A Comparative Kinetic Study on the Efficacious Permanganate Oxidation of Fluorenes in Perchloric and Sulfuric Acid Media

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Abstract

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), by permanganate ion in both perchloric and sulfuric acid media have been investigated using conventional spectrophotometric technique. In both acidic media, the reactions manifested first order kineticsin [permanganate] and less than unit order each in [reductants] and [acid]. Increasing ionic strength had no effect on the oxidation rates. Oxidation rates of fluorenes in perchloric acid were higher than those in sulfuric acid and the order of the oxidation rates was: Fl > Fl-I > Fl-Br > Fl-Cl. Final oxidation products were identified by GC/MS and FT-IR analyses in all cases as 9H-fluorenone derivatives. Reaction constants as well as activation parameters of the second order rate constants were also evaluated.

Keywords

Oxidation, Kinetics, Mechanism, Fluorenes, Permanganate

1. Introduction

Fluorenes (FLs) are an exclusive family of aromatic hydrocarbons. They are amongst products from the burning of gasoline [1] [2]. Fluorene moiety is frequently engaged in the growing of a variety of visual devices with dormant applications in some electronic devices such as solar cells [3], polymer based light-emitting diodes [4] [5] and electroemitting resources [6]. Furthermore, fluorene founded systems enjoy solitary photophysical properties since they exposed

pronounced high fluorescent quantum yield, countless optical nonlinear properties, photo-stability, and outstanding hole-transporting possessions [7] [8]. For these inserting and multi-addressable properties, fluorenes have been used extensively as focused constituents for organic light-emitting diodes, dye-sensitized solar cells, photosensitizers, emission microscopy [9] [10]. Furthermore, fluorene and its substituted derivatives are shown some effective and noticeable precursors for the synthesis of the sounding and promising photochromic di and tetrahydroindolizines [11] [12] [13].

Potassium permanganate is considered as the most powerful multi-electron oxidant employed in the kinetic studies of oxidation of various compounds in different media [14]-[22]. The mechanism of oxidation by this eco-friendly oxidant depends not only on the reductant but also on the reaction medium. Throughout permanganate oxidation, manganese (VII) species in permanganate is reduced to various oxidation states in different media [23]-[28]. However, no work has been reported on the kinetics and mechanism of oxidation of fluorene or its derivatives as well. In view of the above arguments, we tend to investigate the kinetics and mechanism of oxidation of fluorine and its halogenated derivatives with permanganate ion in both perchloric and sulfuric acids media in order to establish the optimum conditions affecting such oxidations and to elucidate a plausible oxidation mechanism.

2. Experimental

2.1. Materials

Fluorene and its derivatives, 2,7-dichloroflourene, 2,7-dibromoflourene and 2,7-diiodoflourene were synthesized as reported [29] [30] and the synthesized fluorene derivatives were characterized by both spectroscopic and analytical tools. For example, the 1H NMR (400 MHz, CDCl$_3$) spectrum of 2,7-dibrom-fluorene 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. A fresh solution of permanganate was prepared and was standardized as reported earlier [31] [32]. All other chemicals were of Aldrich grade.

2.2. Kinetic Measurements

Kinetic runs were carried out under pseudo-first order conditions where the concentration of fluorine derivatives, [S] >> [permanganate]. The reactions temperature (25°C) was controlled within ±0.1°C and the ionic strength was adjusted to 0.5 mol·dm^{-3}. Kinetics of the oxidation reactions were followed spectrophotometrically within the UV-Vis spectral range by recording the disappearance of permanganate absorbance with time at λ = 526 nm. These measurements were performed on a thermostatted Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. Fluorene derivatives were confirmed by both spectroscopic and analytical tools. NMR was recorded on a Bruker Advance 400 MHz and GC-Mass spectra were recorded on a Shimadzu GCMS-QP1000 EX mass spectrometer at 70 eV. The observed-first order rate constants (k_{obs}) were

calculated as slopes of the plots of ln(absorbance) versus time plots, which were straight for about 75% of the oxidation reactions and the such rate constants were reproducible to within 3% - 4%.

3. Results and Discussion

3.1. Stoichiometry and Product Analysis

Various sets of the reactions mixtures containing different ratios of permanganate to fluorine derivatives were mixed at $[H^+] = 0.3$ and $I = 0.5$ mol·dm^{-3} for about 24 hours. Estimation of the remaining permanganate indicate that stoichiometry of the reactions was 5:4 (fluorine:permanganate) as illustrated by the following equation.

