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Electron transfer reactions of methionine peptides with photochemically generated ruthenium(III)–polypyridyl complexes

Dharmaraj Thiruppathi [a], Periyakaruppan Karuppasamy [a], Muniyandi Ganesan [a,*], Veluchamy Kamaraj Sivasubramanian [a,b], Thangamuthu Rajendran [a,c], Seenivasan Rajagopal [d,**]

[a] Post Graduate and Research Department of Chemistry, Vivekananda College, Thiruvedakam West, Madurai 625234, India
[b] Department of Chemistry, K.L.N College of Information Technology, Pottapalayam, Sivagangai 630611, India
[c] Department of Chemistry, PSNA College of Engineering and Technology, Dindigul 624622, India
[d] School of Chemistry, Madurai Kamaraj University, Madurai 625021, India

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ABSTRACT

The dynamics of the oxidation of five methionine carrying peptides with six Ru(III)–polypyridyl complexes in aqueous acetonitrile medium have been followed by spectrophotometric technique. The electron transfer (ET) reaction of $[Ru(NN)_3]^{3+}$ complex (NN = polypyridyl ligand) with peptide containing methionine is sensitive to the change in the structure of ligand of Ru(III) complex and N-terminal component of the peptide Met-Gly Met-Ala Met-Ser Met-Val and Met-Leu. The reaction follows the overall second-order kinetics, first order each in the oxidant and the substrate. Based on the substituent and solvent effects, an outer-sphere electron transfer from the sulfur center of the peptide to Ru(III) has been proposed as the rate controlling step of the reaction. The ET nature of the reaction is confirmed from the recorded transient absorption spectrum of peptide containing methionine sulfur radical cation by laser flash photolysis technique. Marcus theory is successfully applied to the ET reaction.

1. Introduction

Protein-based radicals play an important role in the most elaborate biosyntheses in nature, including photosynthesis and respiration [1,2]. Among the different amino acid residues generally found in proteins, methionine (Met) is one of the two amino acids that contain a sulfur atom (the other amino acid is cysteine) and it is most readily oxidized via electron transfer from its sulfur center. Met residues in peptides and proteins are primarily susceptible to oxidation by numerous reactive oxygen species (ROS) [3,4]. In fact, depending on the nature of the oxidizing species, Met can undergo two-electron transfer oxidation or oxygen transfer reaction (with oxidants HOCl, H_2O_2, ROOH, and $ONOO^-$/ONOOH) to give sulfoxide or one-electron oxidation (with $RS^•$, $HO^•$, $RO^•$, $CO_3^{•-}$, $N_3^•$, and $ROO^•$) to give sulfur radical cations [5,6]. One electron oxidation of Met in peptides is likely to play an important role during the pathological conditions of oxidative stress and neurodegenerative diseases such as Alzheimer's and Parkinson's diseases in addition to biological aging processes [7–9] and age-related human cataract formation [10].

The sulfur radical cation formed due to one electron oxidation of methionine can be stabilized by neighboring groups containing electron-rich heteroatoms present in peptides and proteins through the formation of a two-center three-electron bond with an electron pair donor, :X (=O, N, S) [11]. Such an intermediate species is represented as S∴X. Three types of such two-center three electron bonds S∴O, S∴N and S∴S in Met derivatives have been observed in pulse-radiolysis and flash photolysis experiments in aqueous solution [12–14].

The recent study [15] on the $^•$OH-induced oxidation of cyclic dipeptide c-(L-Met-L-Met) highlighted the formation of sulfur radical cations ($>S^{•+}$) stabilized both by intramolecular sulfur–nitrogen bonding with amide nitrogen atoms in the peptide bonds and by intramolecular sulfur–sulfur two-center, three-electron bonding with the unoxidized sulfur atom in the side chain of the other methionine. The authors monitored the formation of such intermediates using time-resolved optical spectroscopy and conductivity. Theoretical and experimental evidence for the formation of three-electron bonds have been well documented [16].

By using time-resolved optical and conductivity methods, Bobrowski and co-workers [17] also studied the reaction of $HO^•$

* Corresponding author. Tel.: +91 4543 258234; fax: +91 4543 258358.
** Corresponding author. Tel.: +91 452 2458246; fax: +91 452 2459139.
E-mail addresses: mganesan58@ymail.com (M. Ganesan), rajagopalseenivasan@yahoo.com (S. Rajagopal).

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radical with two other cyclic dipeptides, cyclo-Gly-Met and cyclo-D-Met-L-Met to generate the sulfur radical cation which is stabilized through the formation of the stable intramolecular S∴N bonded five-membered radial observed in c-(D-Met-L-Met). In addition to this, the stabilization through intermolecular sulfur-sulfur three-electron bonding with the unoxidized sulfur atom on separate cyclic dipeptide molecules was also observed [17]. Interestingly there is no evidence for the intramolecular stabilization by the unoxidized sulfur atom in the neighboring methionine in cyclo-D-Met-L-Met in contrast to the previously reported intramolecular $(S\therefore S)^+$ radical cations established in the c-(L-Met-L-Met) isomer under the same concentrations and pH conditions [15] This type of contrasting behavior is accounted for by the structural changes in the two isomers as seen through molecular-modeling simulations [17].

Morozova et al. [18] through chemically induced dynamic nuclear polarization (CIDNP) technique studied the photooxidation of two sulfur containing peptides, glycylmethionine (Gly-Met) and methionylglycine (Met-Gly) with triplet 4-carboxybenzophenone (CBP). There are two possible mechanisms for this oxidation reaction: (i) electron transfer from the sulfur atom and (ii) electron/proton transfer from the amino group. The later process takes place only in the Met-Gly not for Gly-Met to form the five-membered cyclic radical with a three electron bond between the S and N atoms. In fact theoretical calculations also predicted that the cyclic sulfur–nitrogen two-center, three-electron bonded intermediate with the N-terminal amino group is probably the most stable structure of the species formed from the one-electron oxidation of methionine in aqueous solution [19,20].

To confirm the formation of peptide containing methionine sulfur radical cation as intermediate of the reaction, we have followed the reaction by nanosecond laser flash photolysis technique from which we are able to get the transient absorption spectrum supporting the formation of the intermolecular sulfur–sulfur dimeric three-electron-bonded radical cation Met $(S\therefore S)^+$ during the course of reaction. These radical cations were detected using nanosecond flash photolysis technique. The interesting results of the spectral and kinetic studies on the reaction of five N-terminal methionyl residues with six ruthenium (III) complexes $[Ru(NN)_3]^{3+}$ are presented in this paper. Though several chemical and electrochemical methods are available for the generation of Ru(III) from Ru(II) complexes, in the present study Ru (III) complexes have been generated using visible light irradiation of $[Ru(NN)_3]^{2+}$ in the presence of molecular oxygen [21–25].

