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Fluorenones Formation via Effective Chromium(VI) Oxidationin Perchlorate Solutions: Kinetic and Mechanistic features

A. Fawzy[1,2*], R. S. Jassas[1], S. A. Ahmed[1,2*], H. M. Ali[2,3], M. Abdallah[1,4],
M. A. S. Abourehab[5,6], N. S. Abbas[7,8]

[1] Chemistry Department., Faculty of Applied Sciences, Umm Al-Qura University, 21955 Makkah, Saudi Arabia
[2] Chemistry Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt
[3] Chemistry Department, Faculty of Science, Aljouf University, Aljouf, Saudi Arabia
Chemistry Department, Faculty of Science, Benha University, Benha, Egypt[4]
[5]Department of Pharmaceutics, Faculty of Pharmacy, Umm Al-Qura University, Makkah, Saudi Arabia
[6]Department of Pharmaceutics and Industrial Pharmacy, Faculty of Pharmacy, Minia University, Minia, Egypt
[7]Department of Chemistry, Faculty of Science, Helwan University, Cairo, Egypt
[8]Department of Chemistry, Faculty of Science, Taibah University, Saudi Arabia

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A. Fawzy and S. A. Ahmed
afsaad13@yahoo.com;
saleh_63@hotmail.com
+966590994316; +966530435760
A..Fawzy

Abstract

Kinetics of chromium(VI) oxidation of fluorene (Fl) and its halogenated derivatives, namely, 2,7-dichlorofluorene (Fl-Cl), 2,7-dibromofluorene (Fl-Br) and 2,7-diiodofluorene (Fl-I), in perchlorate solutions was investigated at a constant ionic strength of 2.0 mol dm^3 and at 25 ^{o}C. The progress of the reactions was followed spectrophotometrically. The reactions showed a first order dependence on [Cr(VI)] and fractional-first order dependences with respect to hydrogen ion and fluorene derivatives concentrations. Under comparable experimental conditions, the order of the oxidation rates of the fluorene derivatives was: Fl > Fl-I > Fl-Br > Fl-Cl. The mechanism of the oxidation reactions was suggested and the rate-law expression was derived. Values of the rate constants of the slow step along with the equilibrium constants were calculated.

1. Introduction

Fluorenes (FLs) are aromatichydrocarbons whichare amongst productsfrom gasoline burning [1,2]. Fluorene moiety is frequently engaged in the growing of various visual devices with dormant applicationssuch as in solar cells [3], polymer based light-emitting diodes [4-6]. Furthermore, fluorene has interestingphotophysical properties since they exposed countless optical nonlinear properties, gigantic photostability, and outstanding hole-transporting possessions [7,8]. For these inserting and multiaddressable 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 synthesisof the sounding and promising photochromic di and tetrahydroindolizines [11-14].

Chromium(VI) is an important oxidant for organic and inorganic compounds [15-31]. A literature survey showed that there are no reports about the kinetics of oxidation of fluorene or its derivatives by any oxidant. For this reason, we investigated the title reactions in organic acidic medium. The purposes of this study are to examine the most favorableconditions affecting oxidation of such noteworthycompounds, to check the selectivity of fluorine derivatives towards chromium(VI), to study the effect of substituted halogens on the kinetics of oxidation of fluorine, and finally to propose a suitable oxidation reactions mechanism.

2. Experimental details

2.1 Materials:

The chemicals used in current work were of Aldrich grades. Fluorene and its derivatives, 2,7-dichloroflourene, 2,7-dibromoflourene and 2,7-diiodoflourene were synthesized as described elsewhere [32,33] and the synthesized fluorenes were identified by both spectroscopic and analytical tools.