Fluorenederivative   9H-fluorenone derivative

This stoichiometric equation is consistent with products characterization (Head-space GC/MS revealed [M$^+$, 100%] at 180 related to the 9H-fluoren-9-one [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-dichloro-9H-fluoren-9-one (as an example) showed the following signals: m/z: 247.98 (100.0%), 249.98 (64.1%), 248.98 (14.1%), 251.97 (10.2%), 250.98 (9.1%), 252.98 (1.5%). Furthermore, FT-IR spectra for both 2,7-dichloro-9H-fluorene (Fl-Cl) and its oxidation product 2,7-dichloro-9H-fluoren-9-one (as an example) are shown in **Figure 1**. The product 2,7-dichloro-9H-fluoren-9-one

Figure 1. FT-IRs spectra of 2,7-dichloro-9H-fluorene (red line) and the oxidized product 2,7-dichloro-9H-fluoren-9-one (black line).

showed a very strong signal at 1712 cm⁻¹ related to the (C=O) group which is absent in the 2,7-dichloro-9H-fluorene (Fl-Cl). In addition, the finger prints of the product were different from that of the corresponding substrate.

3.2. Spectral Changes

Figure 2(a) and Figure 2(b) shows the spectral changes throughout oxidations of fluorene by potassium permanganate in: a) perchloric, and b) sulfuric acid media (as an example). The figure showed gradual disappearance of permanganate band at $\lambda = 526$ nm.

3.3. Order of Reactions

The orders of the oxidation reactions regarding to the reactants concentrations have been evaluated from the plots of log k_{obs} versus log (conc.).

The order with respect to $[MnO_4^-]$ was investigated by changing its concentration from 1.0×10^{-4} to 8.0×10^{-4} mol·dm⁻³ at constant concentrations of other reactants. The order was found to be unity as first order plots were linear for

Table 1. Effect of variation of $\left[MnO_4^-\right]$, [S], [H⁺] and I on the observed first order rate constants (k_{obs}) in the oxidations of fluorene and its derivatives by permanganate ion in perchloric and sulfuric acids media at 25˚C.

$10^4 \left[MnO_4^-\right]$ (mol·dm⁻³)	10^3 [S] (mol·dm⁻³)	10^2 [H⁺] (mol·dm⁻³)	I (mol·dm⁻³)	$10^5\ k_{obs}$ (s⁻¹)							
				Perchloric acid				Sulfuric acid			
				Fl	Fl-Cl	Fl-Br	Fl-I	Fl	Fl-Cl	Fl-Br	Fl-I
1.0	5.0	0.2	0.5	166.2	101.2	113.9	129.2	139.3	86.2	98.7	121.0
2.0	5.0	0.2	0.5	165.7	98.3	117.4	135.6	135.7	87.9	97.8	115.2
4.0	5.0	0.2	0.5	168.1	99.7	116.9	133.1	137.2	88.0	99.3	117.6
6.0	5.0	0.2	0.5	172.1	100.7	115.2	132.2	141.1	85.9	103.2	118.1
8.0	5.0	0.2	0.5	169.3	97.3	118.2	134.1	133.2	89.2	98.2	116.2
4.0	1.0	0.2	0.5	79.8	39.2	48.4	59.7	50.1	32.8	36.3	41.7
4.0	3.0	0.2	0.5	127.3	74.1	85.3	97.2	96.9	62.3	73.1	87.2
4.0	5.0	0.2	0.5	168.1	99.7	116.9	133.1	137.2	88.0	99.3	117.6
4.0	7.0	0.2	0.5	201.0	120.2	139.9	161.0	175.9	108.7	125	145.0
4.0	9.0	0.2	0.5	232.4	141.5	166.2	189.8	204.9	128.2	152	175.4
4.0	5.0	0.1	0.5	105.3	63.1	70.3	81.9	81.6	48.5	55.8	68.9
4.0	5.0	0.2	0.5	139.9	84.7	95.3	111.2	112.0	71.8	83.3	95.2
4.0	5.0	0.3	0.5	168.1	99.7	116.9	133.1	137.2	88.0	99.3	117.6
4.0	5.0	0.4	0.5	195.3	115.0	134.9	158.0	159.3	102.1	115.8	134.3
4.0	5.0	0.5	0.5	216.0	124.9	148.0	181.0	185.0	113.9	132.2	155.0
4.0	5.0	0.2	0.5	168.1	99.7	116.9	133.1	137.2	88.0	99.3	117.6
4.0	5.0	0.2	0.6	169.7	98.3	119.4	135.6	135.7	87.9	101.2	115.2
4.0	5.0	0.2	0.7	171.2	102.7	116.9	134.4	139.2	91.2	99.3	121.6
4.0	5.0	0.2	0.8	172.1	105.7	121.2	137.2	141.1	85.9	103.2	118.1
4.0	5.0	0.2	0.9	167.3	97.4	118.1	134.1	139.2	87.2	104.3	122.2

Ex Experimental error ±3%.

