A Comparative Kinetic and Mechanistic Study on the Oxidation Behaviour of Halogenated Fluorenes by Permanganate in Alkaline Medium

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Abstract: The oxidation kinetics of fluorene (Fl) and its halogenated derivatives, namely, 2,7-dichlorofluorene (Fl-Cl), 2,7-dibromofluorene (Fl-Br) and 2,7-diiodofluorene (Fl-I), using potassium permanganate in alkaline medium has been studied spectrophotometrically at a constant ionic strength of 0.1 mol dm^{-3} and at 25°C. A first order kinetics has been observed in these reactions with respect to [permanganate]. Fractional-first order dependences of the reactions on the [reductants] and [alkali] were revealed. No significant effect on the reaction rates by increasing ionic strength was recorded. Intervention of free radicals was observed in the reactions. The reactions mechanism describing the kinetic results has been proposed which involves formation of 1:1 intermediate complexes between fluorene derivatives and the active species of permanganate. The final reactions products were identified by GC/MS and FT-IR analyses in all cases as the corresponding ketones (9H-fluorenone derivatives). Under comparable experimental conditions, the order of the oxidation rate of fluorine derivatives was: Fl > Fl-I > Fl-Br > Fl-Cl. The reactions constants involved in the different steps of the reactions mechanism have been evaluated. With admiration to rate-limiting step of these reactions, the activation parameters were recorded and discussed.

Keywords: Permanganate, Oxidation, Fluorenes, Kinetics, Mechanism

1. Introduction

Fluorene and its derivatives (Fls) are a unique class of are polycyclic aromatic hydrocarbons (PAHs) exist in the fossil fuels and petrogenic sources are among products from the burning of gasoline [1, 2]. The fluorene unit is regularly employed in the growth of an assortment of visual devices with latent application as dye-sensitized solar cells [3], polymer light-emitting diodes [4, 5] and electro-emitting materials [6]. In addition, fluorene based systems possess sole photophysical properties such as high fluorescent quantum yield, great optical nonlinearities, huge photostability, and excellent hole-transporting properties [7, 8]. Due to these properties, fluorene derivatives have been

used lengthily as purposeful materials for organic light-emitting diodes, solar cells, photosensitizers, fluorescence microscopy [9, 10]. 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. Moreover, fluorene and its derivatives are considered as effective and pronounced precursors for the synthesis of photochromic di and tetrahydroindolizines [11-14].

Potassium permanganate is extensively used as an oxidizing agent for numerous organic molecules in various

media [15-25]. The mechanism of oxidation reactions by permanganate is governed by pH of the medium [26]. Among six oxidation states of manganese from Mn(II) to Mn(VII), permanganate, Mn(VII) is found to be the most powerful oxidation state in both acid and alkaline media. During oxidation by permanganate, it is obvious 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 fluorene or its derivatives. In view of the above arguments, we tend to investigate the kinetics and mechanism of oxidations of fluorine and its halogenated derivatives with permanganate ion in organic alkaline medium. The objectives of the present study are to establish the most favorable conditions affecting oxidations of such noteworthy compounds, to investigate the effect of substituted halogens on the oxidations kinetics of fluorene and to elucidate a plausible reactions mechanism.

2. Experimental

2.1. Materials

The chemical used in the current work were of Aldrich grades. Fluorene and its derivatives, 2,7-dichloroflourene, 2,7-dibromoflourene and 2,7-diiodoflourene were prepared according to the described procedures with some modifications [27, 28]. The absorption spectra of fluorene and its halogenated derivatives are shown in Fig. 1. The synthesized fluorene derivatives were confirmed by both spectroscopic (see the supplementary materials) and analytical tools. For example, the ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of 2,7-dibromfluorene showed the flowing signals (δ = 7.66 (s, 2H, 1,8-CH-arom.), 7.55-7.59 (dd, J = 7.6, 1.5 Hz, 2H, 3.6-CH-arom.), 7.50-7.52 (dd, J = 7.6, 2.4 Hz, 2H, 4,5-CH-arom. All solvents used were of spectroscopic grade and used without

Figure 1. Absorption spectra of fluorene and its halogenated derivatives.

further purifications. The solvents used were checked for the absence of absorbing or any fluorescent impurities. Potassium permanganate freshly solution was prepared and standardized as reported [29]. Sodium hydroxide and sodium perchlorate were used to vary the alkalinity and ionic strength of reactions media, respectively.

2.2. Kinetic Measurements

The kinetic measurements were followed under pseudo-first order conditions where fluorene substrates (abbreviated by S) were exist in large excess over that of permanganate. Initiation of the reactions were done by mixing the formerly thermostatted solutions of permanganate and substrate that also contained the required amounts of NaOH and NaClO$_4$. The courses of the reactions were followed up to not less than two half-lives by monitoring the diminish in the absorbance of permanganate as a function of time at its absorption maximum (λ = 525 nm), whereas the other constituents of the reaction mixtures did not absorb considerably at the determined wavelength. Fluorene derivatives were confirmed by both spectroscopic and analytical tools. The melting points of fluorene derivatives were recorded using a Gallenkamp melting point apparatus. NMR was recorded on a Bruker Advance 400 MHz with CDCl$_3$ and DMSO as solvents with tetramethylsilane (TMS) as the internal reference. Chemical shifts were related to that of the solvent. GC-Mass spectra were recorded on a 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 within ± 0.1°C.

