASCO model UV–Vis spectrophotometer and JASCO FP-770 spectrofluorometer, respectively. The solutions used for emission measurements were deaerated by bubbling dry N_2 gas for 20 min. The quenching rate constant, k_q , was determined by luminescence quenching technique using the Stern–Volmer Eq. (1).

$$\frac{I^0}{I} = 1 + k_q\tau^0[\text{RCOOH}] \quad (1)$$

In Eq. (1), I^0 and I are the emission intensities of $^*\text{Ru}(\text{bpz})_3^{2+}$ in the absence and presence of quencher and τ^0 is the emission lifetime of the metal complex in the absence of quencher. The Stern–Volmer plots for the luminescence quenching of $^*\text{Ru}(\text{bpz})_3^{2+}$ with various organic acids are linear and the sample plots are shown in Fig. 1. The details of the laser flash photolysis studies are described in the previous report [21].

*Corresponding author. Fax: +91-452-85239.

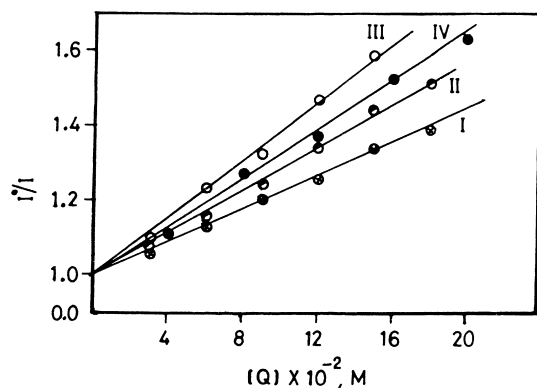


Fig. 1. Stern-Volmer plots for the quenching of $^*\text{Ru}(\text{bpz})_3^{2+}$ with $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ (I), $\text{CH}_3\text{CO}_2\text{H}$ (II), $\text{HSCH}_2\text{CO}_2\text{H}$ (III) and $\text{C}_6\text{H}_5\text{SCH}_2\text{CO}_2\text{H}$ (IV) in acetonitrile at 298 K.

3. Results and discussion

It is well known that $^*\text{Ru}(\text{bpz})_3^{2+}$ ($E^0 = 1.45\text{V}$ versus SCE) is a better oxidant than $^*\text{Ru}(\text{bpy})_2^{3+}$ ($E^0 = 0.80\text{V}$) and its excited state reduction potential is similar to Cr(III)-polypyridyl complexes ($E^0 = 1.44\text{V}$) [22]. Apart from this, the main difference between $\text{Ru}(\text{bpz})_3^{2+}$ and $\text{Ru}(\text{bpy})_2^{3+}$ is that the former has interesting acid-base properties [16,17]. Since the initial report by Crutchely and Lever [11–13] on the synthesis of $\text{Ru}(\text{bpz})_3^{2+}$, many investigations have been devoted to the study of the chemical, photophysical, photochemical, radiation chemical and electrochemical properties of that complex [4–10]. The photoinduced electron and proton transfer reactions of $\text{Ru}(\text{bpz})_3^{2+}$ with different organic compounds have been studied by different groups [11–15,18,19,21]. To learn more on the excited state properties of $\text{Ru}(\text{bpz})_3^{2+}$, its reaction with several carboxylic acids and carboxylate ions has been investigated. The quenching rate constants for $^*\text{Ru}(\text{bpz})_3^{2+}$ with some organic acids in acetonitrile are given in Table 1. From the quenching rate constant data, we understand that the efficiency of quenching depends on the structure of acids. All acids employed here are weak acids and have $\text{p}K_a$ values in the range of 3–5. The observed k_q values are also in a small range $3.0\text{--}15.0 \times 10^6 \text{M}^{-1} \text{s}^{-1}$. It has already been established [11–17]

Table 1

Quenching rate constants (k_q) for the quenching of $^*\text{Ru}(\text{bpz})_3^{2+}$ with organic acids in acetonitrile