2. Experimental

2.1. Chemicals

The ligands, 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmbpy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy), 1,10-phenanthroline (phen), 4,7-diphenyl-1,10-phenanthroline (dpphen) and 4,7-diphenyl-1,10- phenanthroline-disulfonate (BPS) and $RuCl_3{\cdot}3H_2O$ were obtained from Sigma–Aldrich and methionyl-glycine-(Met-Gly), methionyl-alanine-(Met-Ala), methionyl-serine- (Met-Ser), methionine-valine-(Met-Val) and methionyl-leucine-(Met-Leu) (purity > 99%) from Sigma–Aldrich and used without further purification. HPLC grade CH_3CN was obtained from Merck.

2.2. Synthesis and characterization of ruthenium(II)–polypyridyl complexes ($[Ru(NN)_3]^{2+}$

The $[Ru(NN)_3]^{2+}$complexes (where NN = bpy, dmbpy, dtbpy, phen, dpphen and BPS) were synthesized by known procedures [25–29] and characterized by UV–vis, FT-IR, ^1H NMR, ^{13}C NMR and ESI-MS spectral techniques (spectral data are given in the supporting information).

2.3. Photochemical oxidation of $[Ru(NN)_3]^{2+}$ to $[Ru(NN)_3]^{3+}$

The steady-state photolysis of $[Ru(NN)_3]^{2+}$ (2×10^{-5} M) in 2.3 M $HClO_4$, in the presence of molecular oxygen, upon irradiation for 20 min using a 500 W tungsten-halogen lamp led to the formation of the corresponding Ru(III) complex. The infrared (IR) and ultraviolet (UV) radiations were cut-off by passing the light beam through a 30 cm quartz cell filled with water. It was observed that the color of the solution readily changed from orange–yellow to green during irradiation. The formation of $[Ru(NN)_3]^{3+}$ complex was confirmed by recording the absorption spectrum of the irradiated solution. The absorption peak at 450 due to $[Ru(bpy)_3]^{2+}$ disappeared quickly on irradiation for 20 min, resulting in the formation of $[Ru(bpy)_3]^{3+}$ having peaks around 420–430 and 650–670 nm, matching with the reported wavelength of maximum absorption of Ru(III) in acidic aqueous solution [24,30]. These peaks are assigned to charge transfer transitions from the bipyridyl π ligands to the electron-deficient metal (t_{2g}) [31]. The absence of a peak at 450 nm in the absorption spectrum of Ru^{3+} confirms the complete conversion of Ru^{2+} to Ru^{3+}. The absorption spectra of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ are shown in Fig. 1. The percentage conversion of Ru^{2+} to Ru^{3+} determined from the absorption intensity at 650–670 nm is ∼95% in all cases (vide infra). The molar extinction coefficient (ε) of $[Ru(bpy)_3]^{3+}$ at 650–670 nm is 680 $M^{-1}\,cm^{-1}$.

2.4. Kinetic measurements

The absorption spectra of $[Ru(NN)_3]^{2+}$ and $[Ru(NN)_3]^{3+}$ complexes were obtained using a JASCO model 530 UV–vis spectrophotometer. The Ru(III) complexes prepared from the photochemical oxidation of Ru(II) complexes were used for the kinetic study. As the conversion from Ru(II) to Ru(III) is more than 95% (details given in the discussion section), the Ru(III) ion generated in 2.3 M $HClO_4$ was used directly for the oxidation

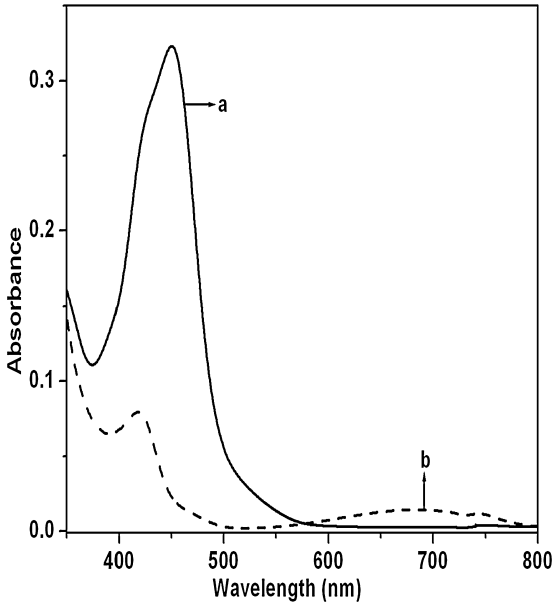


Fig. 1. (a) The absorption spectrum of a solution of 2×10^{-5} M $[Ru(bpy)_3]^{2+}$ complex in oxygen-saturated aqueous CH_3CN (1:1, v/v) solution in the presence of 2.3 M $HClO_4$ and (b) The absorption spectrum of $[Ru(bpy)_3]^{3+}$ obtained from the irradiation of 2×10^{-5} M $[Ru(bpy)_3]^{2+}$ in oxygen saturated aqueous CH_3CN (1:1, v/v) solution in the presence of 2.3 M $HClO_4$.

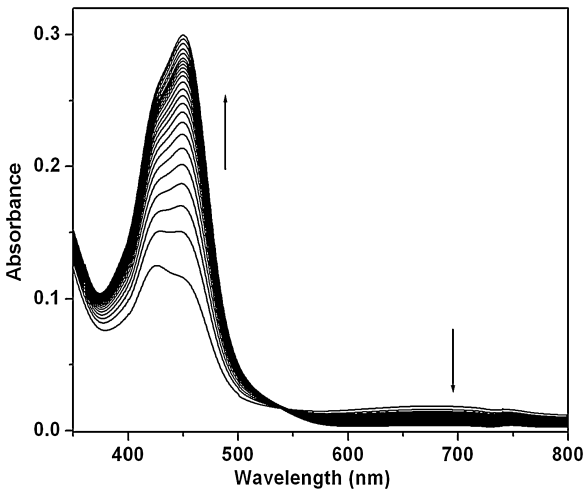


Fig. 2. The absorption spectral changes for the reaction between $[Ru(bpy)_3]^{3+}$ (2×10^{-5} M) and methionylglycine (5×10^{-4} M) in oxygen saturated aqueous CH_3CN (1:1, v/v) solution in the presence of 2.3 M $HClO_4$ at 298 K with 2 min time interval.

reaction. To initiate the reaction 1.5 ml of peptide containing methionine was mixed with 1.5 ml Ru(III) ion in the cuvette. The reaction between the photogenerated $[Ru(NN)_3]^{3+}$ ion with peptide containing methionine was monitored by following the increase in absorbance of $[Ru(NN)_3]^{2+}$ (λ_{max} = 450 nm) at 2 min time interval at 298 K (Fig. 2) [32]. The kinetic studies of oxidation of all peptide containing methionine with $[Ru(NN)_3]^{3+}$ complexes were carried out in aqueous CH_3CN (1:1, v/v) in the presence of 2.3 M $HClO_4$ and molecular oxygen, under pseudo first-order condition. The pseudo first-order rate constant (k_1) for each kinetic run was evaluated from the slope of linear plot of log Abs vs time. A set of duplicate kinetic runs proved that the rate constants were found to be reproducible within ±3%. The second-order rate constant (k_2) is evaluated from the relation $k_2 = k_1/[\text{substrate}]$.