(a)

(b)
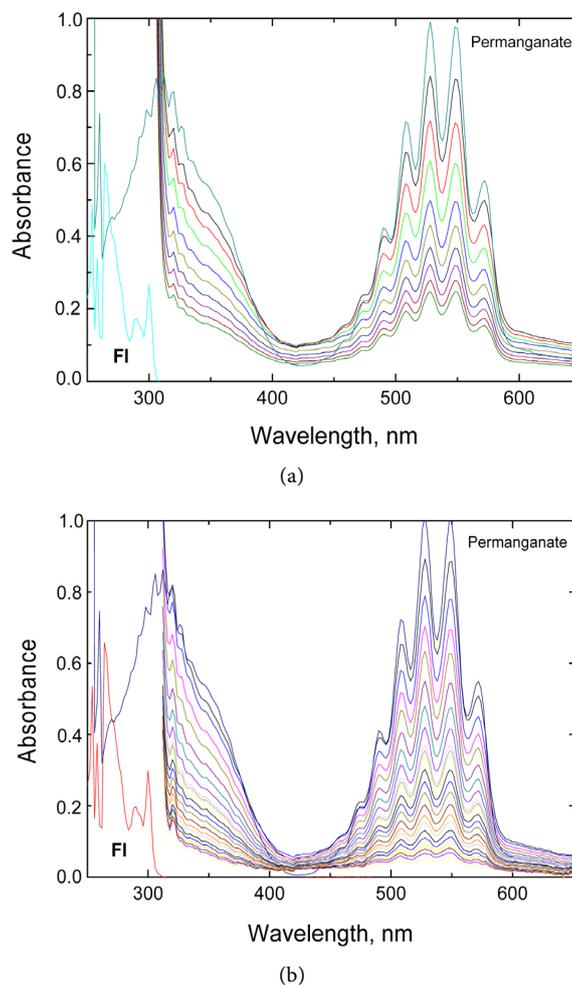
Figure 2. Spectral changes during the oxidations of fluorene by permanganateion in: (a) perchloric, and (b) sulfuric acid media. [S] = 5.0×10^{-3}, $\left[MnO_4^- \right]$ = 4.0×10^{-4}, [H$^+$] = 0.3 and I = 0.5 mol·dm^{-3} at 25°C. Scanning time = 1.0 min.

about 75% of the oxidation reactions. Furthermore, the non-variation of the values of k_{obs} at different initial $\left[MnO_4^- \right]$, as listed in **Table 1**, confirmed the unit order dependence of the reactions in $\left[MnO_4^- \right]$.

The values of k_{obs} were measured at various concentrations of fluorine derivatives (S) at fixed other reactants concentrations. The values of k_{obs} were found to increase with increase [S] as listed in **Table 1**. The plots of k_{obs} versus [S] in both acids were linear with positive intercepts suggesting that the orders of the reactions regarding to [S] were less than unity as shown in **Figure 3**.

The orders of reactions with respect to [H$^+$] were investigated by measuring the oxidation rates at various [H$^+$] (0.1 - 0.5 mol·dm^{-3}) and at fixed other variables. The rate constants were increased as [H$^+$] increased in both acidic media as listed in **Table 1** with less than unit order dependences as the plots of k_{obs} versus [H$^+$], **Figure 4**.

