Electron Transfer Reactions of Photochemically Generated Ruthenium(III)–Polypyridyl Complexes with Methionines

DHARMARAJ THIRUPPATHI,[1] PERIYAKARUPPAN KARUPPASAMY,[1] MUNIYANDI GANESAN,[1] VELUCHAMY KAMARAJ SIVASUBRAMANIAN,[1] THANGAMUTHU RAJENDRAN,[1,2] SEENIVASAN RAJAGOPAL[3]

[1]*Postgraduate and Research Department of Chemistry, Vivekananda College, Thiruvedakam West, Madurai* 625 234, *India*

[2]*Department of Chemistry,* PSNA *College of Engineering and Technology, Dindigul* 624 622, *India*

[3]*School of Chemistry, Madurai Kamaraj University, Madurai* 625 021, *India*

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ABSTRACT: The oxidation of methionine (Met) plays an important role during biological conditions of oxidative stress as well as for protein stability. Ruthenium(III)–polypyridyl complexes, $[Ru(NN)_3]^{3+}$, generated from the photochemical oxidation of the corresponding Ru(II) complexes with molecular oxygen, undergo a facile electron transfer reaction with Met to form methionine sulfoxide (MetO) as the final product. Interaction of $[Ru(NN)_3]^{3+}$ with methionine leads to the formation of $>S^{+\bullet}$ and $(>S.\therefore S<)^{+}$ species as intermediates during the course of the reaction. The interesting spectral, kinetic, and mechanistic study of the electron transfer reaction of four substituted methionines with six $[Ru(NN)_3]^{3+}$ ions carried out in aqueous CH_3CN (1:1, v/v) by a spectrophotometric technique shows that the reaction rate is susceptible to the nature of the ligand in $[Ru(NN)_3]^{3+}$ and the structure of methionine. The rate constants

Correspondence to: Muniyandi Ganesan; e-mail: mganesan58@ymail.com. Seenivasan Rajagopal; e-mail: rajagopalseenivasan@yahoo.com.

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calculated by the application of Marcus semiclassical theory to these redox reactions are in close agreement with the experimental values. Int J Chem Kinet 46: 606–618, 2014

INTRODUCTION

Methionine (Met) is the most important essential sulfur-containing amino acid in human nutrition, that is only available from food sources [1]. It assists in metabolic function, breaks down fats, and is a primary source of sulfur in the living system [2,3]. Met residues in proteins and peptides are susceptible to oxidation by reactive oxygen species to form the corresponding methionine sulfoxide (MetSO) [4] as a result of two-electron oxidation of sulfur. The oxidation of Met residues is related to the pathogenesis of specific diseases such as Alzheimer's disease [5–12], Parkinson's disease [13], and even the aging process [14]. Oxidative damage to Met residue is also considered to be a main reason for the development of cataracts, a leading cause of blindness. Thus Met oxidation is likely to alter physical as well as biochemical properties of proteins of pathophysiological relevance. Although the formation of MetSO from Met is a physiologically reversible process, further oxidation to $MetSO_2$ is believed to be biologically irreversible [15–18]. The first step in the oxidation of Met is the formation of the Met sulfur radical cation, $MetS^{\bullet+}$ due to the one-electron oxidation initiated by species such as peroxyl ($ROO^{\bullet}$), alkoxyl ($RO^{\bullet}$), and hydroxyl ($OH^{\bullet}$) radicals. In particular, the oxidation of Met residues initiated by $OH^{\bullet}$ and other free radical species has attracted a lot of interest [19,20].

The lifetime of the sulfur-centered radical cation formed due to the oxidation of Met is very short, but it is stabilized by complexation with the heteroatoms (O, N, and S) of the peptidic bond or with a sulfur atom of another thioether group [21]. Met sulfur radical cations can be stabilized by an intramolecular sulfur–nitrogen $(>S.\therefore N<)^{+}$ or sulfur–oxygen $(>S.\therefore O<)^{+}$ three-electron bond species or the intermolecular bonding with the unoxidized sulfur atom of the other Met to form a sulfur–sulfur $(>S.\therefore S<)^{+}$ two-center three-electron–bonded dimeric radical cation [12,21–24].

Octahedral ruthenium(II)–polypyridyl complexes, a versatile group of compounds with unique electrochemical and photophysical properties, have extensive applications as oxidation catalysts, dye sensitizers for solar cells, for DNA intercalation, and protein-binding properties [25–29]. Ruthenium complexes with ligands of various structures have been shown to display promising anticancer activities [30–34]. Different mechanisms have been proposed to account for the anticancer activity of ruthenium complexes, and one of them is their redox reactivity [35]. Generally metallodrugs undergo the ligand exchange and redox reaction before they reach the target site. The disturbance of redox balance in living organism is at the center of many diseases, including cancer [36] and neurological disorders [37]. It is proposed that the binding of metallodrugs to sulfur-containing amino acid side chains (methionine and cysteine) of proteins can deactivate their activity [38]. Thus the study of reactivity of redox active ruthenium complexes with Met is important from biochemical and medicinal point of view because ruthenium and iron belong to the same group in the periodic table [39].