2.5. Electrochemical measurements

The reduction potential of $[Ru(NN)_3]^{3+}$ complexes in aqueous CH_3CN (1:1, v/v) medium were measured by cyclic voltammetric technique using computer controlled Potentiostat CH Instruments Model 680 AMP Booster. $HClO_4$ was used as the supporting electrolyte. The oxidation potentials of peptide containing methionine were measured by differential pulse voltammetry (DPV) and tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte. A glassy carbon (working electrode) and a standard (Ag/Ag^+) electrode (reference electrode) were used in the electrochemical measurements. The sample solutions were deaerated by purging dry nitrogen gas for about 30 min before each measurement. The oxidation potential values of five peptide containing methionine and the reduction potential values of six $[Ru(NN)_3]^{3+}$ complexes are shown in Tables 1 and 2. The reduction potential value of $[Ru(NN)_3]^{3+}$ complexes and the oxidation potential value of peptide containing methionine are in good agreement with the reported values [24,33].

2.6. Laser flash photolysis experiment

The formation and decay of the short lived intermediates due to the reaction between $[Ru(NN)_3]^{3+}$ complex and peptide containing methionine is followed using the transient absorption spectral study with a laser flash photolysis technique employing an Applied Photophysics SP-Quanta Ray GCR-2(10) Nd:YAG laser generating 355 nm pulses (~8 ns pulse width) [34]. The transient absorption at preselected wavelengths was monitored using a Czerny–Turner monochromator with a stepper motor control and a Hamamatsu R-928 photomultiplier tube. A 250 W xenon arc lamp was used as the monitor light source. Experiments were carried out using a flash quartz cells (1 cm) with an optical path length of 0.5 cm for the monitoring beam. The reaction condition used for the flash photolysis experiment was similar to that used for the kinetic studies. The concentrations of $[Ru(dmbpy)_3]^{3+}$ and Met-Gly used for all experiments were 1×10^{-3} M and 0.05 M respectively. Typically 3–5 laser shots were averaged for each kinetic trace. All the measurements were carried out at ambient temperature. The solution was flowed and kinetic traces were taken at 10 nm intervals, usually between 320 and 800 nm. The change in the absorbance of the sample on laser irradiation was used to record the time-resolved absorption transient spectrum. The change in the absorbance on flash photolysis was calculated using the expression.

$$\Delta A = \frac{\log I_0}{(I_0 - \Delta I)}$$

$$\Delta I = (I - I_t)$$

where ΔA is the change in the absorbance at time t, I_0, I and I_t are the voltage after flash, the pretrigger voltage and the voltage at particular time respectively. The time-resolved transient absorption spectrum was recorded by plotting the change in absorbance at a particular time vs wavelength. The experiment was carried out in the absence and presence of molecular oxygen. The presence of oxygen was necessary to generate the Ru^{3+} species from Ru^{2+} photochemically [24,30a,35].

2.7. Product analysis

A sample of 0.02 mM of substrate (Met-Gly) was added to a 0.002 mM solution of $[Ru(dmbpy)_3]^{3+}$ complex in 5 ml aqueous CH_3CN (1:1, v/v). The solution was stirred at 298 K for ≈20 min. The products of the reaction were extracted with chloroform and dried and the solvent was removed. The FT-IR spectral analysis of the product obtained from methionine sulfoxide shows the peaks at 1036 cm^{-1} assigned as S=O stretching frequency of sulfoxide.

Table 1
Second order rate constant (k_2, $M^{-1}\,s^{-1}$) values for the oxidation of peptide containing methionines by $[Ru(NN)_3]^{3+}$ in aqueous CH_3CN (1:1, v/v) at 298 K.

Peptides	Oxidation potential, V (Ag/Ag$^+$)	k_2, M^{-1} s^{-1}								
		$[Ru(bpy)_3]^{3+}$ (0.92 V) (I)			$[Ru(dmbpy)_3]^{3+}$ (0.75 V) (II)			$[Ru(dtbpy)_3]^{3+}$ (0.76 V) (III)		
		Observed	Calculated	ΔG° (eV)	Observed	Calculated	ΔG° (eV)	Observed	Calculated	ΔG° (eV)
Met-Gly	1.50	9.7 ± 0.29	4.3	0.58	0.02 ± 0.001	0.01	0.75	0.01 ± 0.0001	0.01	0.74
Met-Ala	1.47	11.2 ± 0.31	13.5	0.55	0.03 ± 0.001	0.02	0.72	0.02 ± 0.001	0.02	0.71
Met-Ser	1.45	14.7 ± 0.38	15.3	0.53	0.05 ± 0.002	0.04	0.70	0.03 ± 0.001	0.04	0.69
Met-Val	1.49	17.6 ± 0.53	5.7	0.57	0.06 ± 0.002	0.02	0.74	0.02 ± 0.001	0.01	0.73
Met-Leu	1.48	20.4 ± 0.62	8.4	0.56	0.07 ± 0.002	0.03	0.73	0.02 ± 0.001	0.01	0.72

General condition: $[Ru(NN)_3]^{3+} = 2 \times 10^{-5}$ M, [Peptide] = 5×10^{-4} M and $[H^+]$ = 2.3 M.

Table 2
Second order rate constant (k_2, $M^{-1} s^{-1}$) values for the oxidation of peptide containing methionines by $[Ru(NN)_3]^{3+}$ in aqueous CH_3CN (1:1, v/v) at 298 K.

Peptides	Oxidation potential, V (Ag/Ag$^+$)	k_2, $M^{-1} s^{-1}$								
		$[Ru(phen)_3]^{3+}$ (0.92 V) (IV)			$[Ru(dpphen)_3]^{3+}$ (0.89 V) (V)			$[Ru(dspphen)_3]^{3+}$ (0.91 V) (VI)		
		Observed	Calculated	ΔG° (eV)	Observed	Calculated	ΔG° (eV)	Observed	Calculated	ΔG° (eV)
Met-Gly	1.50	12.6 ± 0.38	6.8	0.58	10.4 ± 0.31	1.6	0.61	15.5 ± 0.46	5.0	0.59
Met-Ala	1.47	16.1 ± 0.43	15.2	0.55	13.8 ± 0.38	6.7	0.58	19.6 ± 0.52	9.9	0.56
Met-Ser	1.45	18.4 ± 0.46	23.3	0.53	15.2 ± 0.45	9.8	0.56	23.0 ± 0.64	21.1	0.54
Met-Val	1.49	22.1 ± 0.66	6.6	0.57	17.6 ± 0.47	3.4	0.60	25.7 ± 0.77	5.7	0.58
Met-Leu	1.48	26.5 ± 0.74	9.7	0.56	20.8 ± 0.54	4.7	0.59	29.9 ± 0.89	7.2	0.57

General condition: $[Ru(NN)_3]^{3+} = 2 \times 10^{-5}$ M, [Peptide] = 5×10^{-4} M and $[H^+] = 2.3$ M.

