

SPECTROPHOTOMETRIC STUDY OF KINETICS OF REDOX REACTION BETWEEN CAFFEINE AND PERMANGANATE ION IN AQUEOUS ACIDIC MEDIUM

ABSTRACT

The kinetics of redox reaction between caffeine (hereafter referred to as CAF) and permanganate ion $[\text{MnO}_4^-]$ has been studied spectrophotometrically in aqueous sulphuric acid medium. The stoichiometric coefficient of the reactants was 1:1 in terms of mole ratio of $[\text{CAF}]$ and $[\text{MnO}_4^-]$ consumed respectively. The reaction showed first-order kinetics with respect to both $[\text{CAF}]$ and $[\text{MnO}_4^-]$. The investigation was carried out under pseudo-first order condition at $I = 0.5 \text{ mol dm}^{-3}$, (Na_2SO_4) , $T = 24 \pm 0.1^\circ\text{C}$ and $[\text{H}^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$. The reaction obeys the rate law:

$$-d[\text{MnO}_4^-]/dt = (a+b [\text{H}^+]) [\text{CAF}] [\text{MnO}_4^-]$$

The reaction was retarded by increased ionic strength of the reaction medium. The rate of the reaction showed dependence on acid (in the range used). Added anions and cations were observed to catalyze the reaction rate. Spectroscopic investigation and kinetic study did not suggest intermediate complex formation. An outer-sphere mechanism is proposed for the reaction.

Keywords: Redox reaction, caffeine, permanganate ion and spectrophotometric.

1. INTRODUCTION

Caffeine (hereafter referred to as CAF) is an alkaloid naturally found in cocoa beans, tea, and kola nuts *e.t.c.* It is added to some drinks such as red bull and mountain dew [1, 2] It has been reported to be the most widely consumed alkaloid [3] and also possesses some pharmacological properties such as stimulating action on the central nervous system, stimulation of respiratory heart rate and a mild diuretic effect [4]. The addition of caffeine to commonly prescribed pain relief tablets such as ibuprofen and paracetamol improves the potency and efficacy of the tablets [5]. It acts by blocking binding of adenosine to the adenosine receptor, which enhances release of the neurotransmitter acetylcholine [6]. It has a three dimensional structure similar to that of adenosine, which allows it to bind and block its receptor [7]. It also increases cyclic AMP levels through nonselective inhibition of phosphodiesterase [8]. Caffeine is the world's most widely consumed psychoactive drug [9]. In addition, the compound is reported to have significant ability to scavenge highly reactive free radicals and excited state of oxygen thus, protecting crucial biological molecules against these species [10- 14]. The antioxidant ability of caffeine is reported to be similar to that of biological antioxidant glutathione and significantly much higher than that of ascorbic acid [15].

Permanganate ions are widely used as oxidizing agent in both preparative and analytical chemistry [16]. It is a very important oxidant in many organic and inorganic redox reactions involves Mn (VII) which is known for its versatility. The oxidizing ability of Mn (VII) is a function of the pH of the reaction medium. Since caffeine plays a very important role in the biological and biochemical processes, it is therefore, expected that the result of this investigation

will contribute in the better understanding of the redox reaction of caffeine with oxyanions in the biosystem.

2. MATERIALS AND METHODS

2.1 Materials

All solutions were prepared with distilled water. Standard solution of caffeine (BDH) was prepared by dissolving accurately weighed quantity in distilled water. H_2SO_4 and KMnO_4 were prepared and standardized titrimetrically. H_2SO_4 was used as a source of H^+ . Stock solutions of Na_2SO_4 , HCOONa , MgSO_4 , CaSO_4 and NaCO_3 were prepared by dissolving known quantity of the solute in a known volume of distilled water.