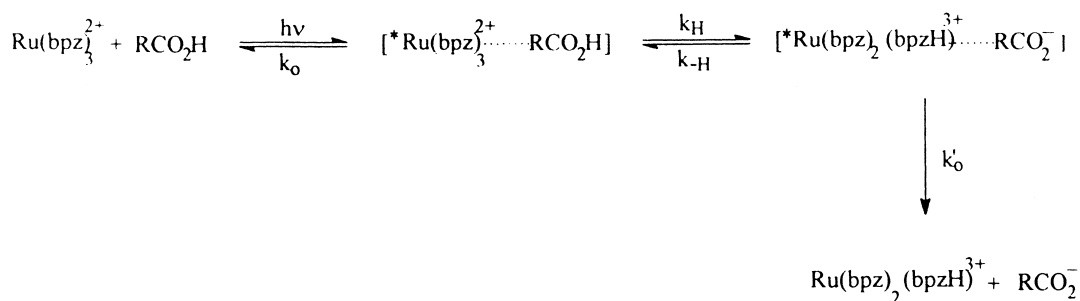
Quencher	$\times 10^{-6} k_q (\text{M}^{-1} \text{s}^{-1})$
CH_3COOH (4.76) ^a	4.7
PhCOOH (4.21)	3.7
PhCH_2COOH (4.31)	15.0
$\text{PhSCH}_2\text{COOH}$ (4.74)	5.5
$\text{PhOCHD}_2\text{COOH}$ (3.17)	4.9 ^b
$\text{PhSO}_2\text{CH}_2\text{COOH}$ (4.50)	8.9
HSCH_2COOH (4.70)	6.3
$\text{S}(\text{CH}_2\text{COOH})_2$ (4.90)	3.3

^a $\text{p}K_a$ values are in water at 25°C.

^bAs this acid is insoluble in water, the k_q value is measured in ethanol medium.

that the emission from $^*\text{Ru}(\text{bpz})_3^{2+}$ is efficiently quenched by protons and the quenching rate constants at appreciable $[\text{H}^+]$ are in the order of diffusion controlled rate. The emission is almost completely quenched if the emission intensity of $^*\text{Ru}(\text{bpz})_3^{2+}$ is recorded with a solution of $[\text{H}^+] > 0.1\text{M}$. i.e., the quenching efficiency depends on $[\text{H}^+]$. As the quenchers used here are weak acids, the available $[\text{H}^+]$ is calculated from the $\text{p}K_a$ values of these acids and the values fall in the range 3.5×10^{-4} – $7.9 \times 10^{-4}\text{M}$. As the concentration of H^+ used in the present study is small compared to the $[\text{H}^+]$ used by Hoffman and co-workers [14,15], the quenching constant is small. Thus, proton transfer mechanism may be proposed for the quenching of $^*\text{Ru}(\text{bpz})_3^{2+}$ with organic acids and the details are summarised in the Scheme 1. Here k_H and k_{-H} are the rate constants for the protonation and deprotonation of the excited states and k_0 and k'_0 are the rate constant for the decay of the deprotonated and protonated excited states, respectively.

It may be pointed out that though the protonated form of $^*\text{Ru}(\text{bpz})_3^{2+}$ is emissive, its lifetime is small compared to the unprotonated complex. The τ values of $^*\text{Ru}(\text{bpz})_3^{2+}$ in the absence and presence of 0.3 M of H^+ are 940 and 47 ns, respectively [14,15] and these τ values reflect the efficiency of quenching of $^*\text{Ru}(\text{bpz})_3^{2+}$ by protons.



Scheme 1. Mechanism for proton transfer quenching

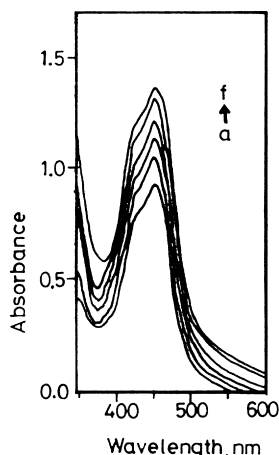


Fig. 2. The change in the absorbance of $\text{Ru}(\text{bpz})_3^{2+}$ with increasing concentration of phenylthioacetate ion in aqueous medium. (a) 0; (b) 3×10^{-2} ; (c) 6×10^{-2} ; (d) 9×10^{-2} ; (e) 12×10^{-2} and (f) 15×10^{-2} M.