In the present study, we have used six $[Ru(NN)_3]^{3+}$ complexes as electron acceptors to understand the role of electrostatic and hydrophobic interactions on the reactivity of these metal complexes with Met. To confirm the formation of the sulfide radical cation as an intermediate including an intermolecular (S.∴S)-bonded radical cation and bipyridyl anion radical of the reaction, we have followed the reaction by a time-resolved technique from which we are able to get the absorption spectrum of the transients supporting the formation of the monomeric sulfide radical cation $(>S^{+\bullet})$ and the intermolecular dimeric radical cation $[>S.\therefore S<]^{+}$ species during the course of the reaction [40]. From these spectral observations for the formation of the sulfur radical cation and successful application of Marcus theory, we conclude that the electron transfer (ET) process is the rate-controlling step for the reaction between $[Ru(NN)_3]^{3+}$ and Met. The results of the spectral and kinetic studies on the reaction of six $[Ru(NN)_3]^{3+}$complexes with four Mets are presented in this article. Although different methods are available for the generation of Ru(III) from Ru(II) complexes, in the present study Ru(III) complexes have been generated by the visible light oxidation of $[Ru(NN)_3]^{2+}$ in the presence of molecular oxygen [41–45], a green process for the generation of an active oxidant.

EXPERIMENTAL

Materials

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 Aldrich (Bangalore, India) and methionine, ethionine, buthionine and *N*-acetylmethionine (purity >99%) from Sigma–Aldrich (Bangalore, India) and used without further purification. HPLC-grade CH_3CN was obtained from Merck (Mumbai, India).

Synthesis and Characterization of Ruthenium(II)–Polypyridyl Complexes

The $[Ru(NN)_3]^{2+}$complexes (where NN is bpy, dmbpy, dtbpy, phen, dpphen, and BPS) were used in the present study synthesized by known procedures [46–49]. All the six Ru(II) complexes synthesized were characterized by UV–vis, IR, ^1H NMR, ^{13}C NMR, and ESI-MS spectral techniques (spectral data are given in the Supporting Information). The spectral data are in close agreement with the reported values [46–49].

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, for 20 min using a 500-W tungsten-halogen lamp led to the formation of the corresponding Ru(III) complex. The IR and 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. Owing to $[Ru(bpy)_3]^{2+}$, the absorption peak at 450 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 the acidic aqueous solution [43,50]. These peaks are assigned to charge transfer transitions from the bipyridyl π ligands to the electron-deficient metal (t_{2g}) [51]. 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}.

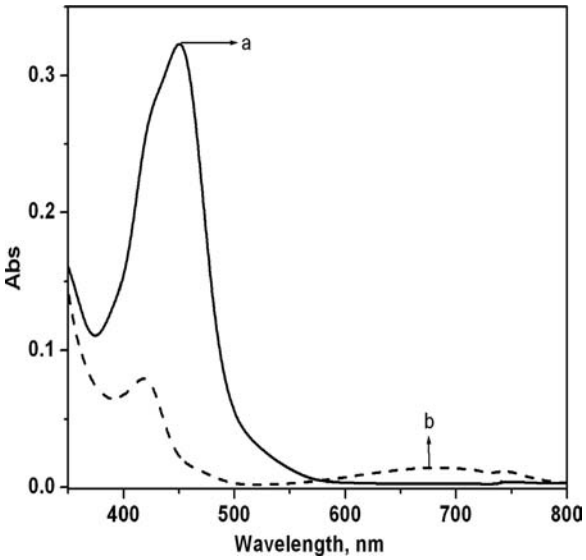


Figure 1 (a) The absorption spectrum of a solution of the 2×10^{-5} M $[Ru(bpy)_3]^{2+}$ complex in aqueous CH_3CN (1:1, v/v) oxygen-saturated 2.3 M $HClO_4$. (b) The absorption spectrum of $[Ru(bpy)_3]^{3+}$ obtained from the irradiation of 2×10^{-5} M $[Ru(bpy)_3]^{2+}$ in the oxygen-saturated solution.

Kinetic Measurements

A Jasco UV–vis absorption spectrophotometer (model V530) was employed to record the absorption spectra of $[Ru(NN)_3]^{2+}$ and $[Ru(NN)_3]^{3+}$ complexes used in the present study and to follow the kinetics of ET reactions of $[Ru(NN)_3]^{3+}$ complexes with Met. The kinetic study was carried out in aqueous CH_3CN (1:1, v/v) under the pseudo–first-order condition by taking an excess substrate over the oxidant. The progress of the reaction was monitored by following the increase in the absorbance of $[Ru(NN)_3]^{2+}$ ($\lambda_{max}^{abs} = 450$ nm) at definite time intervals at 298 K (Fig. 2) [52]. The pseudo-first–order rate constant (k_1) for each kinetic run was evaluated from the slope of a linear plot of log Abs versus time by the method of least squares. The linearity of each fit was confirmed from the values of correlation coefficient (r) and standard deviation(s). The second-order rate constant (k_2) was evaluated from the relation $k_2 = k_1/$ [substrate].