First order plots of ln(absorbance) versus time were recorded to be straight lines up to at least 80% of the reactions completion and the observed first order rate constants (k_{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 within 4%. The orders of the reactions with respect to the reactants were determined from the slopes of the log k_{obs} versus log(concentration) plots by varying the concentrations of substrate and alkali, in turn, while keeping other conditions constant.

3. Results

3.1. Stoichiometry and Product Characterization

The stoichiometry was analyzed periodically by both titrimetric and spectrophotometric techniques at [OH$^-$] = 0.01 and I = 0.1 mol dm^{-3}. The results indicate expenditure of four permanganate ions for one molecule of fluorene derivative to yield the oxidation products as shown in the following equation,
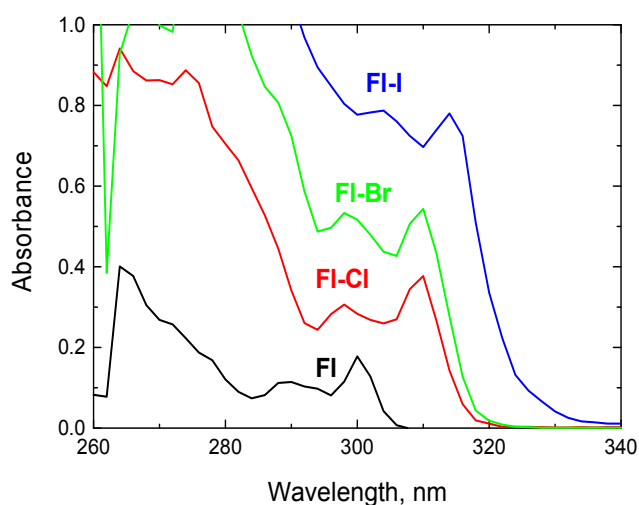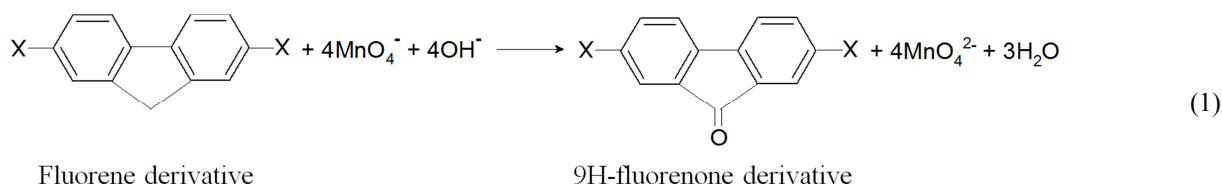
$$\text{X}-\text{(Fluorene derivative)}-\text{X} + 4MnO_4^- + 4OH^- \longrightarrow \text{X}-\text{(9H-fluorenone derivative)}-\text{X} + 4MnO_4^{2-} + 3H_2O$$

(1)

Fluorene derivative   9H-fluorenone derivative

The above stoichiometric equation 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 the 9H-fluoren-9-one (Fig. 2), [M^+, 100%] at 249 related to the 2,7-dichloro-9H-fluoren-9-one, [M^+, 100%] at 338 related to the 2,7-dibromo-9H-fluoren-9-one and [M^+, 100%] at 432 related to the 2,7-

diiodo-9H-fluoren-9-one. The mass spectrometry fragmentation pattern for 2,7-dibromo-9H-fluoren-9-one (as an example) showed the following signals: m/z: 337.88 (100.0%), 335.88 (51.3%), 339.87 (48.6%), 338.88 (14.2%), 336.88 (7.3%), 340.88 (6.9%), 339.88 (1.1%), 152 (26.19%), 125 (4.23%), 115 (1.95%).
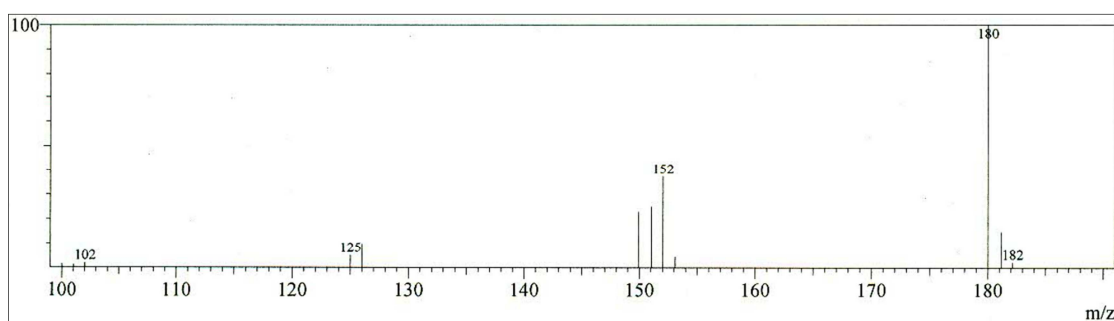