2.2 Methods

2.2.1 Stoichiometry

The stoichiometry of the reaction was determined spectrophotometrically, using the mole ratio method [17- 19]. Concentration of the permanganate ion was kept constant while that of the caffeine was varied in the range $(1.0 - 6.0) \times 10^{-4} \text{ mol dm}^{-3}$ at $[\text{H}^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$ (Na_2SO_4) and $\lambda_{\text{max}} = 530 \text{ nm}$. These reactions were allowed to go to completion. The reaction was taken to complete when the absorbances of the solutions remained constant. The stoichiometry indicated by the point of inflexion, was evaluated from the plot of absorbance versus mole ratio $[\text{CAF}]/[\text{MnO}_4^-]$.

2.2.2 Kinetic measurements

The kinetics of the reaction was investigated by following the decrease in absorbance due to $[\text{MnO}_4^-]$ at $\lambda_{\text{max}} = 530 \text{ nm}$ on Corning Colorimeter 252 model. The investigation was conducted under pseudo- first order condition with $[\text{CAF}]$ in large excess over $[\text{MnO}_4^-]$ at $[\text{H}^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$ (Na_2SO_4) and $T = 23 \pm 0.1^\circ\text{C}$. The pseudo-first order plot of the $\log(A_t - A_\infty)$ versus time was made and from the slope of the plot, the pseudo first-order rate constant (k_{obs}) were determined from the slope of the plots [20, 21, 19]. The second order rate constants were obtained from $k_{\text{obs}}/[\text{CAF}]$.

2.2.3 Effect of hydrogen ion concentration, $[\text{H}^+]$ on the reaction rate

The effect of $[\text{H}^+]$ on the rate of the reaction was investigated using sulphuric acid. The reaction was investigated at acid range of $0.02 - 0.34 \text{ mol dm}^{-3}$ while the concentrations of caffeine and permanganate ion were kept constant at $3.2 \times 10^{-2} \text{ mol dm}^{-3}$ and $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ respectively. The reaction was carried out at $I = 0.50 \text{ mol dm}^{-3}$ (Na_2SO_4) [22- 23].

2.2.4 Effect of ionic strength (I) on the rate of reaction

The effect of ionic strength on the reaction medium was investigated in the range $I = (0.1 - 0.6) \text{ mol dm}^{-3}$ (Na_2SO_4) while the concentrations of other reactants were kept constant. The results are presented in Table 1.

2.2.5 Effect of added anions and cations on the rate of reaction

The influence of added ions (CH_3COO^- , CO_3^{2-} , Ca^{2+} and Mg^{2+}) on the rate of the reaction was investigated by varying the concentrations of the salts in the range $(5.0 - 20.0) \times 10^{-3} \text{ mol dm}^{-3}$. While other conditions were kept constant.

2.2.6 Polymerization test

Addition of acrylamide to the partially oxidized reaction mixture containing various concentrations of solution of caffeine, permanganate ion and hydrogen ion. This was followed by a large excess of methanol. The acrylamide was also added to the solution of caffeine and permanganate ion separately, serving as control [24-26].

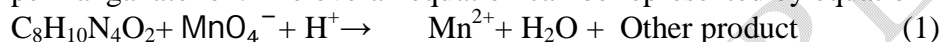
2.2.7 Test for the presence of intermediate complex formation

Spectroscopic test was carried out by comparing the electronic spectrum of the reaction mixture 20 minutes after the start of the reaction with that of the permanganate ion within a wavelength of 400-700nm. Kinetic test was also investigated using Michaelis-Mentens plot of $1/k_{\text{obs}}$ versus $1/[\text{CAF}]$ [24-26].

3. RESULTS AND DISCUSSION

3.1 Stoichiometry and Product Analysis

The result on stoichiometry depicts that one mole of the caffeine was consumed by one mole of permanganate ion. The overall equation can be represented by equation 1.



Similar stoichiometry has been reported for the oxidation of malachite green by permanganate ion [27] and for the oxidation of nicotine by permanganate [28] nicotinic acid [17] and L-tryptophan [24]. Nevertheless in the reaction of permanganate ion with DL-alanine [29] and theobromine [30] one mole of permanganate was consumed by two moles of the reductants respectively.