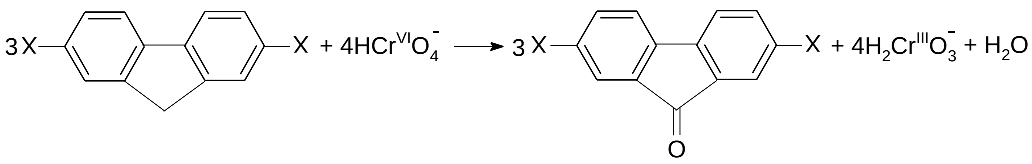
2.2 Kinetic Measurements:

The reactants were formulated such that the reactions were of pseudo-first order kinetics where the fluorine derivatives were added in large excesses relative to chromium(VI) at a temperature of 25°C and ionic strength of 2.0 mol dm^{-3}. The reactions were followed by tracing the decay in Cr(VI) absorbance at λ_{max} = 350 nm, its maximum absorption wavelength, whereas the other constituents of the reactions did not absorb significantly at this wavelength. NMR was recorded on a Bruker Advance 400 MHz with $CDCl_3$ and DMSO as solvents with TMS as a reference. GC-Mass spectra were recorded on a Shimadzu GCMS-QP1000 EX mass spectrometer at 70 eV. The absorbance measurements were performed on a temperature-controlled Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. The observed-first order rate constants (k_{obs}) were calculated as the gradients of ln(absorbance) – time plots, which were straight for about two-half lives of the reactions completion.

3. Results

3.1 Stoichiometry of the Reactions and Identification of the Products

The reactions stoichiometry was determined spectrophotometrically which indicates consumption of four moles of chromium(VI) for three moles of fluorene derivatives to yield the oxidation products as shown in the following equation,



Fluorene derivative

9H-fluorenone derivative

The above equation is consistent with the products identification which confirmed by both head-space GC/MS and FT-IR spectra as the corresponding ketone, namely 9H-fluorenone derivatives.

3.2 Spectral Changes

Figure 1 shows spectral changes throughout oxidation of fluorine derivatives by chromium(VI) in perchlorate solutions. The recorded spectra indicate gradual disappearance of chromium(VI) band with time at λ = 350 nm, as a result of its reduction by the organic substrates. Also, there were changes in the shape of the absorption band of chromium(VI) with small shifts in its absorption maximum in some cases.

3.3 Dependence of [Chromium(VI)]

The oxidant chromium(VI) concentration was varied for all fluorene derivatives from 1.0 x 10^{-4} to 9.0 x 10^{-4} mol dm^{-3}. The reaction order in [Cr(VI)] was found to be unity, as ln(absorbance) against time plots were linear up to about two-half lives of the reactions completion. Furthermore, the non-variation of the values of k_{obs} at different initial [Cr(VI)], as listed in Table 1, confirmed the first order dependence of the reactions on [Cr(VI)].

3.4 Dependence of [Fluorenes]

The k_{obs} values were measured at various concentrations of all derivatives of fluorene (F) keeping other reactants concentrations constant. Plots of k_{obs} versus [F] for all derivatives were linear with non-zero intercepts as shown in Figure 2 indicating that the orders of the reactions on [F] were less than unity.

3.5 Dependence of $[H^+]$

In order to study the effect of $[H^+]$, kinetic runs were performed at different perchloric acid concentrations (0.2 – 1.8 mol dm^{-3}) at constant [F], [Cr(VI)], I and temperature, Table 1. Plots of log k_{obs} versus log $[H^+]$ were linear with slopes of less than unity suggesting that the reactions were fractional-first order in $[H^+]$ as shown in Figure 3.

3.6 Dependence of Ionic Strength

The ionic strength was varied from 2.0 to 4.0 mol dm^{-3} using sodium perchlorate at constant [F] and [Cr(VI)], and at constant pH and temperature. Increasing ionic strength did not affect the oxidation rates as indicated from the data inserted in Table 1.