Figure 2. *GC/MS analysis for detection of the oxidation product 9H-fluoren-9-one (m/z= 180).*
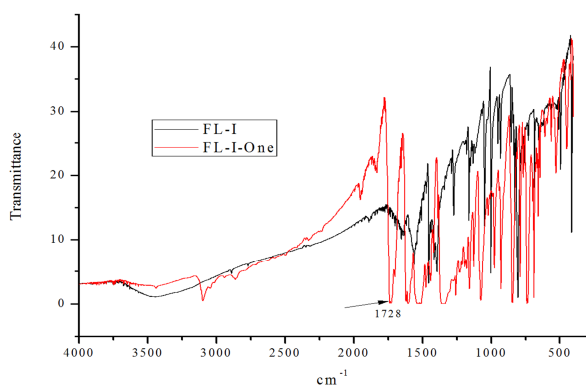

Figure 3. *FT-IRs spectra of 2,7-diiodo-9H-fluorene (black line) and the oxidized product 2,7-diiodo-9H-fluoren-9-one (red line).*

Further assignment of the oxidation products were done by the help of FT-IR spectra as shown in Figure 3 for (as an example) both 2,7-diiodo-9H-fluorene (Fl-I) and its oxidation product 2,7-diiodo-9H-fluoren-9-one. The product 2,7-diiodo-9H-fluoren-9-one showed a very strong signal at 1728 cm^{-1} corresponding to the (C=O) group which is absent in the 2,7-diiodo-9H-fluorene. In addition, the finger prints of the oxidation product are different than before oxidation.

3.2. Spectral Changes

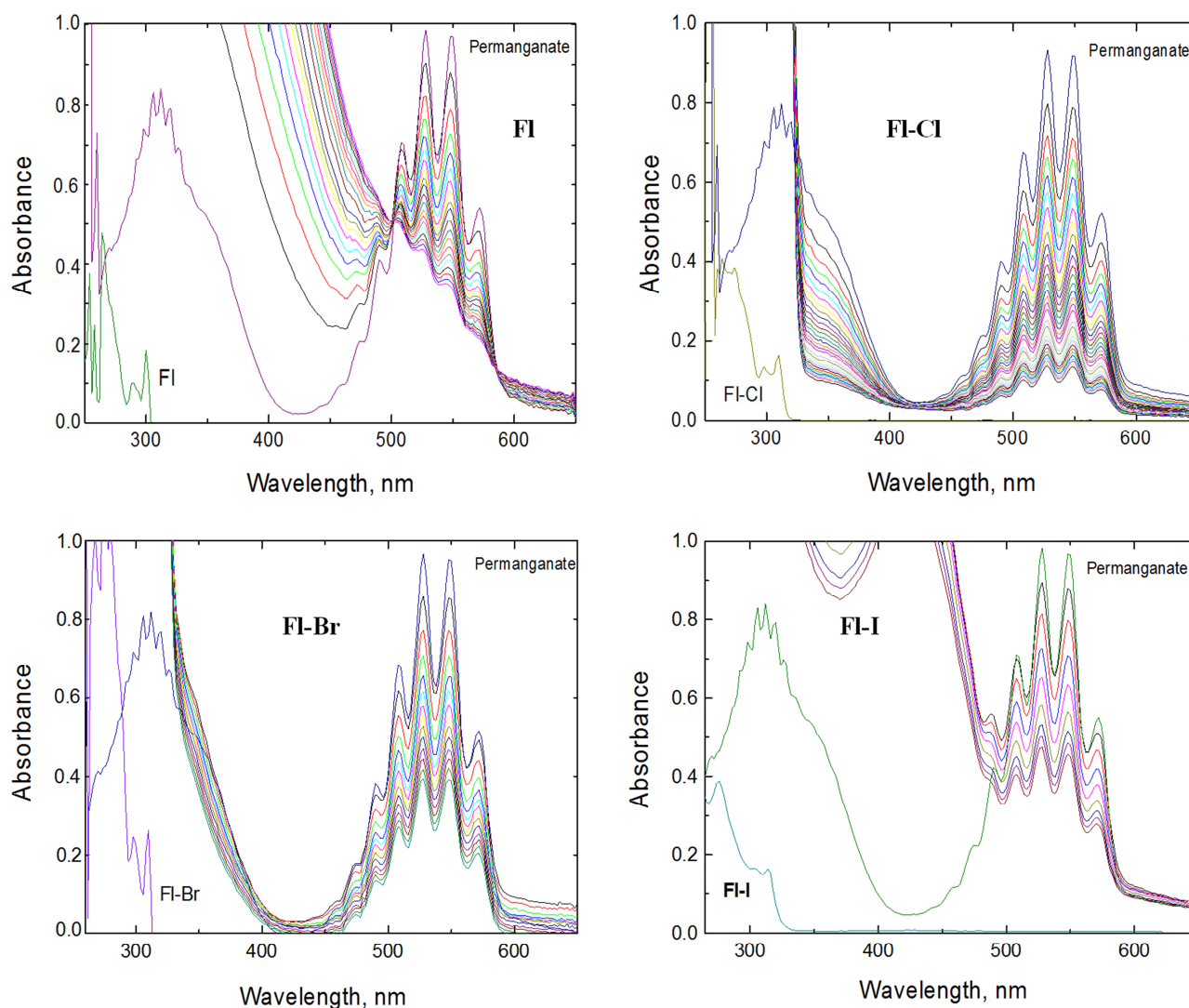The spectral scans during the oxidation of fluorene and its