Sulfoxide product after oxidation of methionine is only major product formed under the present experimental conditions. This was also confirmed from the analysis of the product with ^{1}H NMR. ^{1}H NMR (300 MHz, D_2O): $\delta = 2.30$ (2H, *m*), 2.94 (2H, *t*), 3.71 (2H, dd), 4.10 (1H, *t*) and 2.62 ($SOCH_3$, *s*) values are in good agreement with reported values of methionine sulfoxide [10,18]. ^{1}H NMR and IR spectrum of methionine sulfoxide is given in the supporting information (Figs. S1 and S2).

3. Results and discussion

The generation of the Ru(III) ion from the corresponding $[Ru(NN)_3]^{2+}$ complex is carried out as detailed below. The steady-state photolysis of $[Ru(NN)_3]^{2+}$ (2×10^{-5} M) in 2.3 M $HClO_4$, in the presence of molecular oxygen, upon irradiation for 20 min using a 500 W tungsten-halogen lamp led to the formation of the corresponding $[Ru(NN)_3]^{3+}$ complex. The formation of $[Ru(bpy)_3]^{3+}$ complex was confirmed by recording the absorption spectrum of the irradiated solution. The absorption spectra of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ are shown in Fig. 1. To learn the concentration of Ru^{3+} formed from the photochemical oxidation of Ru^{2+}, we estimated the concentration of the Ru^{3+} ion from the absorbance (Abs) values at 420 and 670 nm. Since the band at 670 nm ($\varepsilon = 680\ M^{-1}\ cm^{-1}$) corresponds to Ru^{3+} with no interference from Ru^{2+}, we considered the concentration estimated from the Abs at 670 nm as more reliable. This estimation shows that the chemical conversion of Ru^{2+} to Ru^{3+} is more than 95% under the present experimental conditions and we have used this Ru^{3+} solution directly for kinetic studies.

When $[Ru(NN)_3]^{2+}$ complexes are irradiated in the presence of molecular oxygen, two processes, energy and electron transfer from the excited state $[Ru(NN)_3]^{2+}$ to molecular oxygen, take place to form singlet oxygen and superoxide anion radical, respectively (Eqs. (1) and (2)). Under high acid concentration, the oxidation of Ru^{2+} to Ru^{3+} is highly favored as indicated in Eq. (3). More than 95% conversion of Ru^{2+} to Ru^{3+} in our present experimental condition also supports our argument that electron transfer from $^*[Ru(NN)_3]^{2+}$ to O_2 to produce $O_2^{\bullet-}$ is the predominant reaction here. The high $[H^+]$ chosen in the present study facilitates the generation of Ru^{3+} from the cage as shown in Eq. (3). Thus we propose that under the conditions used in the present study the formation of singlet oxygen through energy transfer is less favored compared to electron transfer (ET) and most of the Ru^{2+} is converted to Ru^{3+}, which is responsible for the redox reactions of peptide containing methionine.

Chart 1 depicts the structure of ligands and abbreviation of $[Ru(NN)_3]^{3+}$ complexes as well as the structure of substrates used in the present study. The kinetics of electron transfer reaction of six $[Ru(NN)_3]^{3+}$ ions with five peptide containing methionines Met-Gly Met-Ala Met-Ser Met-Val and Met-Leu (Chart 1) has been followed spectrophotometrically, under pseudo first order condition by taking excess of peptide containing methionines over $[Ru(NN)_3]^{3+}$ complex. The kinetics of the reaction has been carried out by mixing the peptide containing methionine with the Ru(III) complex immediately after the preparation of $[Ru(NN)_3]^{3+}$ using photochemical oxidation method as described in the experimental section. The progress of the reaction has been followed by measuring the increase in the absorbance (A) of Ru(II) ion formed

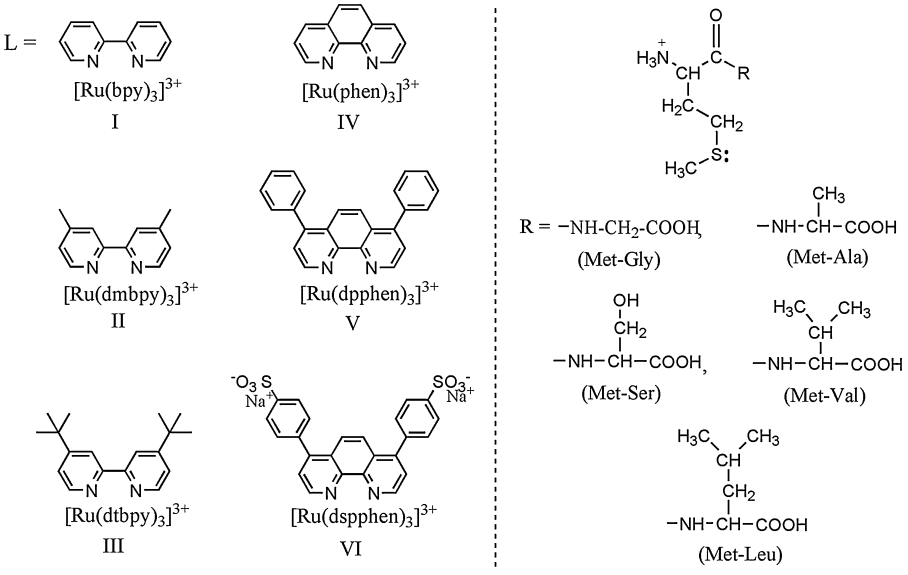


Chart 1. Structure of ligands of $[Ru(NN)_3]^{3+}$ and peptide containing methionines.

(450 nm) as one of the products of the reaction and a sample kinetic run is shown in Fig. 2. The spectral changes collected in Fig. 2 clearly show that during the course of the reaction Ru(III) ion disappears (the peak in the region 600–700 nm) and Ru(II) ion appears (450 nm) with isosbestic point at 542 nm. Thus the reaction Ru(III) → Ru(II) follows simple kinetics without involving any complex mechanism. These experimental observations are strongly in favor of electron transfer (ET) from Met to Ru(III) to form Ru(II) in the rate determining step. The reaction is first-order with respect to Ru(III) complex, the oxidant which is evident from the linear log Abs vs time plot shown in the supporting information (Fig. S3).

