

## Research Article

# Kinetics and Mechanistic Study of Permanganate Oxidation of Fluorenone Hydrazone in Alkaline Medium

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The oxidation kinetics of fluorenone hydrazone (FH) using potassium permanganate in alkaline medium were measured at a constant ionic strength of  $0.1 \text{ mol dm}^{-3}$  and at  $25^\circ\text{C}$  using UV/VIS spectrophotometer. A first-order kinetics has been monitored in the reaction of FH with respect to [permanganate]. Less-than-unit order dependence of the reaction on [FH] and  $[\text{OH}^-]$  was revealed. No pronounced effect on the reaction rate by increasing ionic strength was recorded. Intervention of free radicals was observed in the reaction. The reaction mechanism describing the kinetic results was illustrated which involves formation of 1:1 intermediate complex between fluorenone hydrazones and the active species of permanganate. 9H-Fluorenone as the corresponding ketone was found to be the final oxidation product of fluorenone hydrazone as confirmed by GC/MS analysis and FT-IR spectroscopy. The expression rate law for the oxidation reaction was deduced. The reaction constants and mechanism have been evaluated. The activation parameters associated with the rate-limiting step of the reaction, along with the thermodynamic quantities of the equilibrium constants, have been calculated and discussed.

## 1. Introduction

Fluorene and its derivatives (FLs) are a unique class of polycyclic aromatic hydrocarbons (PAHs) which exist in the fossil fuels and petrogenic sources burning of gasoline [1, 2]. Recently, studies on the exhaust emitting of different types of reformulated diesel fuels showed presence of fluorene as a precedence compound and isomers of methyl fluorene as a hesitant compound in the exhaust [3]. The fluorene unit is regularly employed in the growth of an assortment of visual devices with latent application as dye-sensitized solar cells [4], polymer light-emitting diodes [5, 6], and other electroemissive materials [7]. In addition, fluorene based systems possess sole photophysical properties such as high fluorescent quantum yield, huge photostability, and excellent hole-transporting properties [8, 9]. Furthermore, fluorene is one of the highest plentiful polycyclic aromatic hydrocarbons (PAHs) in the surroundings due to its high volatility. Established to be a neurotoxicant through mouthful of air, it was

also recognized as a contributive PAH to food contagion. Fluorene compounds with intrinsic rigid structures have been attracting much consideration as organic functional materials because of their promising physical and chemical properties such as glass transition temperatures, good solubility, and their amorphous nature, which make them very promising as a move toward optic electric materials [10, 11]. In addition, hydrazone derivatives were found to be biologically important class of compounds [12]. Hydrazone derivatives were found in natural and synthetic products of biological interest [13]. Literature studies revealed that hydrazones and the different substituted derivatives showed a broad spectrum of biological activities. Furthermore, fluorenone hydrazones are used as precursors for the synthesis of photochromic di- and tetrahydroindolizines [14–16] and more recently as efficient corrosion inhibitors [17].

Potassium permanganate is extensively used as an oxidizing agent for numerous organic molecules in various media [18–24]. The oxidation reaction mechanisms by permanganate

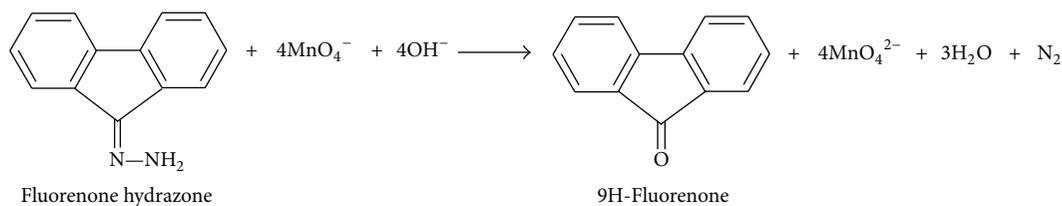


FIGURE 1

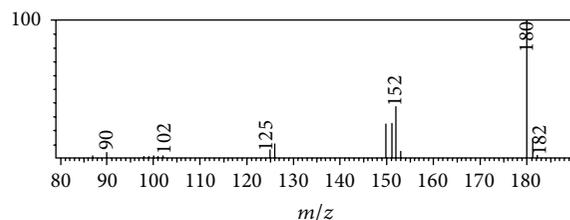
are governed by pH of the medium [25]. Among six oxidation states of Mn(II) to Mn(VII), permanganate, Mn(VII), is found to be the most powerful oxidation state in both acid and alkaline media. By using permanganate as oxidizing agent, it is understandable that the Mn(VII) in permanganate is reduced to a variety of oxidation states in acidic, alkaline, and neutral media.