Electrochemical Measurements

The redox potentials of $[Ru(NN)_3]^{3+}$ complexes in aqueous CH_3CN (1:1, v/v) medium were measured by the cyclic voltammetric technique using a computer-controlled potentiostat (CH Instruments; model 680 AMP Booster). $HClO_4$ was used as the supporting electrolyte. The oxidation potentials of Mets were

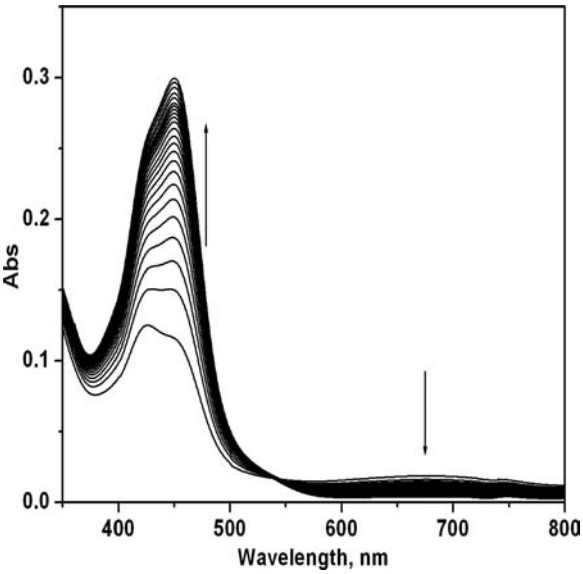


Figure 2 Absorption spectral changes in the reaction between $[Ru(bpy)_3]^{3+}$ (2×10^{-5} M) and methionine (5×10^{-4} M) at 298 K with a 2-min time interval.

measured by differential pulse voltammetry, and tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte. A glassy carbon (working electrode) and a standard (Ag/AgCl) 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 values of the oxidation potential of four-substituted methionines and the reduction potential of six $[Ru(NN)_3]^{3+}$ are presented in Tables I and II. The values of the oxidation potential of methionines and the reduction potential of $[Ru(NN)_3]^{3+}$ are in good agreement with the reported values [43,53,54].

Laser Flash Photolysis Experiments

The short-lived intermediates formed during the course of reaction is followed using the transient absorption spectral study with a laser flash photolysis technique using an Applied Photophysics SP-Quanta Ray GCR-2(10) Nd:YAG laser–generating 355 nm pulses (~8 ns pulse width) [55]. 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 quartz cell (1 cm) with an optical path length of 0.5 cm for the monitoring beam. The concentration of $[Ru(bpy)_3]^{3+}$ (1×10^{-3} M) and Met (0.05 M) was used for all experiments. Typically 3–5 laser shots were averaged for each kinetic trace. All the measurements were carried out at 22 ± 2°C. The 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 following expression:

$$\Delta A = \log I_0/(I_0 - \Delta I)$$

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

Table I Second-Order Rate Constants (k_2; $M^{-1}s^{-1}$) for the Oxidation of Methionines by $[Ru(NN)_3]^{3+}$ in Aqueous CH_3CN 1:1 (v/v) at 298 K

			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)	
No.	Met	Oxidation Potential, V (Ag/AgCl)	Observed Calculated	ΔG^o (eV)	Observed Calculated	ΔG^o (eV)	Observed Calculated	ΔG^o (eV)
1	Methionine	1.34	6.9 ± 0.21 8.2	0.42	0.38 ± 0.01 0.33	0.59	0.19 ± 0.01 0.21	0.58
2	Ethionine	1.47	8.3 ± 0.23 10.1	0.55	0.42 ± 0.01 0.31	0.72	0.23 ± 0.01 0.18	0.71
3	Buthionine	1.49	13.8 ± 0.41 16.2	0.57	0.54 ± 0.01 0.82	0.74	0.27 ± 0.01 0.20	0.73
4	*N*-acetyl methionine	1.42	17.5 ± 0.54 19.9	0.50	0.62 ± 0.02 0.96	0.67	0.32 ± 0.01 0.46	0.66

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

Table II Second-Order Rate Constants (k_2, $M^{-1}s^{-1}$) for the Oxidation of Methionines by $[Ru(NN)_3]^{3+}$ in Aqueous CH_3CN 1:1 (v/v) at 298 K

			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)	
No.	Met	Oxidation Potential,V (Ag/AgCl)	Observed Calculated	ΔG^o (eV)	Observed Calculated	ΔG^o (eV)	Observed Calculated	ΔG^o (eV)
1	Methionine	1.34	9.2 ± 0.25 13.5	0.42	5.8 ± 0.18 4.5	0.45	11.5 ± 0.32 10.6	0.43
2	Ethionine	1.47	12.6 ± 0.37 11.7	0.55	8.3 ± 0.23 11.8	0.58	14.7 ± 0.41 12.3	0.56
3	Buthionine	1.49	17.5 ± 0.48 19.9	0.57	13.8 ± 0.42 14.2	0.60	21.2 ± 0.67 26.5	0.58
4	*N*-acetyl methionine	1.42	25.3 ± 0.75 26.8	0.50	15.4 ± 0.45 18.4	0.53	28.6 ± 0.85 34.8	0.51

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

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 the absorbance at a particular time versus wavelength. The experiment was carried out in the absence and presence of molecular oxygen. The presence of oxygen is necessary to generate the Ru^{3+} species from Ru^{2+} photochemically [43].

Product Analysis

A sample of 0.05 M of substrate (Met) was added to a 0.005 M solution of $[Ru(bpy)_3]^{3+}$ complex in 5 mL aqueous CH_3CN (1:1, v/v). The solution was stirred at 298 K for ~1 h. The products of the reaction were extracted with chloroform and dried, and the solvent was removed. The final compound was then analyzed using IR and ^1H NMR spectroscopy, which confirmed Met sulfoxide as the only major product under the present experimental conditions. The IR spectrum of the product (sulfoxide) was found to have a stretching frequency in the characteristic region 1030 cm^{-1} for the product. ^1H NMR (200 MHz, D_2O): $\delta = 2.1$–2.24 (2H, q), 2.73–3.03 (2H, m), 3.71–3.79 (1H, m), and 2.62 (s, $SOCH_3$) values are in good agreement with reported values of methionine sulfoxide [18,56]. ^1H NMR and IR spectra of methionine sulfoxide are given in the Supporting Information (see Figs. S1 and S2).