3.4. Effect of Ionic Strength

At constant concentrations of the reactants and with other conditions constant,
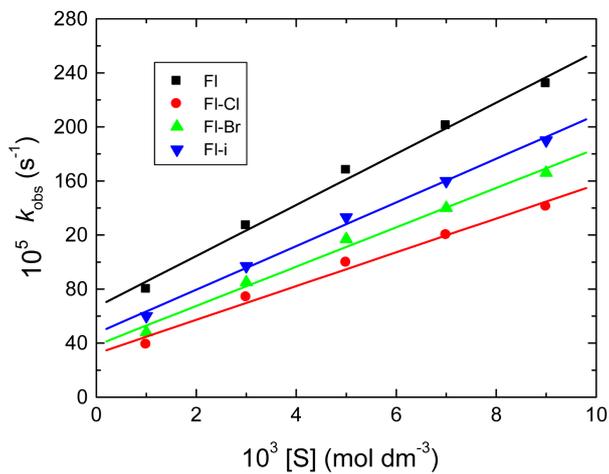
(a)
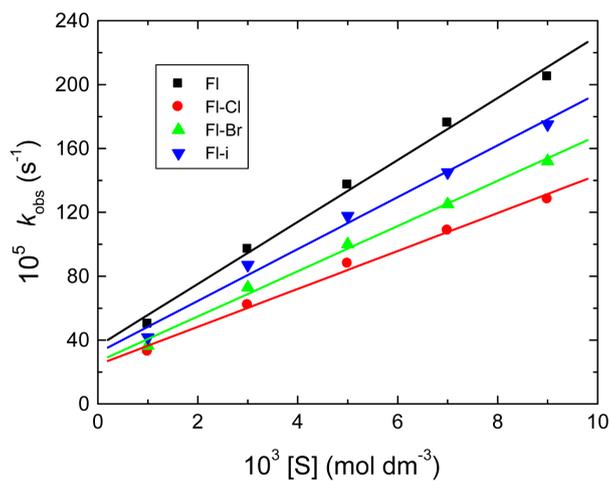
(b)

Figure 3. Plots of the observed first order rate constants (k_{obs}) versus substrate concentrations, [S], in the oxidations of fluorene and its derivatives by permanganate ion in: (a) perchloric, and (b) sulfuric acid media. $\left[MnO_4^-\right] = 4.0 \times 10^{-4}$, $[H^+] = 0.3$ and $I = 0.5$ mol·dm^{-3} at 25˚C.
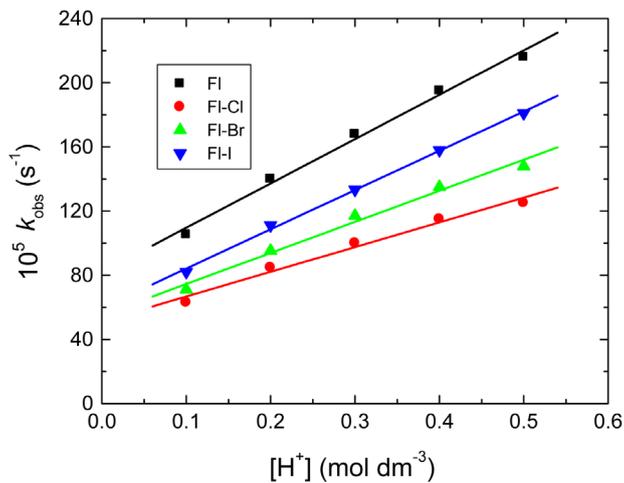
(a)
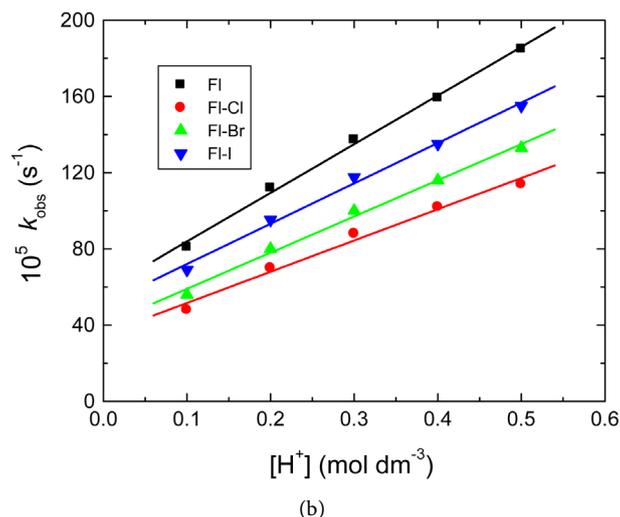
Figure 4. Plots of the observed first order rate constants (k_{obs}) versus acids concentrations in the oxidations of fluorene and its derivatives by permanganate ion in: (a) perchloric, and (b) sulfuric acid media. $\left[MnO_4^- \right] = 4.0 \times 10^{-4}$, [S] = 5.0×10^{-3} and $I = 0.5$ mol·dm^{-3} at 25°C.

the ionic strength of the reactions media was varied (0.5 - 0.9 mol·dm^{-3}) using sodium perchlorate in perchloric acid and sodium sulfate in sulfuric acid medium. The results listed in Table 1 indicated that variation of ionic strength had no significant effect on the oxidation rates.