Photoredox quenching of Cr(III)-polypyridyl complexes with phenylthioacetic acids and phenylthioacetate ions has extensively been studied in this laboratory [23]. The interesting observation is that the quenching proceeds by electron transfer from sulphur centre to Cr(III) in thioacetic acids and from CO_2^- to Cr(III) with thioacetate ions [23]. In order to check whether organic acids and the corresponding carboxylate ions have similar or different behaviour, the reaction of $\text{Ru}(\text{bpz})_3^{2+}$ with several carboxylate ions has been studied by absorption and emission techniques. The absorption and emission spectra of $\text{Ru}(\text{bpz})_3^{2+}$ at different $[\text{RCO}_2^-]$ are shown in Figs. 2 and 3. The absorption intensity of $\text{Ru}(\text{bpz})_3^{2+}$ increases with increasing concentration of carboxylate ion suggesting the complex formation between the two reactants in the ground state. The formation constant of

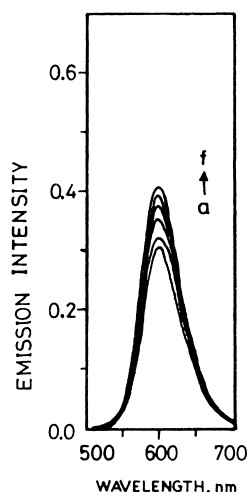
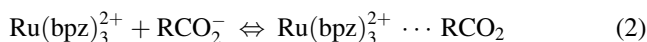


Fig. 3. The change in the emission intensity of $^*\text{Ru}(\text{bpz})_3^{2+}$ with increasing concentration of phenylthioacetate ion in aqueous medium. (a) 0; (b) 3×10^{-2} ; (c) 6×10^{-2} ; (d) 9×10^{-2} ; (e) 12×10^{-2} and (f) 15×10^{-2} M.

the complex between $\text{Ru}(\text{bpz})_3^{2+}$ and RCO_2^- in the ground state (Eq. (2)) is calculated from the change in absorption intensity of $\text{Ru}(\text{bpz})_3^{2+}$ at different $[\text{RCO}_2^-]$ by using Eq. (3) by Benesi–Hildebrand method [24–26].



$$\frac{[\text{oxidant}][\text{substrate}]}{\Delta\text{OD}} = \frac{[\text{oxidant}] + [\text{substrate}]}{\Delta\epsilon} + \frac{K_f}{\Delta\epsilon} \quad (3)$$

In Eq. (3) $\Delta\epsilon$ is the difference in molar absorption coefficient of $\text{Ru}(\text{bpz})_3^{2+}$ in the presence and absence of carboxylate ion, K_f is the equilibrium constant for the formation of the association complex between $\text{Ru}(\text{bpz})_3^{2+}$ and quencher. Similar trend in the emission intensity of $^*\text{Ru}(\text{bpz})_3^{2+}$ with the change of $[\text{RCO}_2^-]$ was also noted. The association constant $\text{Ru}(\text{bpz})_3^{2+} \cdots \text{RCO}_2^-$ ion pair was also evaluated by the modified Benesi–Hildebrand (double reciprocal plot) method [24–26] (Eq. (4)).

$$\frac{1}{I - I_0} = \frac{1}{[Q]aK_f} + \frac{1}{a} \quad (4)$$

In Eq. (4) I and I_0 are the emission intensities of sensitizer in the presence and absence of quencher, respectively, and K_f is the equilibrium constant for the formation of $\text{Ru}(\text{bpz})_3^{2+} \cdots \text{RCO}_2^-$ ion pair and a is a constant. The formation constants of the $\text{Ru}(\text{bpz})_3^{2+} \cdots \text{RCO}_2^-$ ion pair from the absorption and emission spectral studies in aqueous medium evaluated from (Eqs. (3) and (4)) are collected in Table 2. The existence of a complex between $\text{Ru}(\text{bpz})_3^{2+}$ and phenylthioacetate ion in the excited state is also confirmed from the increase in the τ value of $^*\text{Ru}(\text{bpz})_3^{2+}$ from 940 to 1050 ns in the presence of thioacetate ion. This result suggests that the ion pair in the excited state [$^*\text{Ru}(\text{bpz})_3^{2+} \cdots \text{RCO}_2^-$] is emissive.