RESULTS AND DISCUSSION

The generation of the Ru^{3+} ion from the corresponding $[Ru(NN)_3]^{2+}$ ion 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, for 20 min using a 500-W tungsten–halogen lamp led to the formation of the corresponding Ru^{3+} ion. The IR and 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 $[Ru(bpy)_3]^{3+}$ 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 generated from the photochemical oxidation of Ru^{2+} for kinetic studies.

When $[Ru(NN)_3]^{2+}$ complexes are irradiated in the presence of molecular oxygen, two processes, energy and ET 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 ET 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 ET, and most of the Ru^{2+} is converted to Ru^{3+}, which is responsible for the redox reactions of methionines:

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

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

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

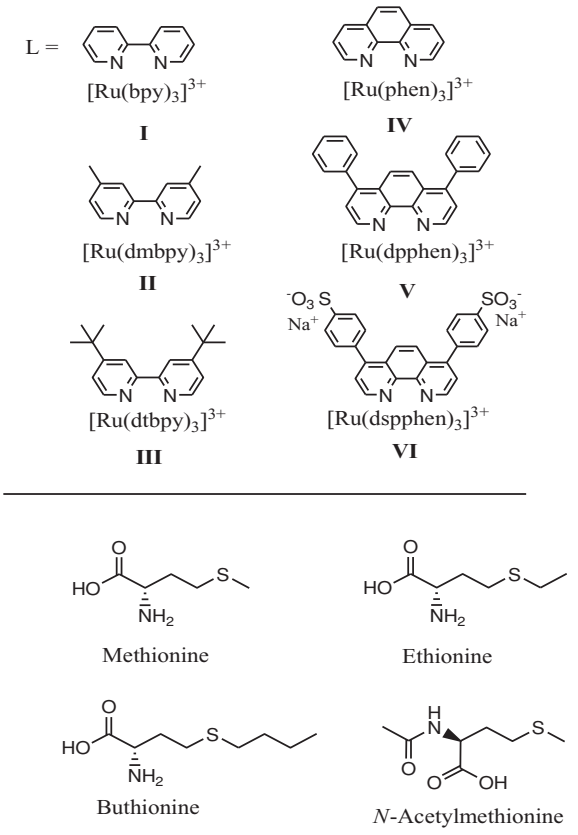


Chart 1 Structure of ligands of $[Ru(NN)_3]^{3+}$, methionine, and substituted methionines.

The dependence of the rate constant of the ET reaction from methionines to $[Ru(NN)_3]^{3+}$ on the reduction potentials of $[Ru(NN)_3]^{3+}$ also supports the formation of Ru^{3+} as the major product when Ru^{2+} is irradiated with visible light in the presence of O_2 under our experimental condition (vide infra).

The structure of ligands of $[Ru(NN)_3]^{3+}$ and Mets used in the present study are shown in Chart 1. The kinetics of the redox reaction between $[Ru(NN)_3]^{3+}$ and Met has been followed spectrophotometrically, under the pseudo–first-order condition by taking excess Met over the $[Ru(NN)_3]^{3+}$ ion in the aqueous CH_3CN (1:1, v/v) mixture. The progress of the reaction has been followed by measuring the increase in the absorbance (A) of the Ru(II) ion formed (450 nm) as one of the products of the reaction, and a sample kinetic run is shown in Fig. 2. Interestingly, the observation of isosbestic point at 538 nm for the reduction of Ru(III) to Ru(II) as shown in Fig. 2, points out that the conversion proceeds neatly and confirms that the reaction follows simple kinetics without involving any complex mechanism. These experimental observations are strongly in favor of 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, which is evident from the linear log Abs versus time plot shown in Fig. S3 in the Supporting Information.

The values of pseudo–first-order rate constant, k_1 plotted as a function of the concentration of Met, are shown in Fig. 3. The linear relationship between k_1 and [Met] and constant k_2 values at different [Met] also points out the first-order dependence in the substrate. The reaction is thus overall second order.

The second-order rate constants determined for the reaction of six $[Ru(NN)_3]^{3+}$ complexes with four-substituted methionines are presented in Tables I and II. It is observed that the introduction of electron-donating groups, such as methyl and *tert*-butyl at the 4- and 4′-position of 2,2′-bipyridine of the Ru(III) complexes, 4,4′-dimethyl-2,2′-bipyridine, and 4,4′-*tert*-butyl-2,2′-bipyridine ligands, retards the rate of oxidation enormously. When we look at the ΔG^o values presented in Table I, we realize that the introduction of the alkyl group in the ligand of $[Ru(NN)_3]^{3+}$ changes the ΔG^o values by 0.17–0.18 eV. Thus the main reason for the substantial change in the rate constant with the change in the structure of the ligand is the change in exergonicity (ΔG^o) of the reaction. On the other hand, the