3.5. Effect of Temperature

To calculate the activation parameters, the observed rate constants were measured at four temperatures, namely 288, 298, 308 and 318 K, at fixed other variables. The observed rate constants were found to increase with raising temperature and the activation parameters of the second order rate constants, k_2, ($k_2 = k_{obs}$/[S]) were evaluated using Arrhenius and Eyring plots (Table 2).

3.6. Polymerization Study

Known quantities of acrylonitrile monomer were added to the reactions mixtures in both acidic media and were kept in an inert atmosphere for about 6 hours. When the reactions mixtures were diluted with methanol, progressive white precipitates were formed suggesting intervention of free radicals during these reactions.

3.7. Reaction Mechanism

It was reported [33] [34] that permanganate ion in acidic medium combines with H$^+$ ion to form a more stronger oxidant called permanganic acid as illustrated by the first step in Scheme 1. This was supported by increasing oxidation rates with increasing acid concentration. On the other hand, many investigators [17]-[24] reported that, most oxidation reactions using permanganate oxidant proceed through formation of intermediate complexes between substrate and

$$MnO_4^- + H^+ \xrightleftharpoons{K_1} HMnO_4$$
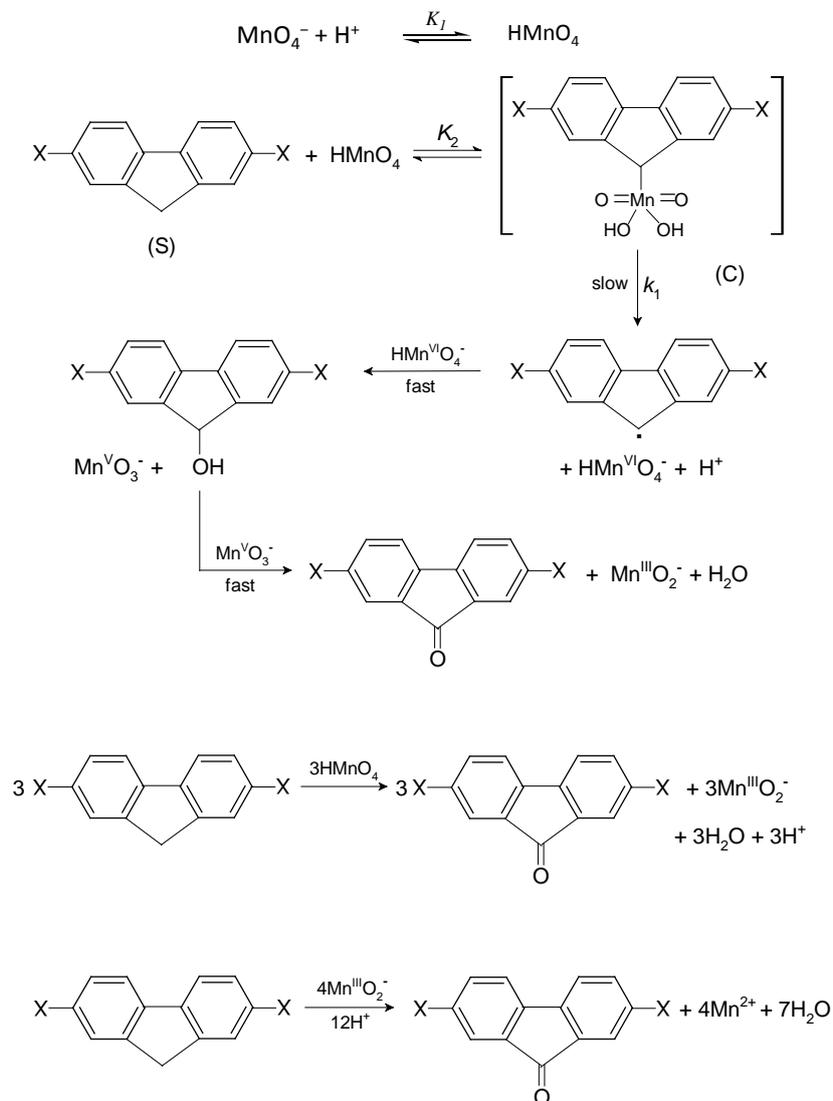
Scheme 1. Mechanism of oxidations of fluorenes by permanganate ion in acid media.

Table 2. Activation parameters of the second order rate constant, k_2, in the oxidations of fluorene and its derivatives by permanganate ion in perchloric and sulfuric acids media. $\left[MnO_4^-\right] = 4.0 \times 10^{-4}$, $[S] = 5.0 \times 10^{-3}$, $[H^+] = 0.3$ and $I = 0.5$ mol·dm^{-3}.