To the best of our knowledge, there are no reports on the kinetics and mechanism of oxidation of fluorenone hydrazone. This motivates us to investigate the kinetics and mechanism of oxidation of fluorenone hydrazone with permanganate ion in alkaline medium. The objectives of the present study aimed to shed more light and establish the most favorable conditions affecting oxidation of such noteworthy compound and to elucidate a plausible oxidation reaction mechanism.

## 2. Experimental

**2.1. Materials.** The chemicals used in the current work were of Aldrich grades. Fluorenone hydrazone was prepared according to the described procedures with some modifications [26, 27]. The synthesized fluorenone hydrazone was confirmed by both spectroscopic and analytical tools. All solvents used were of spectroscopic grade and used without further purification. The solvents used were checked for the absence of absorbing or any fluorescent impurities. Potassium permanganate fresh solution was prepared and standardized as reported [28]. Sodium hydroxide and sodium perchlorate were used to vary the alkalinity and ionic strength of reaction medium, respectively.

**2.2. Kinetic Measurements.** The kinetic measurements were followed under pseudo-first-order conditions where fluorenone hydrazone substrate (abbreviated by FH) existed in a large excess over that of permanganate. Initiation of the reaction was done by mixing the formerly thermostated solutions of permanganate and substrate that also contained the required amounts of NaOH and NaClO<sub>4</sub>. The course of the reaction was followed up to not less than two half-lives by monitoring the absorbance of permanganate as a function of time at its absorption maximum ( $\lambda = 525$  nm), whereas the other constituents of the reaction mixture were not absorbed considerably at the determined wavelength. The melting points of fluorenone derivatives were recorded using Galenkamp melting point apparatus. NMR was recorded on

FIGURE 2: GC/MS analysis for detection of the oxidation product 9H-fluorenone ( $m/z = 180$ ).

Bruker Avance 400 MHz with CDCl<sub>3</sub> and CDCl<sub>3</sub> as solvent with tetramethylsilane (TMS) as the internal reference. Chemical shifts were related to that of the solvent. GC-Mass spectra were recorded on Shimadzu GCMS-QP1000 EX mass spectrometer at 70 eV. The absorption measurements were done in a temperature-controlled Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. The reactions temperature was controlled to  $\pm 0.1^\circ\text{C}$ .

First-order plots of  $\ln(\text{absorbance})$  versus time were recorded to be straight lines up to at least 80% of the reaction completion and the observed first-order rate constants ( $k_{\text{obs}}$ ) were calculated as the gradients of such plots. Ordinary values of at least two independent determinations of the rate constants were taken for the analysis. The rate constants were reproducible to 2-3%. The orders of the reaction with admiration to the reactants were calculated from the slopes of the  $\log k_{\text{obs}}$  versus  $\log(\text{concentration})$  plots by varying the concentrations of both substrate and alkali, in turn, while keeping other conditions constant.

## 3. Results and Discussion

**3.1. Stoichiometry and Product Analysis.** The stoichiometry was analyzed periodically by both titrimetric and spectrophotometric techniques at  $[\text{OH}^-] = 0.01$  and  $I = 0.1$  mol dm<sup>-3</sup> at 25°C. The results indicate expenditure of four permanganate ions for one molecule of fluorenone hydrazone to yield the oxidation products as shown in Figure 1.

Figure 1 is in good agreement with the results of products analysis as confirmed by the head-space GC/MS which revealed a molecular ion peak [ $M^+$ , 100%] at 180 related to 9H-fluorenone (Figure 2). The mass spectrometry fragmentation pattern for 9H-fluorenone showed the following signals:  $m/z$ : 180.06 (100.0%), 181.06 (14.2%), 182.06 (1.1%), 152.23 (33.4%), 125.46 (10.19%), and 102.35 (1.6%).

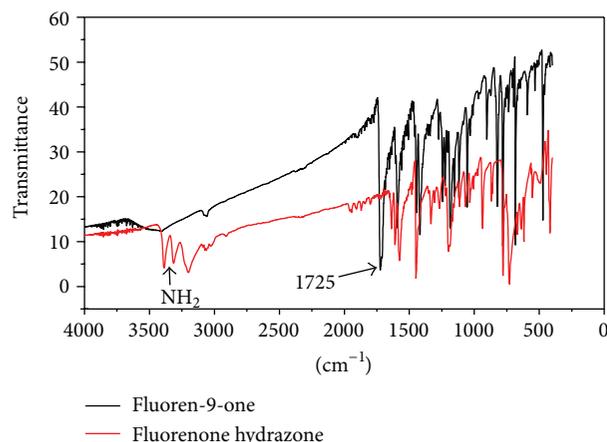


FIGURE 3: FT-IR spectra of fluorenone hydrazone (red line) and the oxidized product 9H-fluorenone (black line).