halogenated derivatives by alkaline permanganate are shown in Fig. 4(a-d). The main characteristic feature manifested in the figure is the gradual decay of permanganate band at its absorption maximum (λ = 525 nm) as a result of reduction of permanganate by fluorene derivatives.
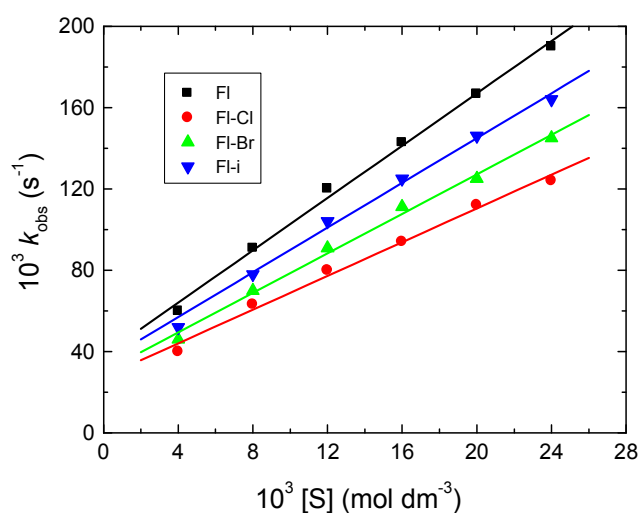
3.3. Effect of Permanganate Concentration

Permanganate ion oxidant was diverse in the concentration range of 1.0×10^{-4} to 8.0×10^{-4} mol dm^{-3} while the rest of the reactant concentrations were kept constant. Both pH and temperature were also reserved constant. It has been found that, plots of ln(absorbance) versus time were linear up to about 80% of the reactions completion. Furthermore, the increase in the oxidant concentration did not change the oxidation rates as listed in Table 1. These results indicate that, the order of reactions with respect to the oxidant is confirmed to be one.

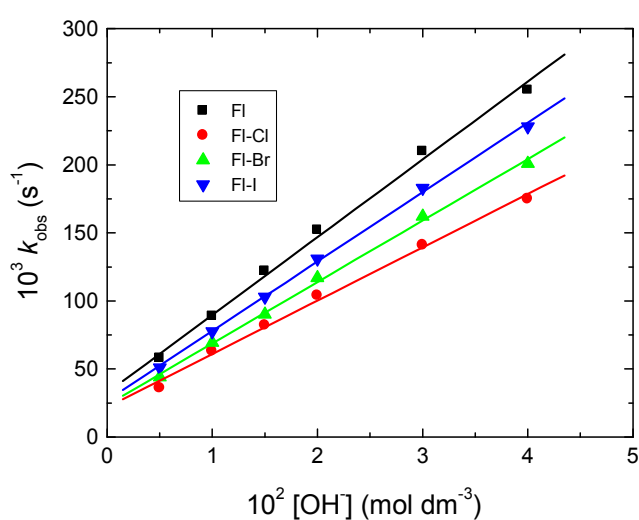### 3.4. Effect of Fluorenes Concentration

The observed first order rate constants were measured at diverse concentrations of the reductants fluorenes keeping others constant. Plots of k_{obs} versus [S] were found to be linear with positive intercepts on k_{obs} axes (Fig. 5) confirming less than unit order dependences with respect to substrates concentration.

Figure 4. *Spectral changes during the oxidations of fluorene and its derivatives by alkaline permanganate. [S] = 8.0 x 10^{-3}, [MnO$_4^-$] = 4.0 x 10^{-4}, [OH$^-$] = 0.01 and I = 0.1 mol dm^{-3} at 25°C.*

Figure 5. *Plots of the observed-first order rate constants (k$_{obs}$) versus substrates concentrations, [S], in the oxidations of fluorene and its derivatives by alkaline permanganate. [MnO$_4^-$] = 4.0 x 10^{-4}, [OH$^-$] = 0.01 and I = 0.1 mol dm^{-3} at 25°C.*

Figure 6. *Plots of the observed-first order rate constants (k$_{obs}$) versus alkali concentration in the oxidations of fluorene and its derivatives by alkaline permanganate. [MnO$_4^-$] = 4.0 x 10^{-4}, [S] = 8.0 x 10^{-3} and I = 0.1 mol dm^{-3} at 25°C.*

3.5. Effect of Alkali Concentration

The influence of alkali on the reaction rates was deliberated at various [OH⁻], keeping all other reactant concentrations constant. An increase in the rate constants with increasing alkali concentration was achieved (Table 1). Plots of k_{obs} versus [OH⁻] were also linear with non-zero intercepts as shown in Fig. 6, suggesting that the orders of reactions with respect to [OH⁻] were less than unity.