Acid	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	−123.22	30.01	66.73	28.61
	Fl-Cl	−133.35	26.03	65.79	26.33
Perchloric	Fl-Br	−149.01	29.51	73.91	29.52
	Fl-I	−113.34	31.47	65.25	29.92
	Fl	−148.41	26.55	70.77	36.72
	Fl-Cl	−131.07	23.33	62.39	33.50
Sulfuric	Fl-Br	−134.27	25.19	65.20	37.36
	Fl-I	−157.81	24.29	71.32	39.07

Experimental error ±4%.

oxidant. This was also evidenced [34] by linear plots of $1/k_{obs}$ and $1/[S]$ as shown in **Figure 5**. The observed insignificant influence of the ionic strength on the oxidations rates indicated that the reactions were between two neutral molecules [35] [36] [37], *i.e.* between fluorene derivative and acid permanganate.

In the light of the above aspects, the following reactions mechanism, illustrated in **Scheme 1**, can be suggested. The mechanism involves reaction of permanganic acid oxidant with fluorene derivative to form a complex (C) and the later decomposes to yield manganate (VI) and fluorene free radical. The free radical is attacked by Mn(VI) forming the secondary alcohol (fluorenol) as an intermediate product and manganese (V) intermediate. In a further fast step, Mn(V) reacts with the intermediate product fluorenol to give the ketone (fluorenone) as the final oxidation product and an intermediate Mn (III) species. This step is followed by other fast steps including reactions of fluorene derivatives with acid permanganate species to form also fluorenone and Mn (III) spe-
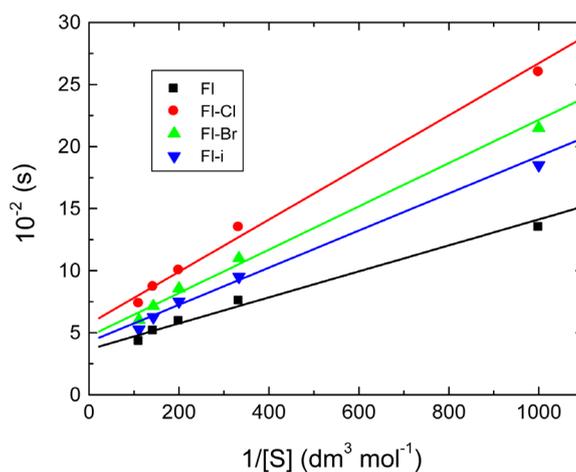
(a)
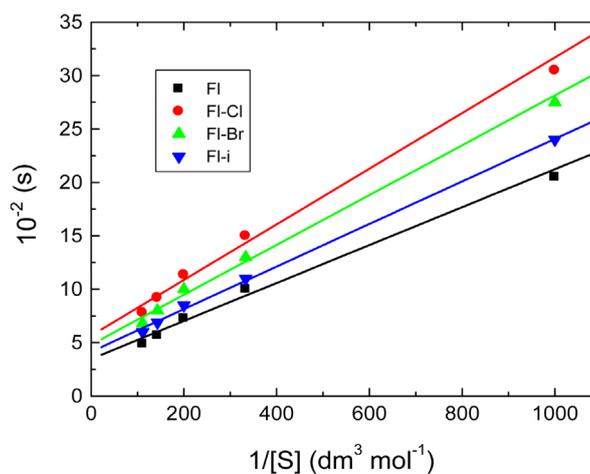
(b)

Figure 5. Verification of equation (4) for the oxidations of fluorene and its derivatives by permanganate ion in: (a) perchloric, and (b) sulfuric acid media. $\left[MnO_4^- \right] = 4.0 \times 10^{-4}$, $[H^+] = 0.3$ and $I = 0.5 \, mol \cdot dm^{-3}$.

cies. The last step is the attack of Mn(III) species on another fluorene molecule to give fluorenone and Mn(II), satisfying the observed stoichiometry.