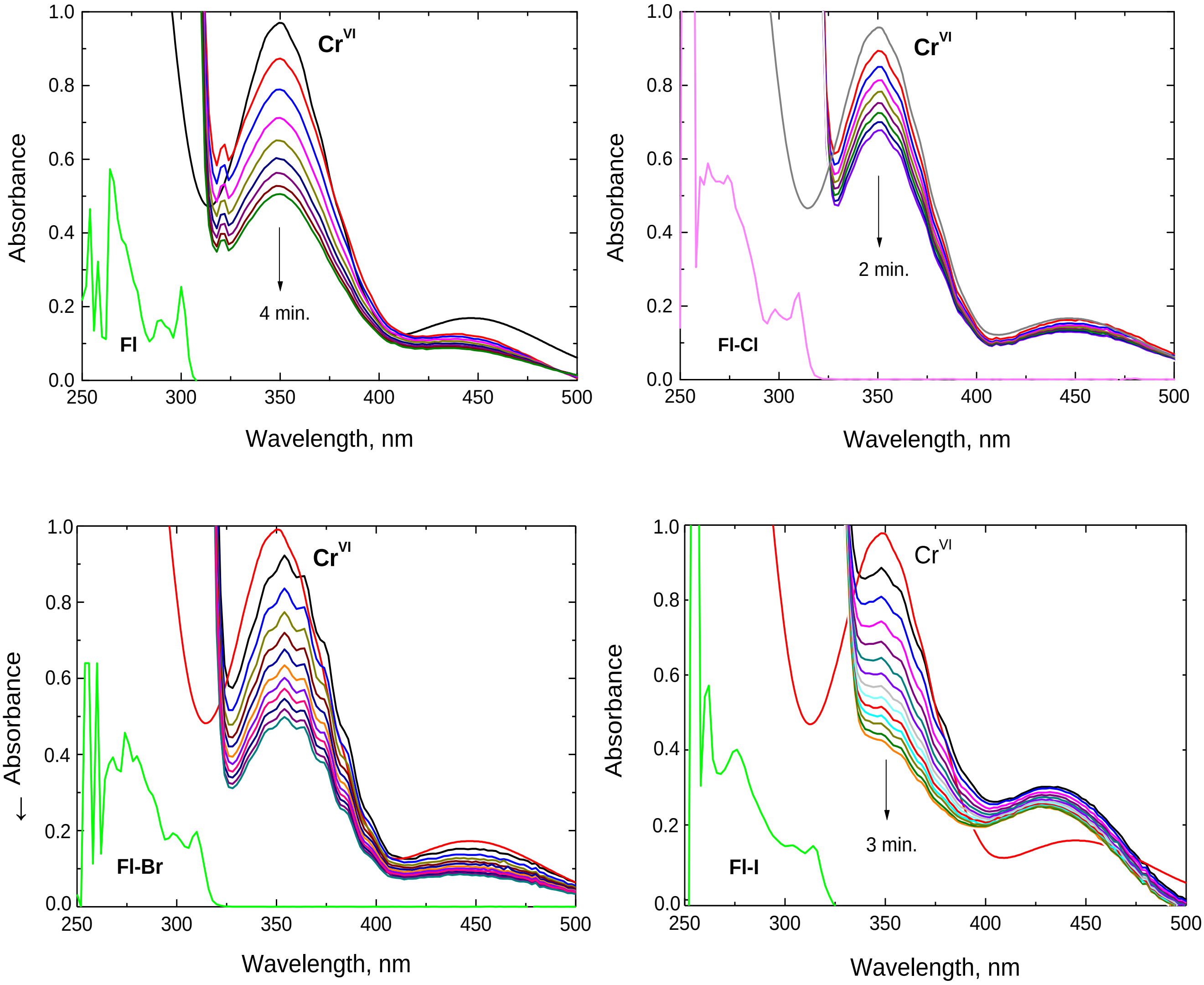


Figure 1 Spectral changes during the chromium(VI) oxidation of fluorine derivatives in perchlorate solutions. [Cr(VI)] = 5.0 x 10^{-4}, [F] = 6.0 x 10^{-3}, [H$^+$] = 1.0 and I = 2.0 mol dm^{-3} at 25 ^{o}C. Scanning time intervals = 3.0 min.

3.7 Effect of [Mn(II)]

The contribution of chromium(VI), as one of chromium intermediate species, in the reactions was examined by addition of various concentrations of manganous ion, Mn(II), to the reactions mixtures up to 8.0 x 10^{-3} mol dm^{-3}. Increasing the added Mn(II) was found to decrease the oxidation rates (Figure not shown).

3.8 Polymerization Test

Known quantities of acrylonitrile were initially added to the reactions mixturesand were kept for about 6 h in an inert atmosphere. On diluting the reactions mixtures with methanol, no white precipitates were formed thus confirming absence of free radicals in the reactions.