Further assignment of the oxidation product was done by the help of FT-IR spectra as represented in Figure 3 for fluorenone hydrazone and its oxidation product, 9H-fluorenone. The product 9H-fluorenone showed a very strong signal at  $1725\text{ cm}^{-1}$  corresponding to the (C=O) group with disappearance of amino group at signals at  $3388$  and  $3316\text{ cm}^{-1}$ . In addition, the fingerprints of the oxidation product are different than before oxidation process.

**3.2. Time-Resolved Spectra.** Time-resolved spectra during the oxidation of fluorenone hydrazone by alkaline permanganate are represented in Figure 4. The main characteristic feature manifested in the figure is the gradual decay of permanganate band at its absorption maximum ( $\lambda = 525\text{ nm}$ ) as a result of reduction of permanganate by fluorenone hydrazone derivatives.

**3.3. Effect of Permanganate Concentration.** Permanganate ion oxidant was diverse in the concentration range of  $1.0 \times 10^{-4}$  to  $8.0 \times 10^{-4}\text{ mol dm}^{-3}$ , while the rest of the reactant concentrations were kept constant. Both pH and temperature were also kept constant. It has been found that plots of  $\ln(\text{absorbance})$  versus time were linear up to about 80% of the reaction achievement. Furthermore, the increase in the oxidant concentration did not change the oxidation rate as listed in Table 1. These results prove and confirm the first-order reaction with respect to the oxidant.

**3.4. Effect of Fluorenone Hydrazone Concentration.** The observed first-order rate constant ( $k_{\text{obs}}$ ) was measured at diverse concentrations of the reductant fluorenone hydrazone keeping others constant. A plot of  $k_{\text{obs}}$  versus [FH] was found to be linear with a positive intercept on  $k_{\text{obs}}$  axis (Figure 5) confirming less-than-unit order dependence with respect to the reductant concentration.

**3.5. Effect of Alkali Concentration.** The influence of alkali on the reaction rate was deliberated at various  $[\text{OH}^-]$ , keeping

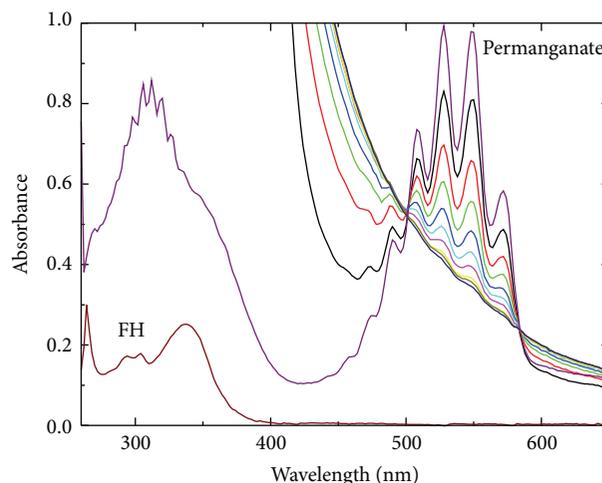


FIGURE 4: Time-resolved spectra during the oxidation of fluorenone by alkaline permanganate:  $[\text{FH}] = 8.0 \times 10^{-3}$ ,  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{OH}^-] = 0.02$ , and  $I = 0.1\text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ . Scanning time intervals are 1 min.

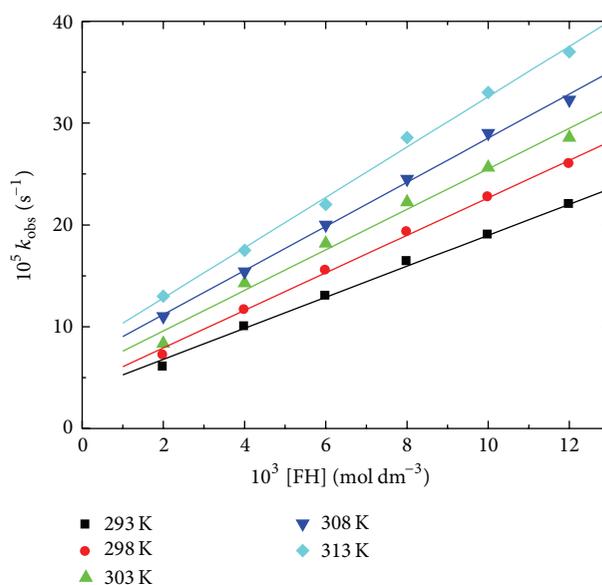


FIGURE 5: Plots of the observed first-order rate constants ( $k_{\text{obs}}$ ) versus [FH], at different temperatures, in the oxidation of fluorenone hydrazone by alkaline permanganate:  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{OH}^-] = 0.02$ , and  $I = 0.1\text{ mol dm}^{-3}$ .