The colourless product obtained at the completion of reaction reacted with potassium perchlorate and a purple colouration was observed suggesting the presence of Mn(II) ion. Potassium perchlorate oxidizes Mn(II) to purple Mn(VII) as can be represented by the equation below.



3.2 Kinetic Measurement

The analysis of the plots of $(\log A_t - A_\infty)$ versus time were linear to more than 70% extent of reaction indicating that the reaction is first order dependence on $[\text{MnO}_4^-]$. And the pseudo-first order rate constants (k_{obs}) were determined from the slope of these plots and are reported in Table (1). Plot of $\log k_{\text{obs}}$ versus $[\text{CAF}]$ showed that CAF- MnO_4^- reaction is first order in $[\text{CAF}]$ as the graph was linear with a slope of 1.0018 (Fig. 1) first order dependence on both reductant and oxidant have been reported by earlier researchers [17, 16, 30]. The reaction was carried out at $I = 0.5 \text{ mol dm}^{-3} (\text{Na}_2\text{SO}_4)$ and $[\text{H}^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$. The rate equation for the reaction can be represented by equation 3:

$$-d[\text{MnO}_4^-]/dt = k_2[\text{MnO}_4^-][\text{CAF}] \quad (3)$$

Table 1: Pseudo-first order and second order rate constants for the reaction of caffeine and MnO_4^- at $[\text{MnO}_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $T = 23 \pm 0.1^\circ\text{C}$, $I = 0.5 \text{ mol dm}^{-3}$ and $\lambda_{\text{max}} = 530 \text{ nm}$

$10^2 [\text{CAF}],$ mol dm^{-3}	$10^1 [\text{H}^+],$ mol dm^{-3}	$10 [\text{I}],$ mol dm^{-3}	$10^3 k_1,$ s^{-1}	$k_2,$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
1.2	1.0	5.0	5.26	0.043
1.6	1.0	5.0	7.04	0.040
2.0	1.0	5.0	9.07	0.045
2.4	1.0	5.0	1.07	0.049
2.8	1.0	5.0	1.20	0.043
3.2	1.0	5.0	1.41	0.044
3.6	1.0	5.0	1.53	0.042
4.0	1.0	5.0	1.78	0.044
4.4	1.0	5.0	1.97	0.044
4.8	1.0	5.0	2.16	0.045
5.2	1.0	5.0	2.30	0.044
3.2	0.2	5.0	0.96	0.030
3.2	0.6	5.0	1.18	0.037
3.2	1.0	5.0	1.38	0.043
3.2	1.4	5.0	1.57	0.049
3.2	1.8	5.0	1.76	0.055
3.2	2.2	5.0	2.10	0.065
3.2	2.6	5.0	2.42	0.073
3.2	3.4	5.0	2.70	0.083
3.2	1.0	1.0	1.98	0.062
3.2	1.0	2.0	1.87	0.058
3.2	1.0	3.0	1.71	0.053
3.2	1.0	4.0	1.48	0.046
3.2	1.0	5.0	1.36	0.044
3.2	1.0	6.0	1.22	0.038