3.9 Effect of Temperature

To evaluate the activation parameters, the observed rate constants were determined at five temperatures in the range of 288 - 308 K, at fixed other variables. The observed rate constants were found to increase with raising temperature and the activation parameters associated with the second order rate constants, k_2,where $k_2 = k_{obs}$ / [F]were evaluated using Arrhenius and Eyring plots (Table 2).

Table 1. Effect of [Cr(VI)], [F], [H^+] and ionic strength (I) on the observed first order rate constant, k_{obs}, in the chromium(VI) oxidation of fluorine derivatives in perchlorate solutions at 25 °C.

10^4 [Cr(VI)] (mol dm^{-3})	10^3 [F] (mol dm^{-3})	[H^+] (mol dm^{-3})	I (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})			
				Fl	**Fl-Cl**	**Fl-Br**	**Fl-I**
1.0	6.0	1.0	2.0	61.3	38.0	51.9	55.3
3.0	6.0	1.0	2.0	64.2	39.7	50.7	57.1
5.0	6.0	1.0	2.0	61.2	38.4	52.1	56.0
7.0	6.0	1.0	2.0	59.8	39.2	49.6	58.0
9.0	6.0	1.0	2.0	61.0	37.1	53.9	55.9
5.0	**2.0**	1.0	2.0	26.3	16.1	19.7	22.0
5.0	**4.0**	1.0	2.0	43.3	27.1	38.0	41.4
5.0	**6.0**	1.0	2.0	61.2	38.4	52.1	56.0
5.0	**8.0**	1.0	2.0	76.0	47.4	65.1	69.4
5.0	**10.0**	1.0	2.0	91.5	55.9	79.2	83.3
5.0	6.0	**0.2**	2.0	27. 8	18.5	23.3	25.6
5.0	6.0	**0.6**	2.0	51.3	32.2	42.5	46.5
5.0	6.0	**1.0**	2.0	61.2	38.4	52.1	56.0
5.0	6.0	**1.4**	2.0	68.9	41.7	58.8	62.5
5.0	6.0	**1.8**	2.0	76.9	45.5	64.5	71.4
5.0	6.0	1.0	**2.0**	61.2	38.4	52.1	56.0
5.0	6.0	1.0	**2.5**	63.2	39.1	53.7	59.1
5.0	6.0	1.0	**3.0**	64.0	37.4	55.1	56.7
5.0	6.0	1.0	**3.5**	62.5	39.7	52.0	58.4
5.0	6.0	1.0	**4.0**	61.4	40.4	53.6	57.1

Experimental error ± 3%

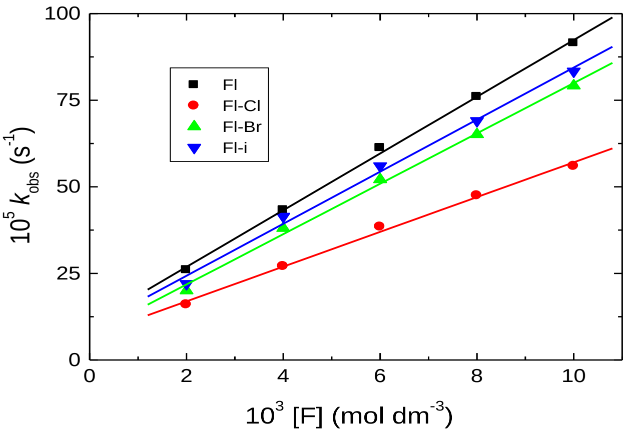


Figure 2 Plots of the observed first order rate constants (k_{obs}) versus fluorene derivatives concentrations, [F], in the chromium(VI) oxidation of fluorine derivatives in perchlorate solutions. [Cr(VI)] = 5.0 x 10^{-4}, [H^+] = 1.0 and I = 2.0 mol dm^{-3} at 25 °C.