all other reactant concentrations constant. An increase in the rate constant with increasing alkali concentration was achieved (Table 1). A plot of  $\log k_{\text{obs}}$  versus  $\log[\text{OH}^-]$  was found to be linear with a slope of 0.75 (figure not shown), suggesting that the reaction order with respect to  $[\text{OH}^-]$  was less than unity.

**3.6. Effect of Ionic Strength.** The effect of the ionic strength was studied through varying the concentration of  $\text{NaClO}_4$  in the reaction medium at constant concentrations of permanganate, fluorenone hydrazone, and alkali. It was found that

TABLE 1: Effect of variation of  $[\text{MnO}_4^-]$ ,  $[\text{FH}]$ ,  $[\text{OH}^-]$ , and  $I$  on the observed first-order rate constants ( $k_{\text{obs}}$ ) in the oxidations of fluorenone hydrazone by alkaline permanganate at 25°C.

$10^4 [\text{MnO}_4^-]$ (mol dm <sup>-3</sup> )	$10^3 [\text{FH}]$ (mol dm <sup>-3</sup> )	$10^2 [\text{OH}^-]$ (mol dm <sup>-3</sup> )	$I$ (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )
<b>1.0</b>	8.0	2.0	0.1	19.8
<b>2.0</b>	8.0	2.0	0.1	20.2
<b>3.0</b>	8.0	2.0	0.1	19.2
<b>4.0</b>	8.0	2.0	0.1	19.6
<b>6.0</b>	8.0	2.0	0.1	18.3
<b>8.0</b>	8.0	2.0	0.1	18.9
4.0	<b>2.0</b>	2.0	0.1	7.3
4.0	<b>4.0</b>	2.0	0.1	12.0
4.0	<b>6.0</b>	2.0	0.1	15.8
4.0	<b>8.0</b>	2.0	0.1	19.6
4.0	<b>10.0</b>	2.0	0.1	22.8
4.0	<b>12.0</b>	2.0	0.1	25.6
4.0	8.0	<b>0.5</b>	0.1	9.8
4.0	8.0	<b>1.0</b>	0.1	14.2
4.0	8.0	<b>1.5</b>	0.1	17.4
4.0	8.0	<b>2.0</b>	0.1	19.6
4.0	8.0	<b>3.0</b>	0.1	23.6
4.0	8.0	<b>4.0</b>	0.1	27.3
4.0	8.0	2.0	<b>0.1</b>	19.6
4.0	8.0	2.0	<b>0.2</b>	18.9
4.0	8.0	2.0	<b>0.3</b>	20.7
4.0	8.0	2.0	<b>0.4</b>	19.2
4.0	8.0	2.0	<b>0.5</b>	18.9
4.0	8.0	2.0	<b>0.6</b>	20.2

Experimental error is  $\pm 3\%$ .

variation in ionic strength did not affect the oxidation rate as observed from the data listed in Table 1.

**3.7. Effect of Temperature.** The oxidation rate was recorded at five different temperatures, 293, 298, 303, 308, and 313 K under varying the concentrations of fluorenone hydrazone and alkali at constant ionic strength. The activation parameters of the rate constant of the slow step ( $k_1$ ) along with thermodynamic parameters of the equilibrium constants involved in the reaction mechanism were evaluated using Arrhenius and Eyring equations and were listed in Table 2.

**3.8. Polymerization Study.** To check the existence of free radicals in the reaction under investigation, the reactions mixtures were mixed with identified quantities of acrylonitrile monomer and stored for 6 hours under dry nitrogen condition. On dilution with methanol, white precipitates were formed, indicating the participation of free radicals in the oxidation reactions. The blank experiments which were carried out with either permanganate or every substrate with acrylonitrile did not induce polymerization under the same experimental conditions.