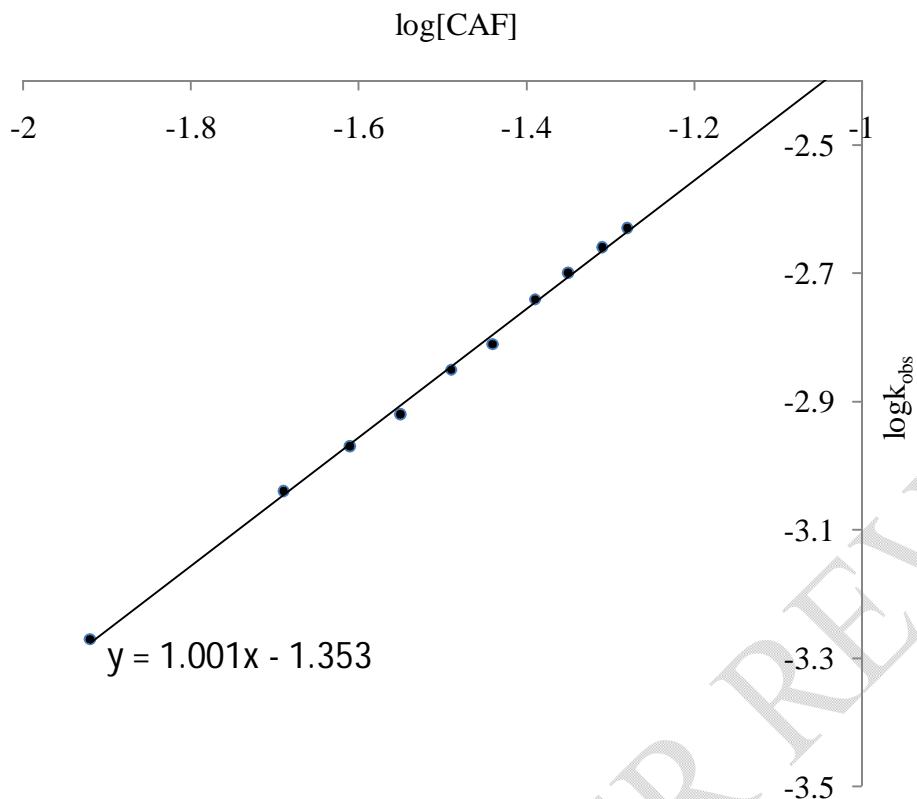


Figure 1: Plot of $\log k_{\text{obs}}$ versus $\log[\text{CAF}]$ for the redox reaction of CAF and MnO_4^- at $[\text{MnO}_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{CAF}] = (1.2 - 5.2) \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$ (Na_2SO_4) and $T = 24 \pm 0.1^\circ\text{C}$.

3.3 Effect of $[\text{H}^+]$ on the Rate of the Reaction

The rate of the reaction was enhanced by increase in $[\text{H}^+]$. Plot of $\log k_{\text{obs}}$ versus $\log[\text{H}^+]$ gave a slope of 1.26, indicating that the reaction is first order with respect to $[\text{H}^+]$. Plot of k_2 versus $[\text{H}^+]$ was linear with positive intercept. The acid rate constant for the reaction can be represented by equation 4:

$$-d[\text{MnO}_4^-]/dt = (a + b[\text{H}^+]) [\text{CAF}] [\text{MnO}_4^-] \quad (4)$$

where $a = 0.26 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ and $b = 1.8 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$.

The rate of reaction displayed two parallel pathways of reaction; one involving the protonated and the other the unprotonated species both reacting to give a product [27, 30, 31, 32].

3.4 Effect of Ionic Strength on the Rate

The rate of the reaction was observed to decrease with increase in the ionic strength of the reaction medium. Linear plot of $\log k_2$ versus $I^{1/2}$ gave a negative slope of -0.469 (Fig. 2), indicating that the reaction displayed a negative Bronsted-Debye salt effect, suggesting that at activated complex there is interaction of both cationic and anionic species. The value of the slope -0.469 implies that some other interactions like parallel reactions, ion-pair interactions might have taken place to account for non-integral value of the slope [17, 18, 24].