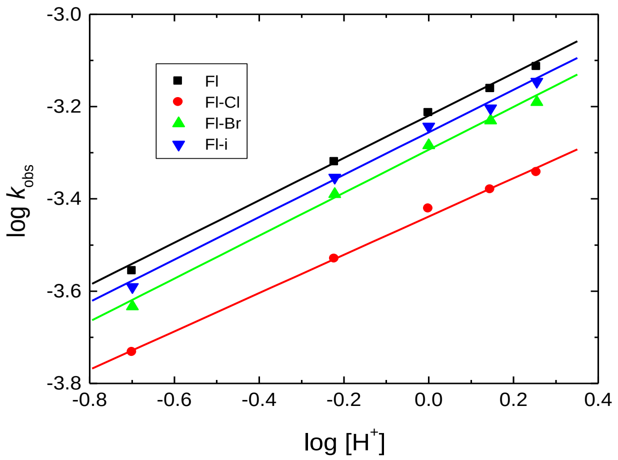


Figure 3 Plots of log k_{obs} versus log [H^+] in the chromium(VI) oxidation of fluorine derivatives in perchlorate solutions. [Cr(VI)] = 5.0 x 10^{-4}, [F] = 6.0 x 10^{-3} and I = 2.0 mol dm^{-3} at 25 °C.

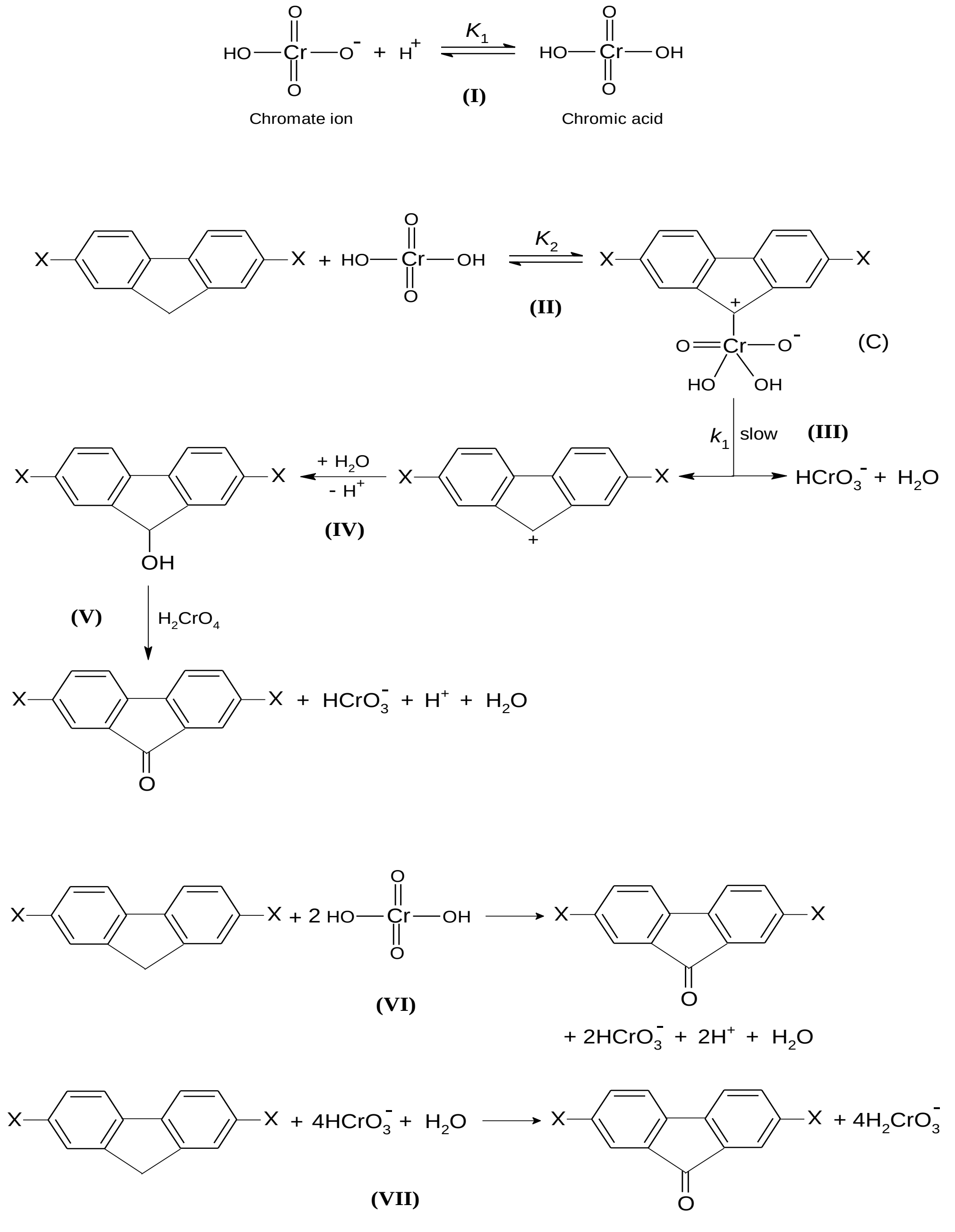
Table2 Activation parameters of the second order rate constant, k_2, in the chromium(VI) oxidation of fluorene derivatives in perchlorate solutions. [Cr(VI)]=5.0 x 10^{-4}, [F]=6.0 x 10^{-3}, [H^+]=1.0 and I=2.0 mol dm^{-3}