**3.9. Reaction Mechanism.** Permanganate ion is found to be a powerful oxidant in aqueous alkaline media and exhibits

some of oxidation states such as Mn(VII), Mn(V), and Mn(VI). At pH > 12, the reduction product of Mn(VII) is stable Mn(VI) and no further reduction is observed [29, 30]. The formation of a manganate(VI) intermediate was confirmed by the green color observed as the reactions proceeded [31, 32] which undergoes a slow decay to give rise to the final oxidation products. The yellow color persisted after achievement of the oxidation reactions; then, finally, discrete brown MnO<sub>2</sub> sol was observed confirming that Mn(V) species, hypomanganate(V), formed and subsequently decomposed to Mn(IV) sol [33]. The latter was coagulated by aging to give a colloidal precipitate of Mn(IV)O<sub>2</sub>.

It was reported [34, 35] that permanganate ion in aqueous alkaline media combines with alkali to produce an alkali-permanganate species,  $[\text{MnO}_4 \cdot \text{OH}]^{2-}$ , in a preequilibrium step, as shown in Scheme 1. This is consistent with the apparent order of less than unity with respect to the alkali. The formation of  $[\text{MnO}_4 \cdot \text{OH}]^{2-}$  in the present systems is further supported by the plots of  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  shown in Figure 7, which are linear with nonzero intercepts.

Many investigators [18–24] have suggested that most of the permanganate ion oxidation reactions in neutral and alkaline media proceed through intermediate complexes formation between the oxidant and substrates. The kinetic evidence for such complex was established by the linearity of the plots between  $1/k_{\text{obs}}$  and  $1/[\text{FH}]$ , Figure 6, in favor of

TABLE 2: Values of  $k_1$ ,  $K_1$ , and  $K_2$  (at different temperatures), activation parameters associated with the slow step ( $k_1$ ), and thermodynamic parameters of the equilibrium constants ( $K_1$  and  $K_2$ ) in the oxidation of fluorenone hydrazone by alkaline permanganate:  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{FH}] = 8.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 0.02$ , and  $I = 0.1 \text{ mol dm}^{-3}$ .

(a) Values of  $k_1$ ,  $K_1$ , and  $K_2$  (at different temperatures)

Constant	Temperature (K)				
	293	298	303	308	313
$10^4 k_1$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )	3.71	4.50	5.39	6.41	7.41
$K_1$ ( $\text{dm}^3 \text{ mol}^{-1}$ )	15.62	17.48	20.11	24.74	29.08
$10^{-2} K_2$ ( $\text{dm}^3 \text{ mol}^{-1}$ )	4.73	4.16	3.61	3.23	3.06

(b) Activation parameters associated with the slow step ( $k_1$ )

$\Delta S^\ddagger$ $\text{J mol}^{-1} \text{ K}^{-1}$	$\Delta H^\ddagger$ $\text{kJ mol}^{-1}$	$\Delta G_{298}^\ddagger$ $\text{kJ mol}^{-1}$	$E_a^\ddagger$ $\text{kJ mol}^{-1}$
$-103.02 \pm 4.1$	$26.52 \pm 1.2$	$57.22 \pm 0.4$	$27.06 \pm 1.3$

(c) Thermodynamic parameters associated with the equilibrium constants ( $K_1$  and  $K_2$ )

Equilibrium constant	$\Delta H^0$ $\text{kJ mol}^{-1}$	$\Delta G_{298}^0$ $\text{kJ mol}^{-1}$	$\Delta S^0$ $\text{J mol}^{-1} \text{ K}^{-1}$
$K_1$	24.28	-7.08	105.25
$K_2$	-17.18	-14.94	-7.51

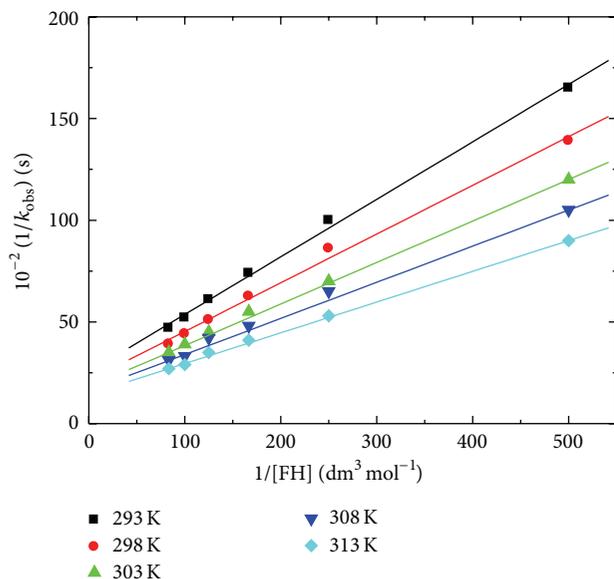


FIGURE 6: Plots of  $1/k_{\text{obs}}$  versus  $1/[\text{FH}]$ , at different temperatures, in the oxidation of fluorenone hydrazone by alkaline permanganate:  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{OH}^-] = 0.02$ , and  $I = 0.1 \text{ mol dm}^{-3}$ .