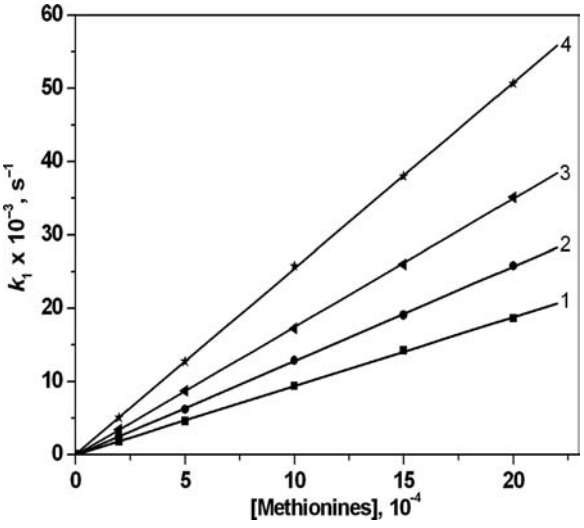


Figure 3 Plot of k_1 versus [Mets] for the oxidation of 1–4 with $[Ru(phen)_3]^{3+}$ in aqueous CH_3CN (1:1, v/v) at 298 K. (The plots 1–4 refer to the Mets given in Table II.)

Table III Effect of Various Solvent Compositions on the Reaction of $[Ru(NN)_3]^{3+}$ with Methionine and Ethionine at 298 K

	k_2 (M^{-1} s^{-1})	
	$[Ru(bpy)_3]^{3+}$	$[Ru(phen)_3]^{3+}$
Solvent Composition CH_3CN:H_2O (v/v)	Methionine	Ethionine
80:20	4.1 ± 0.12	9.3 ± 0.25
70:30	4.8 ± 0.13	10.7 ± 0.32
60:40	5.3 ± 0.15	11.1 ± 0.31
50:50	6.9 ± 0.21	12.4 ± 0.35
40:60	7.2 ± 0.22	14.2 ± 0.38
20:80	8.5 ± 0.24	16.5 ± 0.50

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

introduction of the electron-withdrawing group, disulfonate, in the 1,10-phenanthroline enhances the rate of the reaction slightly (Table II). This is again due to a little change in the ΔG^o value. Thus the effect of changing the substituent in the ligand of the Ru(III) complex on the rate of ET can be accounted for in terms of change in reduction potentials of $[Ru(NN)_3]^{3+}$. Similarly, the change in the structure of methionine has a slight effect on the rate of the reaction, which may be due to the change in the electronic effect of the alkyl group attached to the sulfur atom.

To understand the influence of other parameters on the rate of the reaction, the kinetics of the reaction has been followed at different solvent compositions and the results are presented in Table III. Generally, the increase in the water content favors the reaction when charge development takes place in the transition state of the reaction. Our research group established the fact that an increase in the water content increases the ET reaction between sulfur compounds and Ru(III)-polypyridyl complexes [45b]. Thus the solvent effect supports the formulation of ET in the rate-controlling step.

Transient Absorption Spectral Studies

To understand the transient species formed due to the reaction of $[Ru(NN)_3]^{3+}$ complexes with methionines, the convenient method is monitoring the course of this redox reaction by applying the transient absorption spectroscopy. To get the conclusive evidence for the formation of the transients from the reaction of $[Ru(NN)_3]^{3+}$ with methionine and not from the reaction of the excited state $[Ru(NN)_3]^{2+}$, we have designed the transient spectral study in the following way: We carried out the transient spectral study in the absence and presence of O_2. When we irradiated a mixture of $[Ru(bpy)_3]^{2+}$ and methionine in the absence of O_2 though the excited state, $[Ru(bpy)_3]^{2+}$ was formed; no evidence for the formation methionine sulfur radical was observed. This clearly shows that the excited state $[Ru(bpy)_3]^{2+}$ has no reaction with methionine. But when the reaction of $[Ru(bpy)_3]^{2+}$ with methionine in 2.3 M $[H^+]$ in the presence of molecular O_2 was followed by transient absorption spectroscopy, we are able to get evidence for the formation of the methionine sulfur cation radical. The results of transient spectral study are shown in Figs. 4 and 5. When we look at the spectral changes in the region of 320–800 nm in the absence of molecular O_2, the formation of one intermediate species and bleaching of two species can be noticed (Fig. 4). A sharp absorption band at 370 nm attributed to the formation of bipyridyl radical anion ($bpy^{\bullet -}$) and the bleaching at 450 nm correspond to a relative decrease in the MLCT (metal to ligand charge transfer) transition of the complex in the ground state [57–59]. The bleaching around 600–700 nm corresponds to the light emission from the ground state [60]. In the present experiment, it is pertinent to mention that a lack of absorption band at 480 nm infers a nonformation of the sulfur–sulfur dimeric radical cation $(S.^{\cdot}.S)^+$ even at longer timescales followed in the experiment. Figure 5 shows the spectra of transients formed due to the reaction between the photochemically generated $[Ru(bpy)_3]^{3+}$ ion and methionine in aqueous CH_3CN (1:1, v/v) solution at 298 K. We