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	-88.71	36.09	62.53	38.93
Fl-Cl	-102.91	44.71	75.38	47.82
Fl-Br	-98.18	41.98	71.23	44.01
Fl-I	-89.44	39.99	66.64	41.87

Experimental error ±4%

4. Discussion

It was reported [34] that chromium(VI) oxidation reactions proceed via two suggested mechanisms, successive one-electron transfer through two steps and simultaneous two-electron transfer in one step. Both mechanistic paths may be considered during reduction of chromium(VI) leading to formation of either Cr(V) or Cr(IV) intermediate species, respectively [35-37]. In this study, absence of free radicals in the reactionsindicates absence of Cr(V) as an intermediate species. Also, the decrease of the oxidation rates upon addition of Mn(II) to the reactions medium indicates contribution of Cr(IV) in the reactions[38]. Also, chromium(VI) was suggested [39,40] to exist mainly as acid chromate, H_2CrO_4, in aqueous acid media, as represented by the first step in Scheme 1. This is supported byincreasing oxidation rates with increasing $[H^+]$. This indicates that the protonated species of the chromate oxidant (H_2CrO_4) may be considered as the kinetically reactive species which play the main role in the oxidation kinetics.



Scheme 1 Mechanism of the chromium(VI) oxidation of fluorene derivatives in perchlorate solutions.

The present reactions between chromium(VI) and fluorene derivatives in perchlorate solution showed a stoichiometry of 4:3 (Cr(VI) : F) with a first order dependence on [Cr(VI)] and fractional-first order kinetics with respect to both $[H^+]$ and [F]. The fractional order dependence on fluorenes concentrations suggests formation of complexes between fluorene derivatives and chromium(VI) in the pre-equilibrium step. The formation of the complexes was also proved kinetically by non-zero intercepts of the plots of $1/k_{obs}$ versus 1/[F], similar to Michaelis-Menten kinetics [41], as shown in Fig. 4. Further evidence for complexes formation was obtained from the UV-Vis spectra shown in Fig. 1 as the change in the shape of the absorption band of chromium(VI) with small shifts in its absorption maximum in some cases. The formation of complexes between chromium(VI) and different organic compounds in acid media was also reported [24,42]. Furthermore, the negligible effect of ionic strength was consistent with the reactions occur between neutral molecules [43,44] i.e. between fluorenes and H_2CrO_4.