3.6. Effect of Ionic Strength

The ionic strength effect was studied by varying the concentration of NaClO₄ in the reactions media at constant concentrations of permanganate, fluorenes and alkali. It was found that variation in ionic strength did not affect the rates as observed from the data listed in Table 1.

Table 1. Effect of variation of [MnO₄⁻], [S], [OH⁻] and I on the observed-first order rate constants (k_{obs}) in the oxidations of fluorene and its derivatives by alkaline permanganate at 25°C.

10^4 [MnO₄⁻] (mol dm⁻³)	10^3 [S] (mol dm⁻³)	10^2 [OH⁻] (mol dm⁻³)	I (mol dm⁻³)	10^3 k_{obs} (s⁻¹)			
				Fl	Fl-Cl	Fl-Br	Fl-I
1.0	8.0	1.0	0.1	88.2	61.6	67.7	79.3
2.0	8.0	1.0	0.1	90.0	63.4	70.8	79.0
3.0	8.0	1.0	0.1	90.6	62.9	70.4	75.9
4.0	8.0	1.0	0.1	88.9	63.2	69.3	77.6
6.0	8.0	1.0	0.1	87.2	64.0	67.7	76.8
8.0	8.0	1.0	0.1	87.8	65.1	71.2	75.5
4.0	**4.0**	1.0	0.1	55.8	38.1	43.7	47.1
4.0	**8.0**	1.0	0.1	88.9	63.2	69.3	77.6
4.0	**12.0**	1.0	0.1	119.6	79.7	90.9	104.0
4.0	**16.0**	1.0	0.1	142.8	93.9	111.2	125.3
4.0	**20.0**	1.0	0.1	166.6	112.0	124.9	146.4
4.0	**24.0**	1.0	0.1	190.2	123.9	145.1	164.7
4.0	8.0	**0.5**	0.1	55.7	37.8	43.6	48.9
4.0	8.0	**1.0**	0.1	88.9	63.2	69.3	77.6
4.0	8.0	**1.5**	0.1	122.1	82.3	90.4	103.1
4.0	8.0	**2.0**	0.1	151.8	104.6	117.2	131.0
4.0	8.0	**3.0**	0.1	210.0	141.2	162.4	183.0
4.0	8.0	**4.0**	0.1	254.9	175.3	201.3	228.4
4.0	8.0	1.0	**0.1**	88.9	63.2	69.3	77.6
4.0	8.0	1.0	**0.2**	89.0	61.9	67.4	75.2
4.0	8.0	1.0	**0.3**	87.7	64.3	69.0	76.3
4.0	8.0	1.0	**0.4**	86.1	60.1	66.6	75.3
4.0	8.0	1.0	**0.5**	88.9	64.0	69.8	78.1
4.0	8.0	1.0	**0.6**	87.6	61.3	68.3	75.0

Experimental error ±3%
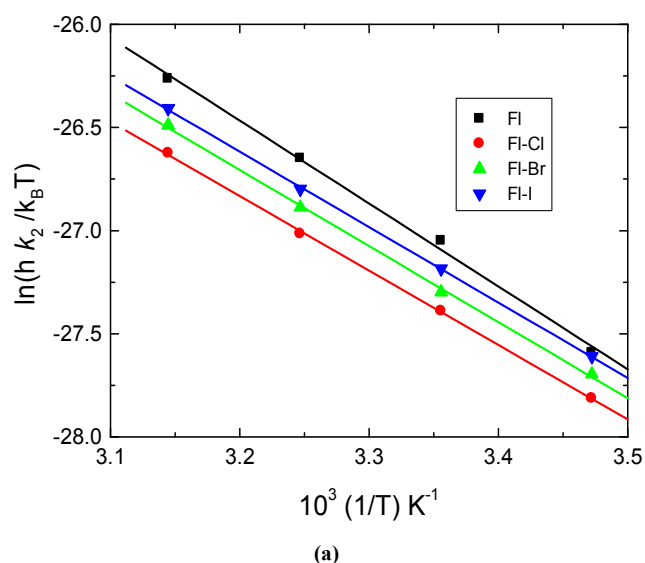
3.7. Effect of Temperature

The rates of the reactions were carried out at four different temperatures, 288, 298, 308 and 318 K at constant concentrations of the reactants and other conditions being constant. The results indicate that the rate constants increased with rise in temperature. The activation parameters of the second order rate constant (k_2) are calculated using Eyring, Fig. 7a, and Arrhenius, Fig. 7b, plots and are listed in Table 2.

Table 2. Activation parameters of the second order rate constant, k_2, in the oxidations of fluorene and its derivatives by alkaline permanganate. [MnO₄⁻] = 4.0 x 10⁻⁴, [S] = 8.0 x 10⁻³, [OH⁻] = 0.01 and I = 0.1 mol dm⁻³.