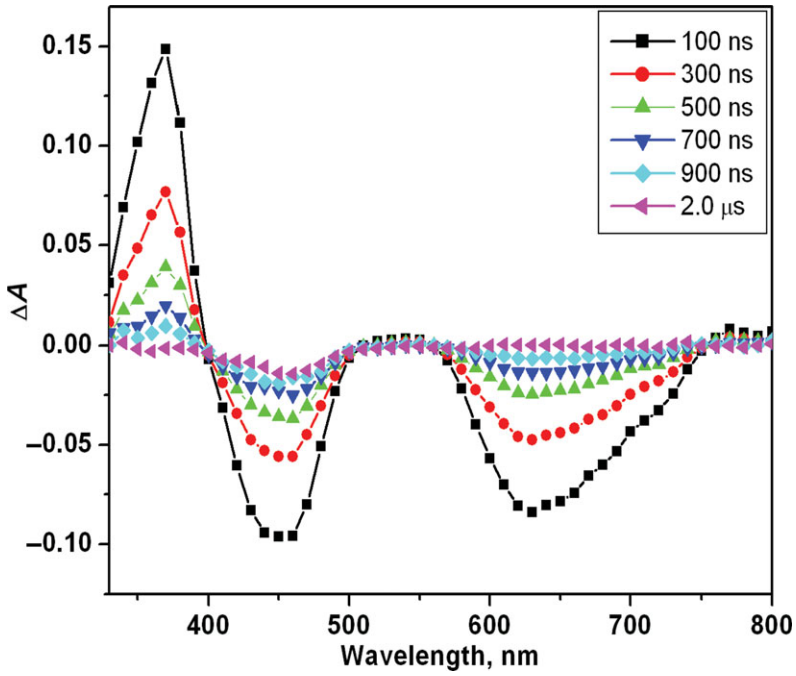


Figure 4 Transient difference spectra of the $[Ru(bpy)_3]^{2+}$ complex with 0.05 M methionine in a deoxygenated aqueous CH_3CN (1:1, v/v) solution obtained at different time delays: from 100 ns to 2 μs.

recorded the absorption spectra of transients formed at different timescales from 100 ns to 2 μs. It exhibits a sharp absorption band at 370 nm attributed to the formation of the bipyridyl radical anion ($bpy^{\bullet-}$). The bleaching at 450 and 650 nm corresponds to the disappearance of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ ions. Interestingly, a new peak around 480 nm appeared at 500 ns, which is assigned to the well-characterized two-center, three-electron–bonded dimeric $(S.\therefore S)^+$ radical cation of methionine [61]. But this short-lived species almost disappeared at 800 ns after the laser pulse (Fig. 5). However, Schoneich et al. were able to get evidence for the appearance of this type of the dimeric radical cation at 8 μs (pH 4.0) [61a]. Since the conditions used in the present study are different from those of Schoneich et al., the lifetime of the transient formed is different. The presence of the intermolecular $(S.\therefore S)^+$-bonded radical cation was previously identified by pulse radiolysis and laser flash photolysis techniques with sulfur-containing amino acids and methionine-containing peptides [61–63]. The point we want to emphasize from these results is that during the course of this reaction the methionine sulfur radical cation $S^{\bullet+}$ and dimeric radical cation $(S.\therefore S)^+$ are formed as the intermediates of the reaction. The flash photolysis study carried out in the absence of methionine in the oxygen-saturated solution indicates almost complete bleaching of Ru^{2+} at 450 nm and the formation of Ru^{3+} (Figs. S4 and S5 in the Supporting Information).

Mechanism of $[Ru(NN)_3]^{3+}$ Oxidation of Methionines

As the progress of the reaction has been followed with an increase in the absorption at 450 nm, the characteristic absorption of the Ru(II) complex, we can presume that the reaction proceeds through the ET mechanism (Fig. 2). It is important to mention that the kinetic data presented in Tables I and II have been obtained using the isolated Ru^{3+} ion, which is obtained from the photolysis of Ru^{2+} in the presence of molecular oxygen. But the flash photolysis study has been carried out by direct irradiation of Ru^{2+} in the presence of molecular oxygen and methionine. Our results suggest that excited state $[Ru(NN)_3]^{2+}$ has no reaction but only Ru^{3+} is the predominant species responsible for the reaction with methionine under high acidic condition. Although Met contains amino, carboxyl, and thioether parts, the site of attack of Ru(III) is on the Met sulfur atom, i.e. the electron is transferred from the sulfur center of Met to the Ru(III) ion. These experimental observations, the formation of the Met