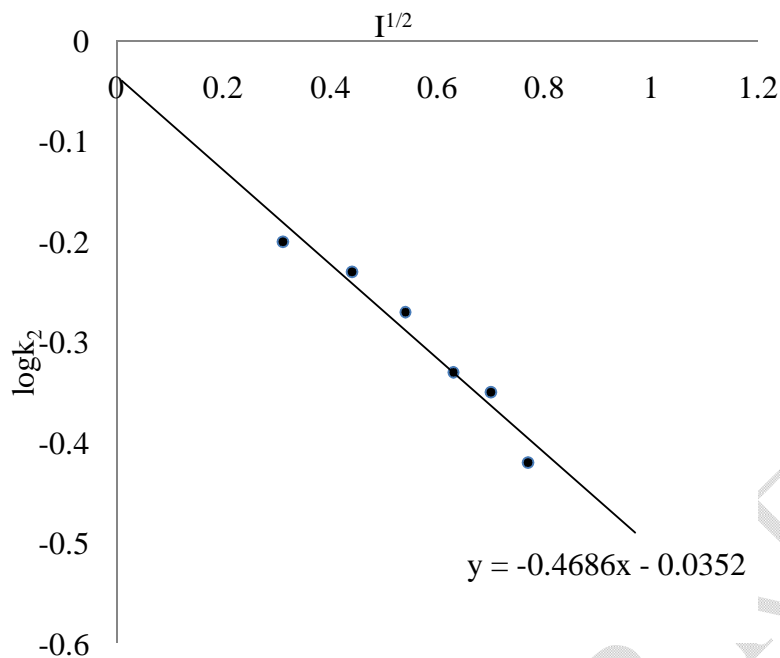


Figure 2: Plot of $\log k_2$ versus $I^{1/2}$ for the redox reaction of CAF and MnO_4^- at $[\text{CAF}] = 3.2 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{MnO}_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, $I = 0.1 - 0.6 \text{ mol dm}^{-3}$ (Na_2SO_4) and $T = 24 \pm 0.1^\circ\text{C}$

3.5 Effect of Added Anions and Cations on the Rate

Added anions (HCOO^- and CO_3^{2-}) and cations (Mg^{2+} and Ca^{2+}) led to the enhancement of the reaction rate (Table 2). Catalysis of the reaction by these added anions and cations is plausibly the characteristic of reactions that occurred through outer-sphere mechanistic pathway. In this kind of reaction the coordination integrity of the reactants are not perturb prior to the electron transfer [30].

3.6 Polymerization Test

Addition acrylamide to partially oxidized reaction mixture of permanganate and caffeine did not polymerized or formed gel, even when a large excess of methanol was added to the CAF-MnO_4^- reaction mixture. The negative result of polymerization test suggests the absence of free radical intermediate in the reaction or the equilibrium constant for the formation of such radicals can be assumed to be negligible [33].

3.7 Intermediate Complex Formation

Spectroscopic study indicates that there was no clear shift from 530nm, the wavelength of maximum absorption of MnO_4^- studied. This indicates absence of spectroscopic intermediate complex formation during the course of the reaction. **Michaelis-Mentens** plot of

Table 2: Rate constants for the effect of cations and anions in the redox reaction of caffeine and permanganate ion at $[CAF] = 3.2 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, $[MnO_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $I = 0.5 \text{ mol dm}^{-3}$ (Na_2SO_4)

$10^3 [Z], \text{ mol dm}^{-3}$	$10^3 k_{obs}, \text{ s}^{-1}$	$k_{2,3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Mg²⁺		
5.00	1.53	4.70
10.0	1.62	5.00
20.0	1.78	5.50
30.0	1.96	6.10
40.0	2.07	6.40
Ca²⁺		
5.00	1.57	4.90
10.0	1.77	5.50
20.0	1.90	5.90
30.0	2.04	6.30
40.0	2.10	6.50
HCOO⁻		
5.00	1.59	4.90
10.0	1.71	5.30
20.0	1.90	5.90
30.0	2.02	6.30
40.0	2.23	
CO₃²⁻		
5.00	1.71	5.31
10.0	1.84	5.72
20.0	1.90	5.90
30.0	2.07	6.44
40.0	2.17	6.70

$1/k_{obs}$ versus $1/[CAF]$ was linear passing through the origin (Fig. 3). This further suggests the absence of intermediate complex formation in the reaction [17, 18, 24, 30].