possible formation of a transient complex flanked by oxidant and substrate comparable with the well-known Michaelis-Menten mechanism [36] for enzyme-substrate reactions. The observed insignificant effect of ionic strength on the reaction rate implies the association of an ion and a neutral molecule

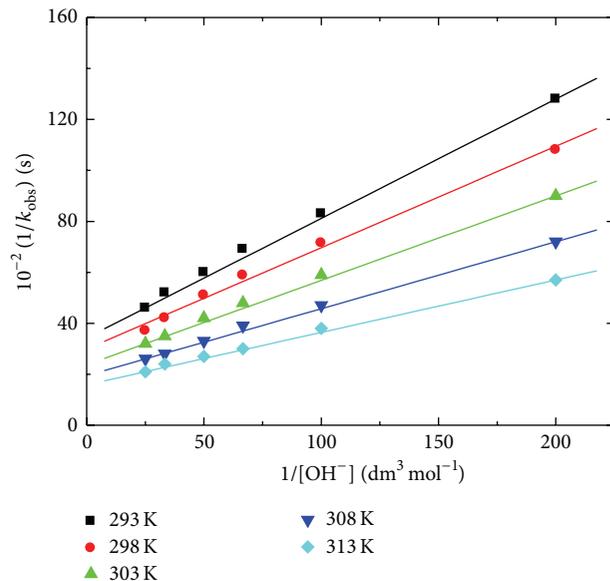


FIGURE 7: Plots of  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$ , at different temperatures, in the oxidation of fluorenone hydrazone by alkaline permanganate:  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{FH}] = 8.0 \times 10^{-3}$ , and  $I = 0.1 \text{ mol dm}^{-3}$ .

[37], that is, between neutral fluorenone hydrazone and negative alkali-permanganate species.

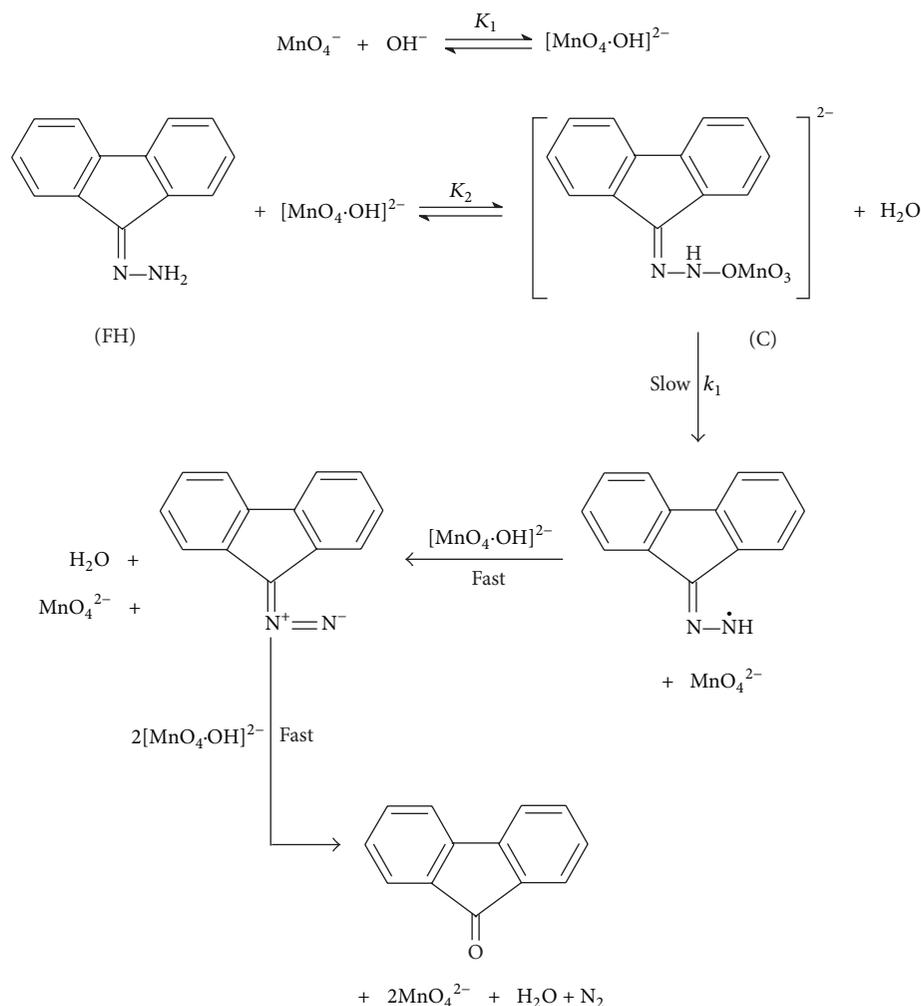
In view of the above arguments, the reaction mechanism shown in Scheme 1 may be suggested. This involves attack of the active species of permanganate,  $[\text{MnO}_4 \cdot \text{OH}]^{2-}$ , on the fluorenone hydrazone substrate leading to the formation of a complex (C) in a preequilibrium step. In this complex, one electron is transferred from the substrate to permanganate. Under slow cleavage of the complex, the formation of a free radical intermediate derived from the substrate and manganate(VI) transient species has been monitored. The intermediate radical is rapidly attacked by another alkali-permanganate species to yield the corresponding diazoderivative which on further oxidation by two moles of permanganate species gives the corresponding ketone (fluorenone) as the final oxidation product.