The values of pseudo first order rate constant, k_1 plotted as a function of concentration of peptide containing methionines is shown in Fig. 3. The linear relationship between k_1 and [peptide] and constant k_2 values at different [peptide] point out the first order dependence in the substrate also. The reaction is thus overall second order. The k_2 values are obtained by dividing the pseudo first order rate constant, k_1 with substrate [peptide] concentration.

The second order rate constant values estimated from the reaction of six $[Ru(NN)_3]^{3+}$ complexes as the oxidants for the one-electron oxidation of five peptide containing methionines are collected in Tables 1 and 2. The kinetic data collected in Table 1 show that the introduction of electron-donating groups like methyl and *tert*-butyl in the 4- and 4′-position of 2,2′-bipyridine of $[Ru(NN)_3]^{3+}$, 4,4′-dimethyl-2,2′-bipyridine and 4,4′-*tert*-butyl-2,2′-bipyridine ligands, leads to decrease in the rate of oxidation by more than two orders compared to unsubstituted 2,2′-bipyridine ligand (Table 1). The change of ligand in $[Ru(NN)_3]^{3+}$ changes the ΔG° value by 0.16 eV. Thus the main reason for the decrease in k_2 values in the order $[Ru(bpy)_3]^{3+} > [Ru(dmbpy)_3]^{3+} \approx [Ru(dtbpy)_3]^{3+}$ may be attributed to the change in the ΔG° value. When we compare the k_2 values observed with $[Ru(dmbpy)_3]^{3+}$ and $[Ru(dtbpy)_3]^{3+}$ the former complex has slightly more k_2 value than the latter though ΔG° values are almost equal. This may be attributed to the steric effect of *tert*-butyl group present in the complex $[Ru(dtbpy)_3]^{3+}$. Similar results were observed by us when we used the excited state $[Ru(NN)_3]^{2+}$ complexes for the oxidation of several phenolate ions [36]. On the other hand the introduction of the electron-withdrawing group, disulfonate, in the ligand 1,10-phenanthroline increases the rate of reaction slightly compared to the parent 1,10-phenanthroline ligand (Table 2). This is because the change in ΔG° value due to the introduction of $-SO_3^-$ is only 0.02 eV. Thus the slightly high k_2 value observed with $[Ru(dspphen)_3]^{3+}$ compared to $[Ru(dpphen)_3]^{3+}$ may be attributed to the change in the ΔG° value.

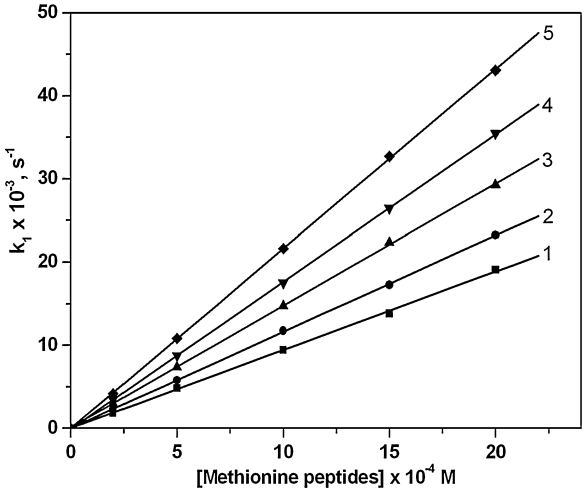


Fig. 3. Plot of k_1 vs [peptide] for the oxidation of peptide containing methionines with $[Ru(bpy)_3]^{3+}$ in oxygen saturated aqueous CH_3CN (1:1, v/v) solution in the presence of 2.3 M $HClO_4$ at 298 K. (The points 1–5 refer to the peptide containing methionine given in Table 1).

When we look at the oxidation potential values of peptide containing methionines (Tables 1 and 2) it is seen that the potential values vary by 0.01–0.05 V with the change of the structure of the peptides. Comparison of kinetic data and ΔG° values compels us to conclude that apart from the ΔG° value other parameters, polar and steric effects, may change the rate constant value with the change of structure of peptide. If the polar effect of the alkyl group present in the peptide alone is the predominant factor in this reaction, then the change of alkyl group should increase the rate constant value in the order methyl (2) < isopropyl (4) < *tert*-butyl (5) because ΔG° value remains almost constant for these three peptides. Interestingly the same trend is observed on the rate constant values for the electron transfer reaction of these three peptides (Tables 1 and 2). The conclusion from this trend is that steric effect plays little role on the electron transfer reaction when the structure of peptide is changed.

In order to understand the influence of other parameters on the rate of the reaction, the kinetics of the reaction has been followed at different solvent (CH_3CN–water) composition and the results are collected in Table 3. Generally the increase in water content favors the reaction when charge development takes place in the transition state of the reaction. As the title reaction involves electron transfer from methionine sulfur atom to Ru(III), positive charge is developed on the sulfur center of the substrate in the transition state. Our research group established the fact that increase in water content increases the rate of the reaction between organic sulfur compounds and Ru(III)–polypyridyl complexes [25a]. Thus the solvent effect supports the operation of electron transfer in the rate-controlling step.

To study the effect of temperature on the reaction rate, kinetics of reaction of $[Ru(NN)_3]^{3+}$ with peptide containing methionines were carried out at four different temperatures 293, 298, 303 and 308 K. The rate constants were found to increase with increase in temperature as presented in Table 4. The enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation evaluated using the Eyring's plot of log k_2/T vs $1/T$ is summarized in Table 4. The negative $\Delta S^{\neq}$ value indicates the compactness of transition state. The thermodynamic parameters $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values, collected in Table 4 show that with the change of structure of peptide containing methionines as well as the ligand in the Ru(III) complex there is little change in the $\Delta H^{\neq}$ as well as $\Delta S^{\neq}$ values. This little change in the thermodynamic parameters with the change of structure of reactants also supports the operation of electron transfer mechanism of the reaction.

3.1. Formation of Met sulfur radical cation

In this work we propose that the reaction of $[Ru(NN)_3]^{3+}$ with methionylglycine produces Met-sulfur radical cation. Ruthenium

Table 3
Effect of varying solvent composition on the reaction of $[Ru(NN)_3]^{3+}$ with peptide containing methionines at 298 K.

Solvent composition CH_3CN:H_2O (v/v)	k_2, M^{-1} s^{-1}	
	$[Ru(bpy)_3]^{3+}$	$[Ru(phen)_3]^{3+}$
	Met-Gly	Met-Ala
80:20	5.3 ± 0.16	11.8 ± 0.35
70:30	6.5 ± 0.18	13.0 ± 0.36
60:40	7.2 ± 0.20	14.3 ± 0.43
50:50	9.7 ± 0.29	16.1 ± 0.43
40:60	12.1 ± 0.32	18.5 ± 0.56
20:80	13.5 ± 0.41	20.8 ± 0.60

General condition: $[Ru(NN)_3]^{3+} = 2 \times 10^{-5}$ M, [Peptide] = 5×10^{-4} M and $[H^+]$ = 2.3 M.