3.7. Reaction Mechanism

On the basis of the above finding, a plausible mechanism is proposed as follows:

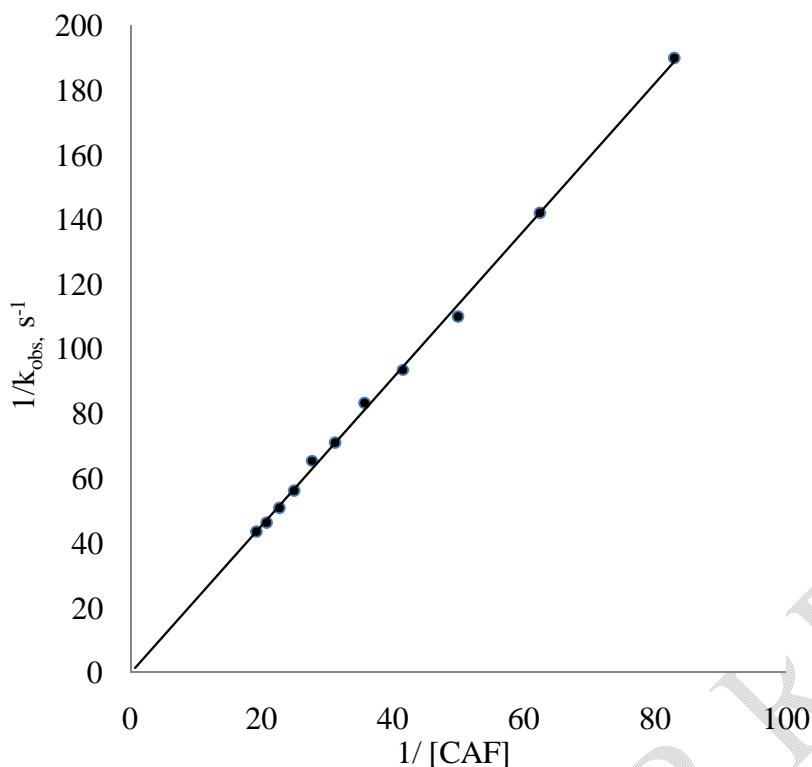
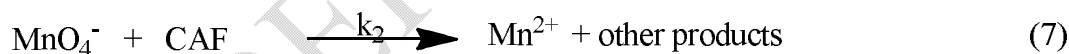
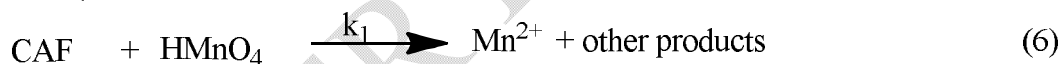
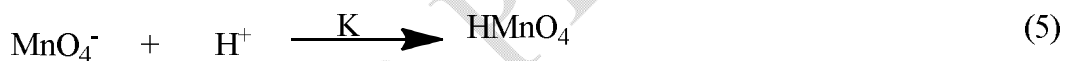


Figure 3: Michealis–Mentens plot of $1/k_1$ versus $1/[CAF]$ at $[MnO_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[CAF] = (1.20 - 5.20) \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$ (Na_2SO_4) and $T = 24.0 \pm 0.1^\circ C$.



$$\text{Rate} = k_1 [CAF][HMnO_4] + k_2 [CAF][MnO_4^-] \quad (8)$$

$$\text{But, } [HMnO_4] = K [H^+] [MnO_4^-] \quad (9)$$

Substituting equation 5 into equation 9

$$\text{Rate} = Kk_1 [CAF] [MnO_4^-] [H^+] + k_2 [CAF][MnO_4^-] \quad (10)$$

$$\text{Rate} = (Kk_1 [H^+] + k_2) [CAF][MnO_4^-] \quad (11)$$

$$(Kk_1 [H^+] + k_2) \approx k_3$$

Therefore

$$\text{Rate} = k_3 [CAF][MnO_4^-] \quad (12)$$

4. CONCLUSION

The redox reaction of caffeine by permanganate ion in aqueous sulphuric acid medium showed a 1:1 stoichiometry. The first order kinetics was observed with respect to both [CAF] and $[\text{MnO}_4^-]$. The rate of the reaction was enhanced by added CO_3^{2-} , HCOO^- , Mg^{2+} and Ca^{2+} . However, the rate of the reaction was inhibited by increase in the ionic strength of the reaction medium. From the above findings, it can be inferred that the kinetic and spectroscopic evidences are in support of the occurrence of outer-sphere mechanism in the caffeine–permanganate redox reaction.

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