Owing to the suggested mechanism, rate of oxidation reaction can be expressed by the following rate law:

$$\text{Rate} = \frac{-d\left[MnO_4^-\right]}{dt} = k_1[C] \tag{1}$$

The relationship between the oxidation rate and the oxidant, substrate and hydrogen ion concentrations is deduced (See **Appendix A**) to give the following equation:

$$\text{Rate} = \frac{k_1 K_1 K_2 \left[MnO_4^-\right][S]\left[H^+\right]}{1 + K_1\left[H^+\right] + K_1 K_2[S]\left[H^+\right]} \tag{2}$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d\left[MnO_4^-\right]}{dt} = k_{obs}\left[MnO_4^-\right] \tag{3}$$

From Equations (2) and (3),

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1\left[H^+\right]}{k_1 K_1 K_2\left[H^+\right]}\right)\frac{1}{[S]} + \frac{1}{k_1} \tag{4}$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 K_1 K_2[S]}\right)\frac{1}{\left[H^+\right]} + \left(\frac{1}{k_1 K_2[S]} + \frac{1}{k_1}\right) \tag{5}$$

Regarding to Equations (4) and (5), plots of $1/k_{obs}$ versus $1/[S]$ at constant $[H^+]$ and $1/k_{obs}$ versus $1/[H^+]$ at constant $[S]$ should be linear with positive intercepts on the $1/k_{obs}$ axes as were obtained, **Figure 5** and **Figure 6**, respectively. The slopes and intercepts of such plots lead to calculation of the values of k_1, K_1 and K_2 (**Table 3**).

Table 3. Values of k_1, K_1 and K_2 in the oxidations of fluorene and its derivatives by permanganate ion in perchloric and sulfuric acid media. $\left[MnO_4^-\right]$ = 4.0 × 10^{-4}, [S] = 5.0 × 10^{-3}, [H$^+$] = 0.3 and I = 0.5 mol·dm^{-3}.

Acid	Substrate	Constant		
		$10^3\ k_1$, s^{-1}	$10^2\ K_1$, dm^3·mol^{-1}	$10^{-3}\ K_2$, dm^3·mol^{-1}
Pechloric	Fl	2.51	29.41	5.24
	Fl-Cl	1.80	28.80	3.26
	Fl-Br	2.12	28.32	3.31
	Fl-I	2.43	29.53	3.18
Sulfuric	Fl	2.41	28.90	4.90
	Fl-Cl	1.73	27.61	3.15
	Fl-Br	2.21	28.84	3.10
	Fl-I	2.34	28.53	3.34
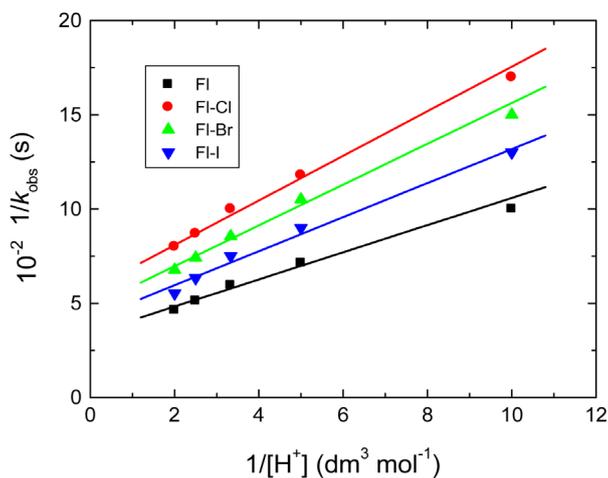
(a)
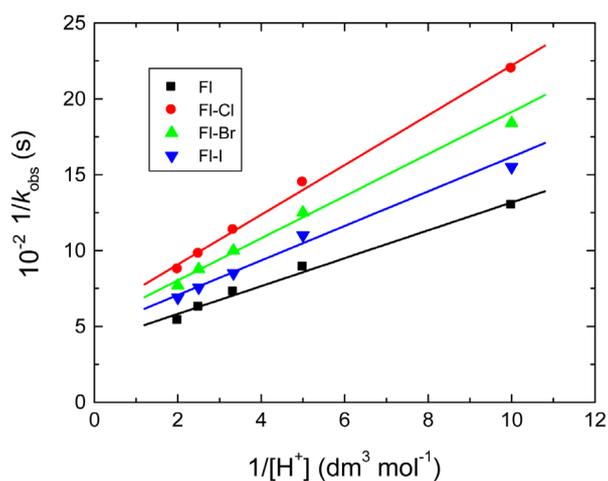
(b)

Figure 6. Verification of equation (5) for the oxidations of fluorene and its derivatives by permanganate ion in: (a) perchloric, and (b) sulfuric acid media. $\left[MnO_4^-\right]$ = 4.0×10^{-4}, [S] = 5.0×10^{-3} and I = 0.5 mol·dm^{-3}.

On the other hand, the negative values of entropy of activation ($\Delta S^{\neq}$) listed in **Table 2** supports formation of compacted intermediate complexes [38]. The positive values of both enthalpy of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) indicates endothermic intermediate complexes and their non-spontaneities, respectively.