The relationship between reaction rate and substrate (FH), hydroxyl ion, and oxidant concentrations can be deduced (see Appendix) to give the following equation:

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{FH}] [\text{OH}^-] [\text{MnO}_4^-]}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{FH}] [\text{OH}^-]}. \quad (1)$$

The rate law under pseudo-first-order condition can be expressed by

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}} [\text{MnO}_4^-]. \quad (2)$$



SCHEME 1: Mechanism of oxidation of fluorenone hydrazone by alkaline permanganate.

Comparing (1) and (2) and with rearrangement, we obtain the following equations:

$$\frac{1}{k_{\text{obs}}} = \left( \frac{1 + K_1 [\text{OH}^-]}{k_1 K_1 K_2 [\text{OH}^-]} \right) \frac{1}{[\text{FH}]} + \frac{1}{k_1} \quad (3)$$

$$\frac{1}{k_{\text{obs}}} = \left( \frac{1}{k_1 K_1 K_2 [\text{FH}]} \right) \frac{1}{[\text{OH}^-]} + \left( \frac{1}{k_1 K_2 [\text{FH}]} + \frac{1}{k_1} \right). \quad (4)$$

According to (3) and (4), with other conditions being constant, plots of  $1/k_{\text{obs}}$  versus  $1/[\text{FH}]$  at constant  $[\text{OH}^-]$  and  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  at constant  $[\text{FH}]$  should be linear with positive intercepts on  $1/k_{\text{obs}}$  axes and are certainly found to be so as shown in Figures 6 and 7, respectively. The slopes and intercepts of such plots lead to calculation of values of  $k_1$ ,  $K_1$ , and  $K_2$  (at different temperatures) as listed in Table 2. The obtained values of  $K_1$  are in a good agreement with those

reported in the literature [18–20]. Also, the activation parameters of  $k_1$  along with thermodynamic parameters of  $K_1$  and  $K_2$  were calculated and were listed also in Table 2.

It has been previously reported [38] that the entropy of activation tends to be more negative for reactions of inner-sphere nature, whereas the reactions of positive  $\Delta S^\ddagger$  values proceed via outer-sphere mechanism. The obtained large negative values of entropy of activation (Table 2) suggest that one-electron transfer of inner-sphere nature is the more plausible mechanism for the current oxidation reaction. On the other hand, positive values of both  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  specify that the formation of the complex is endothermic and non-spontaneous, respectively.

#### 4. Conclusions

The kinetics of oxidation of fluorenone hydrazone by alkaline permanganate has been studied. The oxidation product of fluorenone hydrazone was identified by GC/MS and FT-IR analyses as the corresponding ketone (9H-fluorenone). The

reaction constants involved in the reaction mechanism have been evaluated. The activation and thermodynamic parameters have been evaluated and discussed.

## Appendix

### Derivation of the Rate Law Expression

According to suggested mechanistic scheme,

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_1 [\text{C}] \quad (\text{A.1})$$

$$K_1 = \frac{[\text{MnO}_4 \cdot \text{OH}^{2-}]}{[\text{MnO}_4^-] [\text{OH}^-]} \quad (\text{A.2})$$

Therefore,

$$[\text{MnO}_4 \cdot \text{OH}^{2-}] = K_1 [\text{MnO}_4^-] [\text{OH}^-] \quad (\text{A.3})$$

$$K_2 = \frac{[\text{C}]}{[\text{FH}] [\text{MnO}_4 \cdot \text{OH}^{2-}]} \quad (\text{A.4})$$