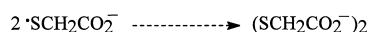
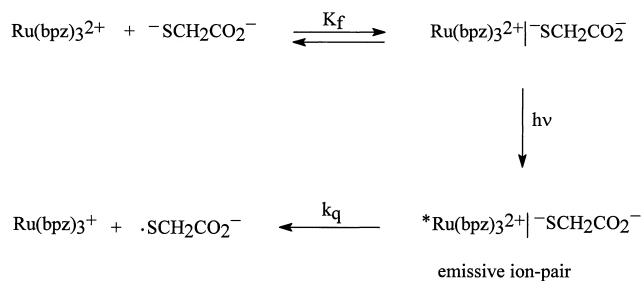
The K_f values given in Table 2 indicate that generally the ion pair association constants estimated from absorption and emission techniques are comparable confirming our postulate of ion pair formation between $\text{Ru}(\text{bpz})_3^{2+}$ and RCO_2^- . These association constant values are small compared to the values observed for the ion pair formed between $\text{Ru}(\text{bpz})_3^{2+}$ and inorganic ions like $\text{S}_2\text{O}_8^{2-}$, PtCl_4^{2-} , $\text{Cr}(\text{CN})_6^{3-}$ etc., which are in the range of 200–3600 M^{-1} [27,28]. But the present values are close to the values calculated from the

Table 2

Formation constant (k_f) values of the complex formed between $\text{Ru}(\text{bpz})_3^{2+}$ and RCO_2^- in aqueous medium

Substrate	$K_f(\text{abs})$	$K_f(\text{em})$
CH_3COO^-	11.4	3.50
PhCOO^-	8.00	2.50
$\text{PhCH}_2\text{COO}^-$	9.60	5.60
$\text{PhOCH}_2\text{COO}^-$	1.2	2.30
$\text{PhSO}_2\text{CH}_2\text{COO}^-$	7.40	7.00
$^- \text{SCH}_2\text{COO}^-$	19.8	q
$\text{S}(\text{CH}_2\text{COO}^-)_2$	13.7	11.3

q , quenching rate constant; $k_q = 2.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.



Scheme 2.

classical Fuoss–Bjerrum model of electrostatic attraction [29]. Further the values are sensitive to the structure of the carboxylate ion. Replacement of alkyl by phenyl groups lowers the K_f value and replacement of oxygen by sulphur leads to appreciable increase in K_f value. Compared to the phenyl group, the methyl group is electron releasing and thus the electron density of $-\text{CO}_2^-$ is high, thereby favouring ion-pair formation. Similar explanation can be offered when the K_f value of $\text{PhSCH}_2\text{CO}_2^-$ is compared with $\text{PhOCH}_2\text{CO}_2^-$ and $\text{PhSO}_2\text{CH}_2\text{CO}_2^-$. Phenylthio group is electron releasing compared to phenoxy and PhSO_2 is electron attracting group. In the case of thioglycollate ion, ET quenching process takes place in the excited state. The quenching rate constant for the reductive quenching of $*\text{Ru}(\text{bpz})_3^{2+}$ with thioglycollate ion is similar to those of organic sulphides [30]. This may point out that the quenching process proceeds through ET from sulphur centre to $*\text{Ru}(\text{bpz})_3^{2+}$ and the tentative mechanism (static quenching) shown in Scheme 2 may be postulated for the quenching process.

That the electron is transferred from sulphur centre to $*\text{Ru}(\text{bpz})_3^{2+}$ and not from $-\text{CO}_2^-$ is evident by comparing the results observed with $^-\text{SCH}_2\text{CO}_2^-$ and $\text{S}(\text{CH}_2\text{CO}_2^-)_2$. Though luminescence quenching is the process with the former, luminescence enhancement takes place with the latter. It is interesting to recall that sulphur centre is the site of attack when sulphur containing amino acids are used as the quenchers for the excited state aromatic ketones [31–34]. The enhancement in emission may be attributed to the formation of emissive ion-pair complex.

In the luminescence quenching of $*\text{Ru}(\text{bpz})_3^{2+}$ with organic sulphides we have established the formation of exciplex between $*\text{Ru}(\text{bpz})_3^{2+}$ and R_2S from the solvent effect study [30]. Through luminescence quenching is the major process in polar solvents like CH_3CN and aqueous CH_3CN , the increase in the emission intensity and lifetime has been noticed in the less polar solvent, dichloromethane. The low quenching constant ($2.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) observed here similar to organic sulphides leads the authors to presume that here also the exciplex formation is competing with ET process.

Acknowledgements

One of the authors (P.T.) thanks the CSIR for the award of Senior Research Fellowship. The authors thank Prof. P. Natarajan and Dr. P. Ramamurthy, University of Madras for their help in laser flash photolysis studies.