Table 4
Second order rate constant (k_2) values and activation parameters for the oxidation of peptide containing methionines by $[Ru(bpy)_3]^{3+}$ in aqueous CH_3CN (1:1, v/v) at four different temperatures.

Peptides	k_2, $M^{-1}\,s^{-1}$				$\Delta H^{\neq}$ kJ mol^{-1}	$-\Delta S^{\neq}$ J K^{-1} mol^{-1}
	293 K	298 K	303 K	313 K		
Met-Gly	7.3 ± 0.2	9.7 ± 0.3	13.6 ± 0.4	18.5 ± 0.5	35.6 ± 1.1	197.1 ± 5.9
Met-Ala	8.1 ± 0.2	11.2 ± 0.3	15.5 ± 0.4	20.7 ± 0.6	35.1 ± 1.0	197.1 ± 5.4
Met-Ser	11.3 ± 0.3	14.7 ± 0.4	20.3 ± 0.5	26.5 ± 0.8	34.7 ± 0.99	197.1 ± 5.3
Met-Val	13.1 ± 0.4	17.6 ± 0.5	24.4 ± 0.7	30.9 ± 0.9	35.6 ± 1.0	197.1 ± 5.7
Met-Leu	15.2 ± 0.1	21.7 ± 0.6	27.9 ± 0.8	36.5 ± 1.0	36.4 ± 1.1	197.1 ± 5.8

General condition: $[Ru(NN)_3]^{3+} = 2 \times 10^{-5}$ M, [Peptide] = 5×10^{-4} M and $[H^+] = 2.3$ M.

(III) complexes (I–VI), $[Ru(NN)_3]^{3+}$, are one-electron oxidants and the proposal of ET mechanism can be confirmed if the short lived transient radical, formed during the course of the reaction, is identified by nanosecond laser flash photolysis technique (Fig. 4). The experiment was designed as follows: the reaction mixture consisting of $[Ru(dmbpy)_3]^{2+}$ and methionylglycine taken in aqueous CH_3CN (1:1, v/v), was purged with molecular oxygen for 20 min in the presence of 2.3 M $HClO_4$. This reaction mixture was utilized for the flash photolysis study. When this reaction mixture was irradiated with flash of light using the flash photolysis set up it resulted in the appearance of the absorption peaks corresponding to various transients depending as a function of time. The irradiation of $[Ru(dmbpy)_3]^{2+}$ in the presence of O_2 leads to the formation of Ru(III) species which is formed due to the oxidative quenching of $^*[Ru(NN)_3]^{2+}$ with molecular oxygen particularly at high $[H^+]$ as per reactions shown in Eqs. (1)–(3) (Scheme 1). Thus the transients formed are due to the reaction between $[Ru(dmbpy)_3]^{3+}$ and methionylglycine as shown in Fig. 4.

Fig. 4 shows the formation of three new species and decay of two species. The peak at 370 nm corresponds to the dmbpy radical anion on the basis of its similarity with the spectrum of 2,2′-bipyridyl anion radical and 420 nm assigned to the absorption maximum of Ru(III) ion. The bleaching around 450 nm is due to the loss of ground state absorption, $d\pi$–π^* (MLCT) transition, [37–39] while the disappearance of a peak at 650 nm corresponds to the emission of the excited state of Ru(II) ion. Interestingly a new peak is appeared around 480 nm at 1 μs, which is assigned to the well-characterized two-center, three-electron-bonded $(S\therefore S)^+$ dimeric radical cation of methionylglycine (Met-Gly) [17,18]. But this short-lived species almost completely disappeared at 2 μs after the laser pulse (Fig. 4). Bobrowski et al. [40–42] previously reported the formation of dimeric radical cation with different kind of methionine peptides at 480 nm. The point that we want to emphasize from these results is that during the course of this reaction methionine sulfur radical cation $S^{\bullet+}$ and dimeric radical cation $(S\therefore S)^+$ are formed as the intermediates of the reaction. It is important to quote that at low pH 0–1 the formation of $S\therefore S$ species is more favorable compared to $S\therefore N$ and $S\therefore O$ species in the oxidation of peptide containing methionines [40].

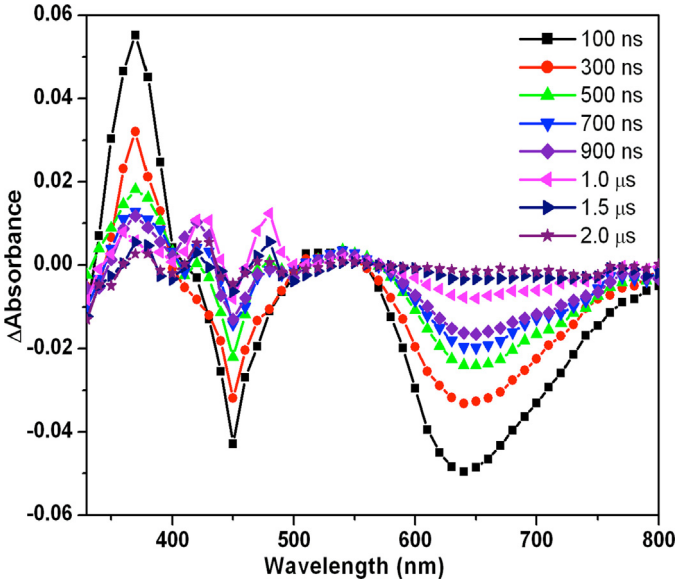


Fig. 4. Spectra of transients formed due to the reaction between the photochemically generated $[Ru(dmbpy)_3]^{3+}$ with 0.05 M methionylglycine in an oxygen-saturated aqueous CH_3CN (1:1, v/v) solution in the presence of 2.3 M $HClO_4$ obtained at different time delays, from 100 ns to 2.0 μs, by laser flash photolysis experiment.

When we irradiated a mixture of $[Ru(dmbpy)_3]^{2+}$ and methionylglycine (Met-Gly) in the absence of O_2 with 2.3 M $HClO_4$ no evidence for the formation of Ru^{3+} and methionine sulfur radical cation is observed (Fig. 5). This clearly shows that the excited state $[Ru(NN)_3]^{2+}$ has no reaction with methionylglycine (Met-Gly). When we look at the spectral changes indicated in Fig. 5 in the region 330–800 nm the formation of one intermediate species and bleaching of two species can be noticed. A sharp absorption band at 370 nm is attributed to the formation of dmbpy radical anion on the basis of its similarity with the spectrum of 2,2′-bipyridyl anion radical. The bleaching around 450 nm is due to the loss of ground state absorption, $d\pi$–π^* (MLCT) transition, [37–39] while the disappearance of 650 nm correspond to the emission of the excited state of Ru(II) ion. In the present experiment it is pertinent to mention that a lack of absorption band at 480 nm infers that sulfur-sulfur dimeric radical cation is not formed even at longer time scales followed in the experiment.