4. Conclusion

Oxidations of fluorene derivatives by potassium permanganate in acidic medialed to formation of the corresponding ketones (9H-fluorenone derivatives) and the oxidations rate was: Fl > Fl-I > Fl-Br > Fl-Cl. Reaction constants as well as activation parameters were evaluated.

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Appendix A. Derivation of the Rate-Law Expression

$$\text{Rate} = \frac{-\mathrm{d}\left[\mathrm{MnO_4^-}\right]}{\mathrm{d}t} = k_1[\mathrm{C}] \tag{A1}$$

$$K_1 = \frac{[\mathrm{HMnO_4}]}{\left[\mathrm{MnO_4^-}\right]\left[\mathrm{H^+}\right]}, \quad [\mathrm{HMnO_4}] = K_1\left[\mathrm{MnO_4^-}\right]\left[\mathrm{H^+}\right] \tag{A2}$$

$$K_2 = \frac{[\mathrm{C}]}{[\mathrm{S}][\mathrm{HMnO_4}]}, \quad [\mathrm{C}] = K_2[\mathrm{S}][\mathrm{HMnO_4}] = K_1 K_2 [\mathrm{S}]\left[\mathrm{MnO_4^-}\right]\left[\mathrm{H^+}\right] \tag{A3}$$

From Equations (A1) and (A3),

$$\text{Rate} = k_1 K_1 K_2 [\mathrm{S}]\left[\mathrm{MnO_4^-}\right]\left[\mathrm{H^+}\right] \tag{A4}$$

The total concentration of $\mathrm{MnO_4^-}$ is given by (where "T" and "F" stand for total and free),

$$\left[\mathrm{MnO_4^-}\right]_{\mathrm{T}} = \left[\mathrm{MnO_4^-}\right]_{\mathrm{F}} + [\mathrm{HMnO_4}] + [\mathrm{C}] \tag{A5}$$

$$\left[\mathrm{MnO_4^-}\right]_{\mathrm{T}} = \left[\mathrm{MnO_4^-}\right]_{\mathrm{F}} + K_1\left[\mathrm{MnO_4^-}\right]_{\mathrm{F}}\left[\mathrm{H^+}\right] + K_1 K_2\left[\mathrm{MnO_4^-}\right]_{\mathrm{F}}[\mathrm{S}]\left[\mathrm{H^+}\right] \tag{A6}$$

$$\left[\mathrm{MnO_4^-}\right]_{\mathrm{F}} = \frac{\left[\mathrm{MnO_4^-}\right]_{\mathrm{T}}}{1 + K_1\left[\mathrm{H^+}\right] + K_1 K_2 [\mathrm{S}]\left[\mathrm{H^+}\right]} \tag{A7}$$

Because of [H$^+$] was high,

$$\left[\mathrm{H^+}\right]_{\mathrm{T}} = \left[\mathrm{H^+}\right]_{\mathrm{F}} \tag{A8}$$

Similarly

$$[\mathrm{S}]_{\mathrm{T}} = [\mathrm{S}]_{\mathrm{F}} \tag{A9}$$

Substituting Equations (A7), (A8) and (A9) into Equation (A4) (and omitting "T" and "F" subscripts) gives:

$$\text{Rate} = \frac{k_1 K_1 K_2\left[\mathrm{MnO_4^-}\right][\mathrm{S}]\left[\mathrm{H^+}\right]}{1 + K_1\left[\mathrm{H^+}\right] + K_1 K_2 [\mathrm{S}]\left[\mathrm{H^+}\right]} \tag{A10}$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-\mathrm{d}\left[\mathrm{MnO_4^-}\right]}{\mathrm{d}t} = k_{\mathrm{obs}}\left[\mathrm{MnO_4^-}\right] \tag{A11}$$

From Equations (A10) and (A11),

$$k_{\mathrm{obs}} = \frac{k_1 K_1 K_2 [\mathrm{S}]\left[\mathrm{H^+}\right]}{1 + K_1\left[\mathrm{H^+}\right] + K_1 K_2 [\mathrm{S}]\left[\mathrm{H^+}\right]} \tag{A12}$$

and with rearrangement of Equation (A12),

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[\mathrm{H^+}]}{k_1 K_1 K_2[\mathrm{H^+}]}\right)\frac{1}{[\mathrm{S}]} + \frac{1}{k_1} \tag{A13}$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 K_1 K_2[\mathrm{S}]}\right)\frac{1}{[\mathrm{H^+}]} + \left(\frac{1}{k_1 K_2[\mathrm{S}]} + \frac{1}{k_1}\right) \tag{A14}$$

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