References

- [1] E. Pelizzetti, M. Schiavello (Eds.), Photochemical Conversion and Storage of Solar Energy, Kluwer, Dordrecht, The Netherlands, 1991.
- [2] B. O'regan, M. Gratzel, *Nature* 353 (1991) 737.
- [3] M. Gratzel, *Comments Inorg. Chem.* 12 (1991) 93.
- [4] J. Klaffer, J.M. Drake, (Eds.), *Molecular Dynamics in Restricted Geometries*, Wiley, New York, 1989.
- [5] M. Gratzel, K. Kalyanasundaram, (Eds.), *Kinetics and Catalysis in Microheterogeneous Systems*, Marcel Dekker, New York, 1991.
- [6] O. Horvath, K.L. Stevenson, *Charge Transfer Photochemistry of Coordination Compounds*, VCH, New York, 1993.
- [7] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 1992.
- [8] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* 84 (1988) 85.
- [9] K. Kalyanasundaram, M. Gratzel, (Eds.), *Photosensitization and Photocatalysis using Inorganic and Organometallic Compounds*, Kluwer Academic, Dordrecht, 1993.
- [10] G.J. Kavarnos, *Fundamentals of Photoinduced Electron Transfer*, VCH, New York, 1993.
- [11] M.A. Haga, E.S. Dodsworth, G. Eryavec, P. Seymour, A.B.P. Lever, *Inorg. Chem.* 24 (1985) 1901.
- [12] D.R. Prasad, M.Z. Hoffman, *J. Phys. Chem.* 108 (1986) 2568.
- [13] R.J. Crutchely, A.B.P. Lever, *Inorg. Chem.* 21 (1982) 2766.
- [14] H. Sun, M.Z. Hoffman, *J. Phys. Chem.* 97 (1993) 5014.
- [15] T. Ohno, A. Yoshimura, N. Mataga, S. Tazuke, Y. Kawanishi, N. Kitamura, *J. Phys. Chem.* 93 (1989) 3546.
- [16] J.G. Vos, *Polyhedron* 11 (1992) 2285.
- [17] R.J. Crutchley, N. Kress, A.B.P. Lever, *J. Am. Chem. Soc.* 105 (1983) 1170.
- [18] H. Sun, M.Z. Hoffman, *J. Phys. Chem.* 98 (1994) 11719.
- [19] S. Nishida, Y. Harima, K. Yamashita, *Inorg. Chem.* 28 (1989) 4073.
- [20] Y. Kawanishi, N. Kitamura, S. Tazuke, *Inorg. Chem.* 28 (1989) 2968.
- [21] P. Thanasekaran, T. Rajendran, S. Rajagopal, C. Srinivasan, R. Ramaraj, P. Ramamurthy, B. Venkatachalapathy, *J. Phys. Chem. A* 101 (1997) 8195.
- [22] G. Allen Gnanaraj, S. Rajagopal, C. Srinivasan, K. Pitchumani, *Tetrahedron* 49 (1993) 4721.
- [23] G. Allen Gnanaraj, S. Rajagopal, C. Srinivasan, *Tetrahedron* 50 (1994) 9447.
- [24] H.A. Benesi, J.H. Hildebrand, *J. Am. Chem. Soc.* 71 (1949) 2703.
- [25] H. Kondo, H. Naleatani, K. Hiromi, *Biochemistry* 79 (1976) 393.
- [26] W.B. Person, *J. Am. Chem. Soc.* 87 (1965) 167.
- [27] H.S. White, W.G. Becker, A.J. Bard, *J. Phys. Chem.* 88 (1984) 1840.
- [28] J.N. Demas, J.W. Addington, *J. Am. Chem. Soc.* 98 (1976) 5800.
- [29] R.M. Fuoss, *J. Am. Chem. Soc.* 80 (1958) 5059.
- [30] P. Thanasekaran, S. Rajagopal, C. Srinivasan, R. Ramaraj, *Radiation Phys. Chem.* 49 (1997) 103.
- [31] G.L. Hug, B. Marciniak, K. Bobrowski, *J. Phys. Chem.* 100 (1996) 14914.
- [32] G.L. Hug, B. Marciniak, K. Bobrowski, *J. Photochem. Photobiol. A: Chem.* 95 (1996) 81.
- [33] K. Bobrowski, B. Marciniak, G.L. Hug, *J. Am. Chem. Soc.* 114 (1992) 10279.
- [34] B. Marciniak, K. Bobrowski, G.L. Hug, *J. Phys. Chem.* 97 (1993) 11937 and references cited therein.