Substrate	$\Delta S^{\neq}$ J mol⁻¹ K⁻¹	$\Delta H^{\neq}$ kJ mol⁻¹	$\Delta G^{\neq}_{298}$ kJ mol⁻¹	$E_a^{\neq}$ kJ mol⁻¹
Fl	-113.07	33.42	67.11	34.92
Fl-Cl	-126.37	29.93	67.59	32.51
Fl-Br	-124.38	30.59	67.65	33.17
Fl-I	-123.87	30.35	67.27	32.92

(a)

Figure 7. *a) Eyring and, b) Arrhenius plots of the second order rate constant, k_2, in the oxidations of fluorene and its derivatives by alkaline permanganate. $[MnO_4] = 4.0 \times 10^{-4}$, $[S] = 8.0 \times 10^{-3}$, $[OH] = 0.01$ and $I = 0.1$ mol dm^{-3}.*
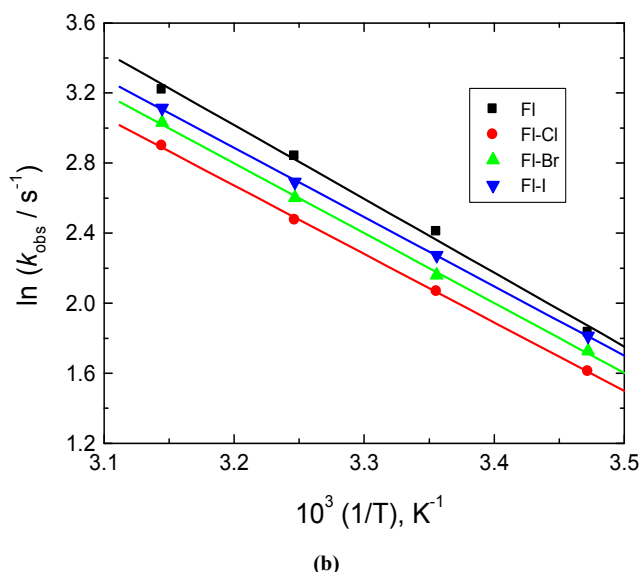
3.8. Polymerization Study

To check the existence of free radicals in the reactions under investigations, the reactions mixtures were mixed with identified quantities of acrylonitrile monomer and kept for 6 hours under nitrogen. 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 alone with acrylonitrile did not induce polymerization under the same experimental conditions.
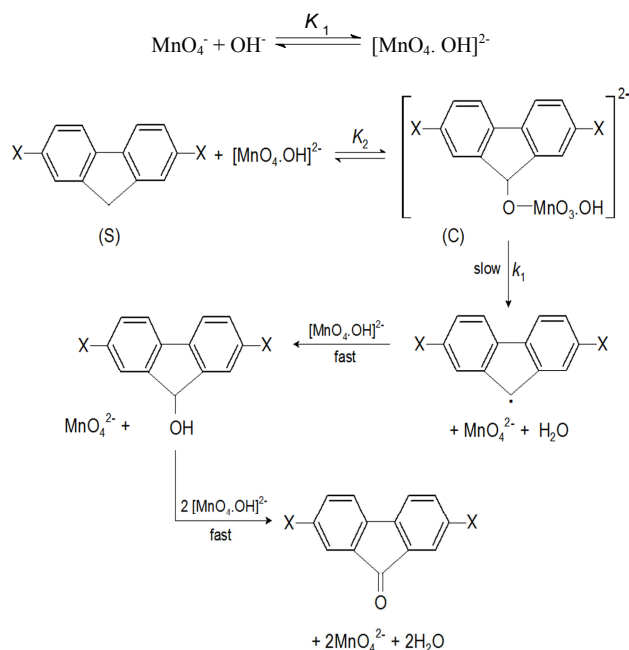
4. Discussion

Permanganate ion is a powerful oxidant in aqueous alkaline media and exhibits a variety of oxidation states, such as Mn(VII), Mn(V) and Mn(VI). Simandi et al. [30, 31] reported that, at pH > 12, the reduction product of Mn(VII) is stable Mn(VI) and no further reduction is observed. The formation of a manganate(VI) intermediate was confirmed by the green color observed as the reactions proceeded [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_2 sol was observed confirming that the 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 MnO_2.

It was reported [34, 35] that, permanganate ion in aqueous alkaline media combines with alkali to produce an alkali-permanganate species, $[MnO_4.OH]^{2-}$, in a pre-equilibrium 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 $[MnO_4.OH]^{2-}$ in the present systems is further supported by the plots of $1/k_{obs}$ versus $1/[OH^-]$ shown

in Fig. 9, which are linear with non-zero intercepts.

Many investigators [17-25] 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 evidences for such complexes were established by the linearity of the plots between $1/k_{obs}$ and $1/[S]$, Fig. 8, in favor of 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 rates implies the association of an ion and a neutral molecule [37, 38], i.e. between neutral fluorene derivative 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, $[MnO_4.OH]^{2-}$, on the fluorene substrate leading to the formation of a complex (C) in a prior equilibrium step. In this complex, one electron is transferred from the fluorene substrate to permanganate. Slow cleavage of the complex leads to the formation of a free radical intermediate derived from the substrate, and manganate(VI) transient species. The intermediate radical is rapidly attacked by another alkali-permanganate species to yield the corresponding secondary alcohols (fluorenol). A further oxidation of the intermediate product by permanganate species takes place leading to formation of the corresponding ketone (fluorenone) as the final oxidation product.