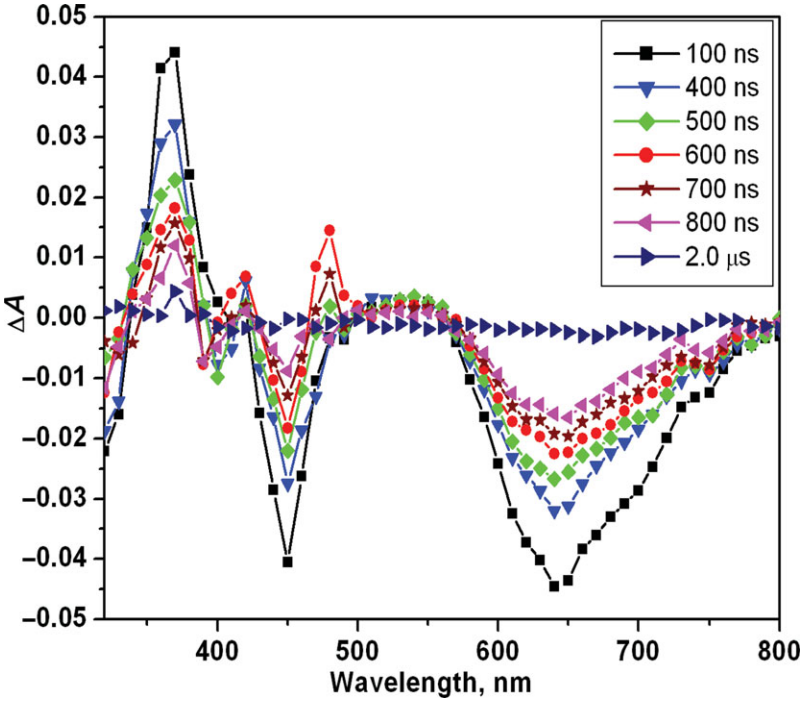
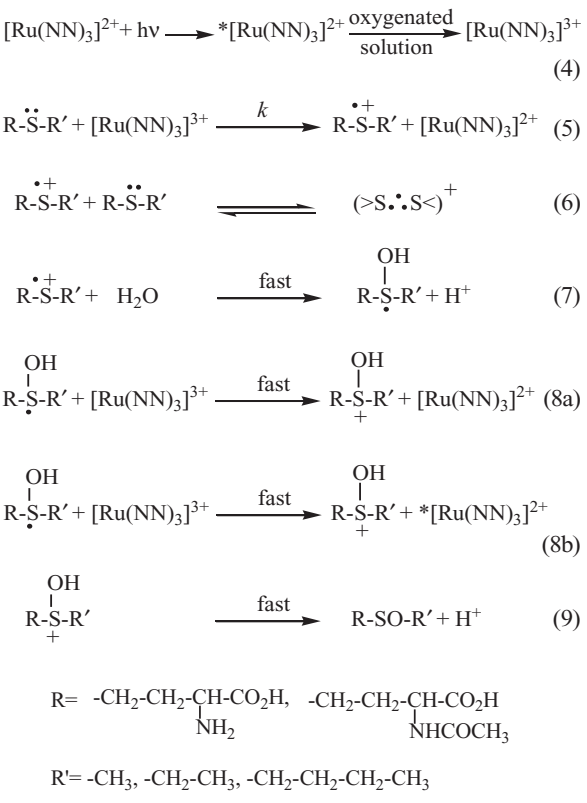


Figure 5 Spectra of transients formed due to the reaction between the photochemically generated $[Ru(bpy)_3]^{3+}$ complex with methionine (0.05 M) in an oxygen-saturated aqueous CH_3CN (1:1, v/v) solution obtained at different time delays: from 100 ns to 2 μs.

radical cation ($>S^{\bullet+}$) and Ru (II) as the products in the rate-determining step (Step 5), are strongly in favor of ET from Met to Ru(III). It has been proved earlier that the sulfur radical cation formed from Met can be stabilized either by the formation of the intermolecular $(S.\therefore S)^+$ two-center three-electron–bonded dimeric radical cation or intramolecular three-electron sulfur–nitrogen $(S.\therefore NH_2)^+$ or sulfur–oxygen $(S.\therefore O)^+$ bonded species [21,22]. Since in the present study the reaction has been carried out under high acidic condition ($[H^+] = 2.3$ M), the carboxylic and amino groups are protonated and thus the intramolecular sulfur–oxygen and sulfur–nitrogen three-electron–bonded species not identified. Thus the monomeric sulfur radical cation ($>S^{\bullet+}$) is stabilized only through the formation of the intermolecular sulfur–sulfur $(S.\therefore S)^+$ two-center three-electron–bonded dimeric radical cation (Step 6), which is supported by the formation of absorption band around 480 nm observed using the nanosecond laser flash photolysis technique. The initially formed Met sulfur cation radical further reacts with the water molecule present in the solvent medium to form the hydroxyl sulfuranyl radical (Step 7). Finally, the formation of sulfoxide as the major product of the reaction helps us to confirm that the major portion of the Met sulfur radical cation is consumed by the solvent, water even though the fragmentation and back ET may be competing processes. The formation of Met sulfoxide from the Met sulfur radical cation may be shown as a three-step process (Eqs. (7)–(9) in Scheme 1). Furthermore, a good agreement between the experimentally observed second-order rate constants and rate constants calculated from the Marcus semiclassical theory also supports the proposed mechanism (Scheme 1). The reaction between $[Ru(NN)_3]^{3+}$ and Met also leads to the formation of the Ru(II) complex in the excited state ($*[Ru(NN)_3]^{2+}$) (Eq. (8b) in Scheme 1), which is supported by the peak observed at 600–700 nm in the transient absorption spectrum (Fig. 5). The mechanism proposed here is similar to the one postulated for the $[Ru(NN)_3]^{3+}$ oxidation of organic sulfoxides and sulfides [45].

Application of Marcus Semiclassical Theory to the ET Reaction of $[Ru(NN)_3]^{3+}$ with Methionines

After proposing the ET as the rate-controlling step of the reaction, we applied the semiclassical theory of ET (Eq. (10)) [64–67] to the above redox reaction. The rate of ET from a donor to an acceptor



Scheme 1 Mechanism for the oxidation of Met by $[Ru(NN)_3]^{3+}$.

molecule in a solvent is controlled by free energy change in the reaction (ΔG^0), the reorganization energy (λ) and the ET distance between the donor and the acceptor.

$$k_{et} = 4\pi^2/h\,|H_{DA}|^2\,(4\pi\lambda kT)^{-1/2}\sum_{m=0}^{\alpha}\left(e^{-s}S^m/m!\right) \times \exp\left[-(\lambda + \Delta G^{\circ} + mhv)^2/4\lambda kT\right] \quad (10)$$