We have also carried out flash photolysis study of the deoxygenated solution of $[Ru(bpy)_3]^{2+}$ in the absence of methionine and the absorption spectral changes are shown in the supporting information (Fig. S4). The spectral changes collected in the supporting information show that during this photolysis study both the formation of excited state Ru^{2+} and decay of $^*Ru^{2+}$ are observed. The important point we want to emphasize from the flash photolysis study is that no transient with absorption maximum at 480 nm is observed in the absence of oxygen.

$$^*[Ru(NN)_3]^{2+} + {}^3O_2 \xrightarrow[\text{transfer}]{\text{energy}} [Ru(NN)_3]^{2+} + {}^1O_2 \quad (1)$$

$$^*[Ru(NN)_3]^{2+} + {}^3O_2 \xrightarrow[\text{transfer}]{\text{electron}} [Ru(NN)_3]^{3+} + O_2^{\bullet-} \quad (2)$$

$$\underset{\text{cage}}{\left[[Ru(NN)_3]^{3+} \ldots O_2^{-}\right]} + H^+ \rightleftharpoons [Ru(NN)_3]^{3+} + HO_2^{\bullet} \quad (3)$$

Scheme 1. Reaction of excited state $[Ru(NN)_3]^{2+}$ with molecular oxygen.

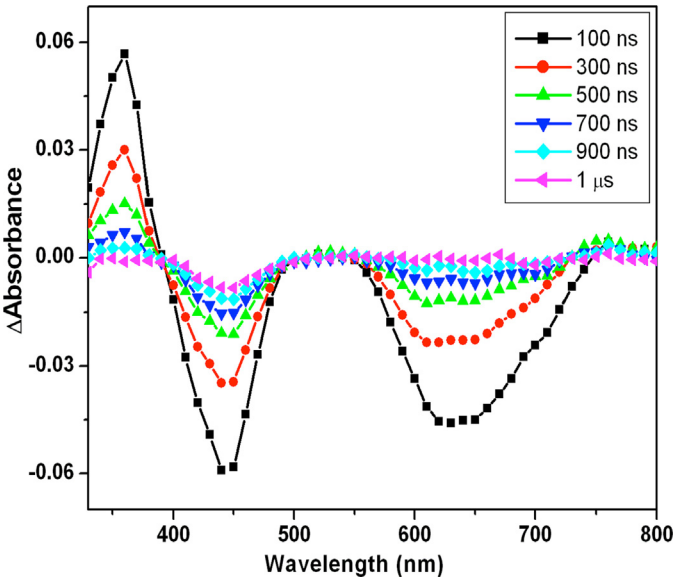


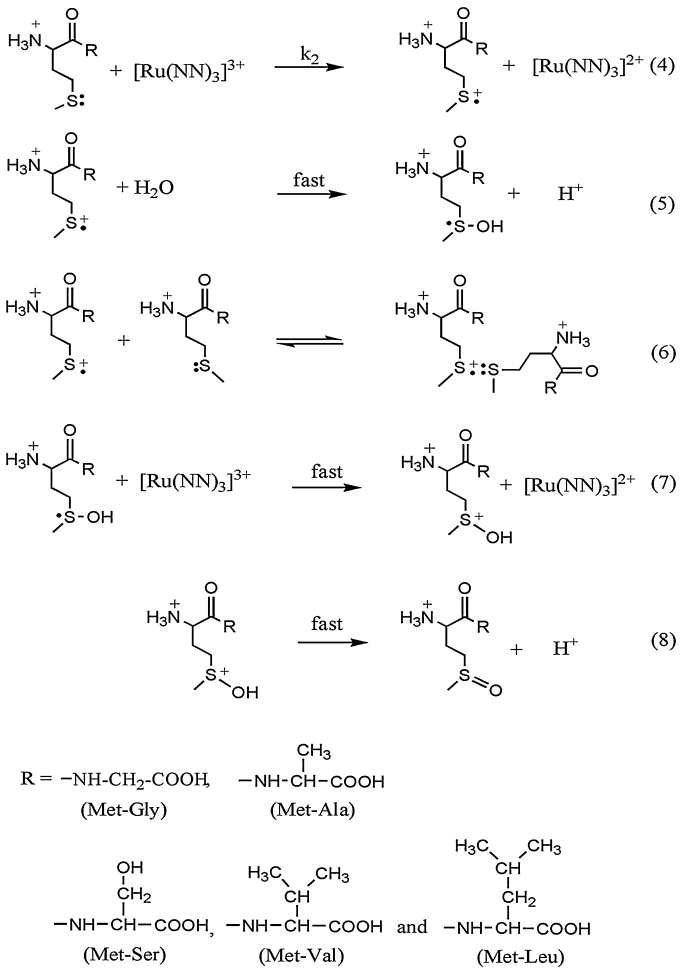
Fig. 5. Transient difference spectra of the $[Ru(dmbpy)_3]^{2+}$ complex with 0.05 M methionylglycine in a deoxygenated aqueous CH_3CN (1:1, v/v) solution in the presence of 2.3 M $HClO_4$ obtained at different time delays, from 100 ns to 1.0 μs, by laser flash photolysis experiment.

3.2. Mechanism of $[Ru(NN)_3]^{3+}$ oxidation of methionine peptides

The one electron transfer from sulfur atom of methionyl peptide to $[Ru(NN)_3]^{3+}$ is proposed as the rate controlling step of the reaction (Eq. (4). The sulfur-center radical cation (>$S^{\bullet+}$) and $[Ru(NN)_3]^{2+}$ are formed as the products of this step. The initially formed sulfur radical cation can react with either water molecule present in the solvent medium to form the hydroxyl sulfuranyl radical (Eq. (5)) or another molecule of methionyl peptide to form the dimer (Eq. (6)). Since the present reaction has been carried out at high $[H^+]$ (2.3 M) the following steps are suggested to account for the overall reaction and transients detected. (i) in the presence of higher thioether concentration, monomeric sulfur radical cation combines with a unoxidized Met residue according to equilibrium (Eq. (6)) to form the intermolecular two-center, three-electron-bonded dimeric radical cation $(S\therefore S)^+$ – species which has an absorption maximum at 480 nm confirmed by laser flash photolysis study. (ii) $[Ru(NN)_3]^{3+}$ abstracts an electron from the hydroxysulfuranyl radical ($^{\bullet}$S—OH) in a fast step to produce the protonated sulfoxide (Eq. (7)). (iii) Finally the deprotonation of hydroxysulfuranyl cation yields sulfoxide as the major product of the reaction (Eq. (8)) is confirmed by FT-IR and ^{1}H NMR techniques. The electron transfer mechanism of the reaction is supported from a satisfactory correlation between the experimentally observed second-order rate constants and the values calculated by Marcus semiclassical theory also support the proposed mechanism. This mechanism is similar to the one proposed by us for the $[Ru(NN)_3]^{3+}$ and $[Fe(NN)_3]^{3+}$ oxidation of organic sulfides and sulfoxides [25,43,44] (Scheme 2).