X = H for Fl, X = Cl for Fl-Cl, X = Br for Fl-Br and X = I for Fl-I,

Scheme 1. *Mechanism of oxidations of fluorenes by alkaline permanganate.*

Again, it has been previously reported [39] that, the entropy of activation tends to be more negative for reactions of inner-sphere nature, whereas the reactions of positive $\Delta S^{\neq}$

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 present oxidation reactions. On the other hand, the positive values of both $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate that the complex formation is endothermic and non-spontaneous, respectively.

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

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{S}][\text{OH}^-][\text{MnO}_4^-]}{1 + K_1[\text{OH}^-] + K_1 K_2 [\text{S}][\text{OH}^-]} \quad (2)$$

Under pseudo-first order condition the rate law can be expressed by Eq. (3),

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{obs}[\text{MnO}_4^-] \quad (3)$$

Comparing equations (2) and (3) and with rearrangement we obtain the following equations,

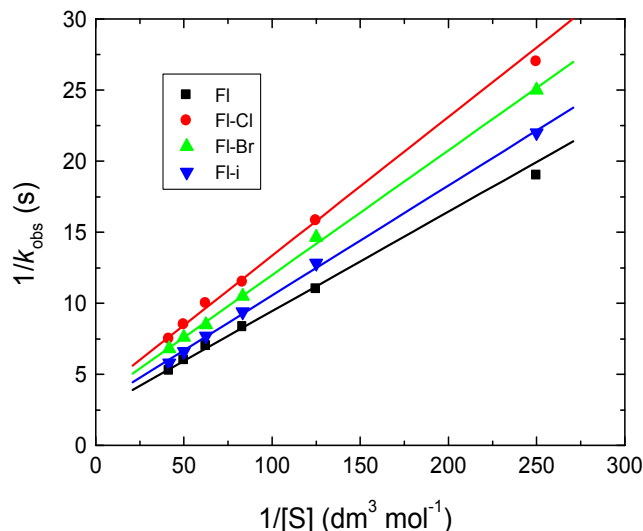$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[\text{OH}^-]}{k_1 K_1 K_2 [\text{OH}^-]} \right) \frac{1}{[\text{S}]} + \frac{1}{k_1} \quad (4)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 K_1 K_2 [\text{S}]} \right) \frac{1}{[\text{OH}^-]} + \left(\frac{1}{k_1 K_2} \frac{1}{[\text{S}]} + \frac{1}{k_1} \right) \quad (5)$$

According to equations (4) and (5), other conditions being constant, plots of $1/k_{obs}$ versus $1/[\text{S}]$ at constant $[\text{OH}^-]$ and $1/k_{obs}$ versus $1/[\text{OH}^-]$ at constant $[\text{S}]$ should be linear with positive intercepts on the $1/k_{obs}$ axes and are certainly found to be so as shown in Figs. 8 and 9, respectively. The slopes and intercepts of such plots lead to calculation of the values of k_1, K_1 and K_2 as listed in Table 3. The obtained values of K_1 are in a good agreement with those reported in the literature [16-19].
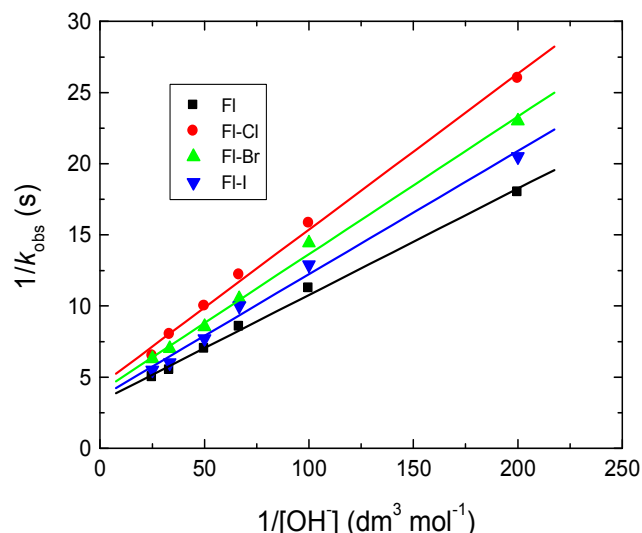
Table 3. *Values of k_1, K_1 and K_2 in the oxidations of fluorene and its derivatives by alkaline permanganate. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[S] = 8.0 \times 10^{-3}$, $[OH] = 0.01$ and $I = 0.1$ mol dm^{-3} at 25°C.*

Substrate	Constant		
	k_1, s^{-1}	K_1, dm^3 mol^{-1}	K_2, dm^3 mol^{-1}
Fl	0.41	6.86	554.31
Fl-Cl	0.28	14.45	312.05
Fl-Br	0.31	10.96	368.41
Fl-I	0.38	9.82	373.23