Thus,

$$[\text{C}] = K_2 [\text{FH}] [\text{MnO}_4 \cdot \text{OH}^{2-}] \quad (\text{A.5})$$

Substituting (A.3) into (A.5) leads to

$$[\text{C}] = K_1 K_2 [\text{FH}] [\text{OH}^-] [\text{MnO}_4^-] \quad (\text{A.6})$$

Substituting (A.6) into (A.1) yields

$$\text{Rate} = k_1 K_1 K_2 [\text{FH}] [\text{OH}^-] [\text{MnO}_4^-] \quad (\text{A.7})$$

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{FH}] [\text{OH}^-] [\text{MnO}_4^-]}{(1 + K_1 K_2 [\text{OH}^-] [\text{MnO}_4^-]) (1 + K_1 [\text{MnO}_4^-]) (1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{FH}] [\text{OH}^-])} \quad (\text{A.17})$$

In view of low concentration of  $[\text{MnO}_4^-]$  used, both first and second terms in the denominator of (A.17) approximate to unity. Therefore, (A.17) becomes

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{FH}] [\text{OH}^-] [\text{MnO}_4^-]}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{FH}] [\text{OH}^-]} \quad (\text{A.18})$$

Under pseudo-first-order conditions, the rate law can be expressed as

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}} [\text{MnO}_4^-] \quad (\text{A.19})$$

Comparing (A.18) and (A.19), the following relationship is obtained:

$$k_{\text{obs}} = \frac{k_1 K_1 K_2 [\text{FH}] [\text{OH}^-]}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{FH}] [\text{OH}^-]} \quad (\text{A.20})$$

The total concentration of fluorenone hydrazone is given by

$$[\text{FH}]_{\text{T}} = [\text{FH}]_{\text{F}} + [\text{C}], \quad (\text{A.8})$$

where  $[\text{FH}]_{\text{T}}$  and  $[\text{FH}]_{\text{F}}$  stand for total and free concentrations of the substrate.

Substituting (A.6) into (A.8) gives

$$[\text{FH}]_{\text{T}} = [\text{FH}]_{\text{F}} + K_1 K_2 [\text{FH}] [\text{OH}^-] [\text{MnO}_4^-] \quad (\text{A.9})$$

$$[\text{FH}]_{\text{T}} = [\text{FH}]_{\text{F}} (1 + K_1 K_2 [\text{OH}^-] [\text{MnO}_4^-]) \quad (\text{A.10})$$

Therefore,

$$[\text{FH}]_{\text{F}} = \frac{[\text{FH}]_{\text{T}}}{1 + K_1 K_2 [\text{OH}^-] [\text{MnO}_4^-]} \quad (\text{A.11})$$

Similarly,

$$[\text{MnO}_4^-]_{\text{T}} = [\text{MnO}_4^-]_{\text{F}} + [\text{MnO}_4 \cdot \text{OH}^{2-}] + [\text{C}] \quad (\text{A.12})$$

$$[\text{MnO}_4^-]_{\text{T}} = [\text{MnO}_4^-]_{\text{F}} (1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{FH}] [\text{OH}^-] [\text{MnO}_4^-]) \quad (\text{A.13})$$

$$[\text{MnO}_4^-]_{\text{F}} = \frac{[\text{MnO}_4^-]_{\text{T}}}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{FH}] [\text{OH}^-]} \quad (\text{A.14})$$

Also,

$$[\text{OH}^-]_{\text{T}} = [\text{OH}^-]_{\text{F}} + [\text{MnO}_4 \cdot \text{OH}^{2-}] \quad (\text{A.15})$$

$$[\text{OH}^-]_{\text{F}} = \frac{[\text{OH}^-]_{\text{T}}}{1 + K_1 [\text{MnO}_4^-]} \quad (\text{A.16})$$

Substituting (A.11), (A.14), and (A.16) into (A.7) (and omitting "T" and "F" subscripts), we get

And with rearrangement, the following equations are obtained:

$$\frac{1}{k_{\text{obs}}} = \left( \frac{1 + K_1 [\text{OH}^-]}{k_1 K_1 K_2 [\text{OH}^-]} \right) \frac{1}{[\text{FH}]} + \frac{1}{k_1} \quad (\text{A.21})$$

$$\frac{1}{k_{\text{obs}}} = \left( \frac{1}{k_1 K_1 K_2 [\text{FH}]} \right) \frac{1}{[\text{OH}^-]} + \left( \frac{1}{k_1 K_2 [\text{FH}]} + \frac{1}{k_1} \right) \quad (\text{A.22})$$

### Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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