3.3. Application of Marcus semiclassical theory to the electron transfer reaction of $[Ru(NN)_3]^{3+}$ with methionine peptides.

After establishing the electron transfer nature of the reaction, we applied the semiclassical theory of electron transfer (Eq. (9)) [45–47] to the above redox reaction. The rate of ET from a donor to an acceptor molecule in a solvent is controlled by free energy change of the reaction (ΔG°), the reorganization energy (λ) and the electron transfer distance between the donor and the acceptor (Eq. (9)).



Scheme 2. Mechanism for the oxidation of methionine peptides by $[Ru(NN)_3]^{3+}$.

$$k_{et} = \frac{4\pi^2}{h}|H_{DA}|^2(4\pi\lambda kT)^{1/2}\sum_{m=0}^{\alpha}\left(\frac{e^{-s}S^m}{m!}\right) \times \exp\left[\frac{-(\lambda + \Delta G^\circ + mh\nu)^2}{(4\lambda kT)}\right] \quad (9)$$

In Eq. (9), H_{DA} is the electronic coupling matrix element, the reorganization energy λ is composed of solvational λ_0 and vibrational λ_i contributions with $s = \lambda_i/h\nu$, ν is the high-energy vibrational frequency associated with the acceptor and m is the density of product vibrational levels. The terms h and k are Planck's and Boltzmann's constants, respectively. The free-energy change (ΔG°) of electron transfer can be calculated from Eq. (10).

$$\Delta G^\circ = E_{(D/D^+)} - E_{(A/A^-)} \quad (10)$$

where $E_{(D/D^+)}$ is the oxidation potential of electron donor and $E_{(A/A^-)}$, the reduction potential of acceptor. The reorganization energy (λ) is the sum of two contributions, $\lambda = \lambda_0 + \lambda_i$, where λ_i represents the activation of the vibrational modes of the reactants and λ_0 represents the changes in the solvent structure around the reactants, which strongly dependent on the solution medium. According to the Marcus theory of electron transfer, the λ_0 value is given by Eq. (11) [48].

$$\lambda_0 = e^2/4\pi\varepsilon_0\{(1/2r_D + 1/2r_A - 1/d)(1/D_{op} - 1/D_s)\} \quad (11)$$

Here e is the transferred electronic charge, ε_0 the permittivity of free space, D_{op} and D_s the optical and static dielectric constants,

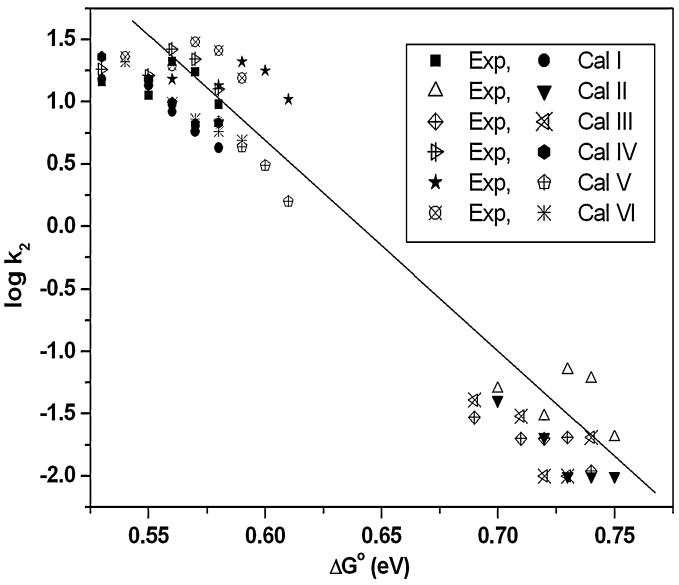


Fig. 6. Plot of log k_2, $M^{-1}\,s^{-1}$ vs ΔG°, eV for the reaction of $[Ru(NN)_3]^{3+}$ with peptide containing methionines (Exp- experimental value, Cal- values calculated using Marcus theory).

respectively. The terms r_D and r_A are the radii of the electron donor and acceptor, respectively and d is the sum of radii, $r_D + r_A$. The values of r_D and r_A are estimated by MM2 molecular model and the values are 5.4–6.5 Å and 6.1–12.6 Å. The value of λ_0 calculated using Eq. (11) is 0.64 eV for Met-Gly 0.55 eV for Met-Ala 0.56 eV for Met-Ser 0.57 eV for Met-Val and 0.60 eV for Met-Lue. The value of λ_i is found to be 0.2 eV and is employed in the calculation of the rate constant for ET reaction [49,50]. Thus the total reorganization energy, λ, value for this redox system is in the range of 0.75–0.84 eV. Since ΔG° and λ values are known, the value of rate constant for electron transfer from Met to $[Ru(NN)_3]^{3+}$ can be calculated using Eq. (9). The experimental and calculated k_2 values were plotted against ΔG° values (Fig. 6). The data given in Fig. 6 show a close agreement between the experimental and calculated values. The scrutiny of Fig. 6 indicates that generally with an increase of ΔG° value the rate constant for electron transfer reaction (k_2) decreases in accordance with the Marcus equation. When we compare the observed and calculated values we see considerable deviation between these two values only in the case of complexes V and VI. The ligands of both complexes carry five phenyl rings which may facilitate hydrophobic interaction between the oxidant and substrate. Thus, the data collected in Tables 1 and 2 and Fig. 6 show that the semiclassical theory of electron transfer (ET) reproduces the experimental results favorably confirming the success of the theory of ET and the operation of ET mechanism of the reaction.

4. Conclusion

The oxidation of peptide containing methionines with photochemically generated $[Ru(NN)_3]^{3+}$ complexes proceeds through overall second-order kinetics, first order each in $[Ru(NN)_3]^{3+}$ and peptide. Though the second-order rate constant, k_2 value is highly sensitive to the change of structure of ligand in $[Ru(NN)_3]^{3+}$ it is slightly sensitive to the structure of peptide. The k_2 values are in accordance with the free energy change, ΔG°, of the reaction. The detection of methionine sulfur cation radical as the intermediate of the reaction from flash photolysis technique and successful application of Marcus theory to this redox reaction support the postulation of electron transfer mechanism.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2014.09.003.

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