Experimental error ± 4%

Figure 8. *Verification of equation (4) for the oxidations of fluorene and its derivatives by alkaline permanganate. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[OH^-] = 0.01$ and $I = 0.1$ mol dm^{-3} at 25°C.*

Figure 9. *Verification of equation (5) for the oxidations of fluorene and its derivatives by alkaline permanganate. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[S] = 8.0 \times 10^{-3}$ and $I = 0.1$ mol dm^{-3} at 25°C.*

5. Conclusions

The kinetics of oxidations of fluorene and its halogenated derivatives by alkaline permanganate has been studied. The oxidation products of fluorenes were identified by GC/MS and FT-IR analyses as the corresponding ketones (9H-fluorenone derivatives). Under comparable experimental conditions, the order of the oxidation rate of fluorene derivatives is: Fl > Fl-I > Fl-Br > Fl-Cl.

Appendix A

Derivation of the Rate-Law Expression

According to suggested mechanistic scheme,

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = k_1[C] \qquad (A1)$$

$$K_1 = \frac{[MnO_4 \cdot OH^{2-}]}{[MnO_4^-][OH^-]} \qquad (A2)$$

Therefore,

$$[MnO_4 \cdot OH^{2-}] = K_1[MnO_4^-][OH^-] \qquad (A3)$$

$$K_2 = \frac{[C]}{[S][MnO_4 \cdot OH^{2-}]} \qquad (A4)$$

Thus,

$$[C] = K_2[S][MnO_4 \cdot OH^{2-}] \qquad (A5)$$

Substituting Eq. (A3) into Eq. (A5) leads to,

$$[C] = K_1K_2[S][OH^-][MnO_4^-] \qquad (A6)$$

Substituting Eq. (A6) into Eq. (A1) yields,

$$\text{Rate} = k_1K_1K_2[S][OH^-][MnO_4^-] \qquad (A7)$$

The total concentration of the substrate is given by,

$$[S]_T = [S]_F + [C] \qquad (A8)$$

where $[S]_T$ and $[S]_F$ stand for total and free concentrations of the substrate.

Substituting Eq. (A6) into Eq. (A8) gives,

$$[S]_T = [S]_F + K_1K_2[S][OH^-][MnO_4^-] \qquad (A9)$$

$$[S]_T = [S]_F(1 + K_1K_2[OH^-][MnO_4^-]) \qquad (A10)$$

Therefore,

$$[S]F = \frac{[S]_T}{1 + K_1K_2[OH^-][MnO_4^-]} \qquad (A11)$$

Similarly,

$$[MnO_4^-]_T = [MnO_4^-]_F + [MnO_4 \cdot OH^{2-}] + [C] \qquad (A12)$$

Substituting Eqs. (A3) and (A5) into Eq. (A12) gives,

$$[MnO_4^-]_T = [MnO_4^-]_F(1 + K_1[OH^-] + K_1K_2[S][OH^-][MnO_4^-]) \qquad (A13)$$

$$[MnO4^-]F = \frac{[MnO_4^-]_T}{1 + K_1[OH^-] + K_1K_2[S][OH^-]} \qquad (A14)$$

Also,

$$[OH^-]_T = [OH^-]_F + [MnO_4 \cdot OH^{2-}] \qquad (A15)$$

$$[OH-]F = \frac{[OH^-]_T}{1 + K_1[MnO_4^-]} \qquad (A16)$$

Substituting Eqs. (A11), (A14) and (A16) into Eq. (A16) (and omitting 'T' and 'F' subscripts) we get,

$$\text{Rate} = \frac{k_1K_1K_2[S][OH^-][MnO_4^-]}{(1 + K_1K_2[OH^-][MnO_4^-])(1 + K_1[MnO_4^-])(1 + K_1[OH^-] + K_1K_2[S][OH^-])} \qquad (A17)$$

In view of low concentration of $[MnO_4^-]$ used, both first and second terms in the denominator of Eq. (21) approximate to unity. Therefore, Eq. (21) becomes,

$$\text{Rate} = \frac{k_1K_1K_2[S][OH^-][MnO_4^-]}{1 + K_1[OH^-] + K_1K_2[S][OH^-]} \qquad (A18)$$

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

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = k_{obs}[MnO_4^-] \qquad (A19)$$

Comparing Eqs. (A18) and (A19), the following relationship is obtained,

$$k_{obs} = \frac{k_1K_1K_2[S][OH^-]}{1 + K_1[OH^-] + K_1K_2[S][OH^-]} \qquad (A20)$$

and with rearrangement, the following equations are obtained,

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[OH^-]}{k_1K_1K_2[OH^-]}\right)\frac{1}{[S]} + \frac{1}{k_1} \qquad (A21)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1K_1K_2[S]}\right)\frac{1}{[OH^-]} + \left(\frac{1}{k_1K_2}\frac{1}{[S]} + \frac{1}{k_1}\right) \qquad (A22)$$

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