In Eq. (10), H_{DA} is the electronic coupling matrix element, the reorganization energy λ is composed of solvational λ_o 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^0) of ET can be calculated from (Eq. (11)):

$$\Delta G^{\circ} = E_{(D/D^+)} - E_{(A/A^-)} \quad (11)$$

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, $\lambda = \lambda_o + \lambda_i$, where λ_i represents the activation of the vibrational modes of the reactants and λ_o represents the changes in the solvent structure around the reactants, which is strongly dependent on the solution medium. The value of λ_o is evaluated by using the dielectric continuum model (Eq. (12)):

$$\lambda_o = e^2/4\pi\varepsilon_o\,(1/2r_D + 1/2r_A - 1/d) \times \left(1/D_{op} - 1/D_s\right) \quad (12)$$

where e is the transferred electronic charge, ε_o the permittivity of free space and D_{op} and D_s are the optical and static dielectric constants, 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 the MM2 molecular model, and the values are 4.7–6.3 Å and 6.1–12.6 Å. The value of λ_o calculated using Eq. (12) is 0.73 eV for methionine, 0.70 eV for ethionine, 0.61 eV for buthionine, and 0.69 eV for *N*-acetylmethionine. The value of λ_i is found to be 0.2 eV and is employed in the calculation of the rate constant for the ET reaction [68–70]. Thus the total reorganization energy λ value for this redox system is in the range of 0.81–0.93 eV. Since ΔG^0 and λ values are known, the value of the rate constant for ET from Met to $[Ru(NN)_3]^{3+}$ can be calculated using Eq. (10). The experimental and calculated k_2 values are presented in Tables I and II. These data show a close agreement between the experimental and calculated values. Thus, the semiclassical theory of ET reproduces the experimental results favorably confirming the success of the theory of ET and the operation of the ET mechanism of the reaction.

Thermodynamic Parameters

The ET reaction of $[Ru(NN)_3]^{3+}$ with Mets has been studied in four different temperatures, and the enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation are evaluated from the kinetic data. The rate constants obtained at four temperatures and the thermodynamic data are presented in Table IV, and the Eyring plots are shown in Fig. 6. The negative values of $\Delta S^{\neq}$ indicate the compactness of transition state. A comparison of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values shows that with the change in the structure of methionine there is little change in the $\Delta S^{\neq}$ but there is a significant change in the $\Delta H^{\neq}$ value. Thus it seems that the reaction is enthalpy controlled.

Table IV Second-Order Rate Constants (k_2) and Activation Parameters for the Oxidation of Methionines by $[Ru(phen)_3]^{3+}$ in Aqueous 1:1 (v/v) CH_3CN at Different Temperatures

		k_2 (M^{-1} s^{-1})					
No.	Met	293 K	298 K	303 K	313 K	$\Delta H^{\neq}$ (kcal mol^{-1})	$-\Delta S^{\neq}$ (cal K^{-1} mol^{-1})
1	Methionine	7.6	9.2	12.5	17.4	8.5	47.1
2	Ethionine	9.7	12.4	15.2	22.6	6.1	47.1
3	Buthionine	14.3	17.5	22.7	32.4	6.1	47.1
4	*N*-acetyl-methionine	20.5	25.7	32.4	49.3	6.0	47.1

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

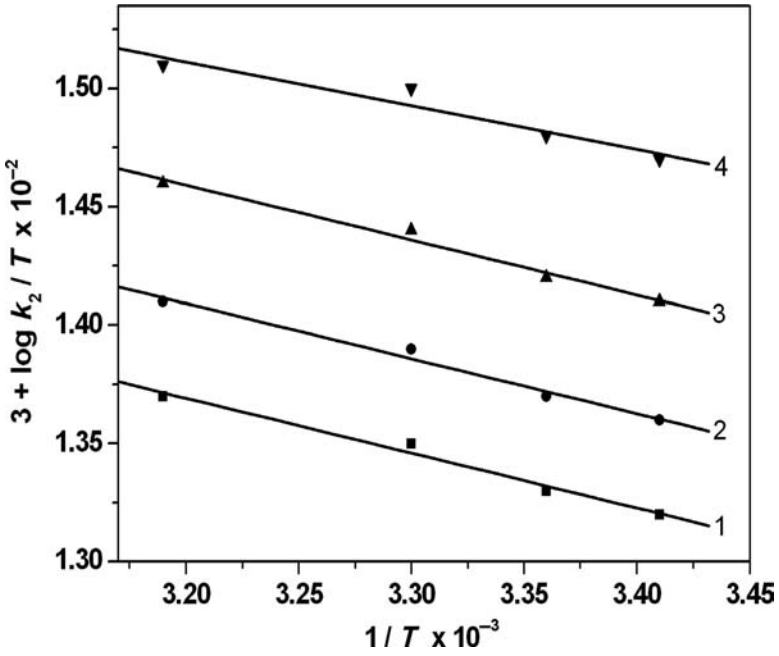


Figure 6 Eyring's plots for the oxidation of amino acids by $[Ru(phen)_3]^{3+}$ in aqueous CH_3CN (1:1, v/v) at 298 K. (The plots 1–4 refer to the amino acids given in Table IV.)

CONCLUSION

The oxidation of four substituted Mets with six $[Ru(NN)_3]^{3+}$ ions proceeds through rate-determining ET from the substrate to the oxidant. The ET nature of the reaction is confirmed by the identification of the sulfur cation radical using the nanosecond laser flash photolysis technique and formation of the Ru(II) ion as the product of the reaction. Met sulfoxide is the major product of the reaction. The rate constants calculated by using Marcus semiclassical theory are in close agreement with the experimental values.

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