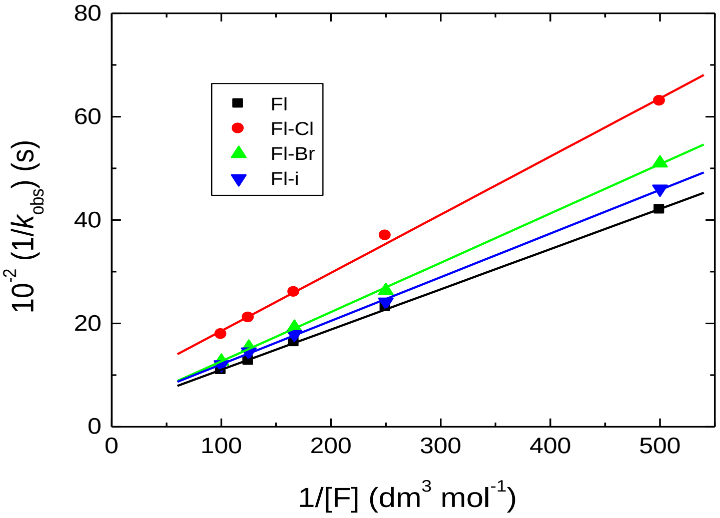


Figure 4 Plots of $1/k_{obs}$ versus 1/[F] at constant $[H^+]$ in the oxidation of fluorene derivatives by chromium(VI) in perchlorate solutions. [Cr(VI)] = 5.0 x 10^{-4}, $[H^+]$ = 1.0 and I = 2.0 mol dm^{-3} at 25 °C.

Hence, the most reasonable reactions mechanism which may be suggested (see Scheme I), involves a fast complexation between the reductant fluorene derivative and chromium(VI) oxidant, step (II), to form the complex (C). The latter was slowly decomposed in the rate-determining step to give the corresponding cation which rapidly hydrolyzed to the corresponding secondary alcohols (fluorenol). This is followed by subsequent fast steps to yield the final oxidation products.

The suggested mechanistic Scheme 1 leads to the following rate-law expression,

$$\text{Rate} = \frac{k_1 K_1 K_2 [\mathrm{HCrO_4}^-][\mathrm{F}][\mathrm{H}^+]}{1 + K_1[\mathrm{H}^+] + K_1 K_2 [\mathrm{F}][\mathrm{H}^+]} \quad (1)$$

Under pseudo-first order conditions,

$$\text{Rate} = \frac{-d[\mathrm{HCrO_4}^-]}{dt} = k_{obs}[\mathrm{HCrO_4}^-] \qquad (2)$$

Comparison of Eqs. (1) and (2) gives,

$$k_{obs} = \frac{k_1 K_1 K_2 [\mathrm{F}][\mathrm{H}^+]}{1 + K_1[\mathrm{H}^+] + K_1 K_2 [\mathrm{F}][\mathrm{H}^+]} \qquad (3)$$

and with rearrangement of Eq. (3) leads to the following equations,

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[\mathrm{H}^+]}{k_1 K_1 K_2 [\mathrm{H}^+]}\right)\frac{1}{[\mathrm{F}]} + \frac{1}{k_1} \quad (4) \qquad \frac{1}{k_{obs}} = \left(\frac{1}{k_1 K_1 K_2 [\mathrm{F}]}\right)\frac{1}{[\mathrm{H}^+]} + \left(\frac{1}{k_1 K_2 [\mathrm{F}]} + \frac{1}{k_1}\right) \quad (5)$$

Owing to Eqs. (4) and (5), plots of $1/k_{obs}$ versus 1/[F] at constant $[H^+]$ and plots of $1/k_{obs}$ versus $1/[H^+]$ at constant [F] should give straight lines with positive intercepts on the $1/k_{obs}$ axes, as were experimentally observed (Figs. 4 and 5, respectively). Values of the rate constants of the slow step (k_1) along with the equilibrium constants K_1 and K_2 were calculated and were listed in Table 3. From Table 2, the negative values of $\Delta S^{\neq}$suggestcompactness of the formed intermediate complexes [45]. Also, the positive values of both enthalpy of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) confirm endothermic formation of the intermediate complexes and their non-spontaneities, respectively.

Table3 Values of k_1, K_1 and K_2 in the chromium(VI) oxidation of fluorene derivatives in perchlorate solutions. [Cr(VI)] = 5.0 x 10^{-4}, [F] = 6.0 x 10^{-3} , [H^+] = 1.0 and I = 2.0 mol dm^{-3} at 25 °C

Substrate	**Constant**		
	10^3k_1, s^{-1}	**K_1, dm^3 mol^{-1}**	**K_2, dm^3 mol^{-1}**
Fl	3.07	1.49	71.93
Fl-Cl	1.38	1.62	104.65
Fl-Br	2.42	1.42	78.60
Fl-I	2.71	1.51	70.01

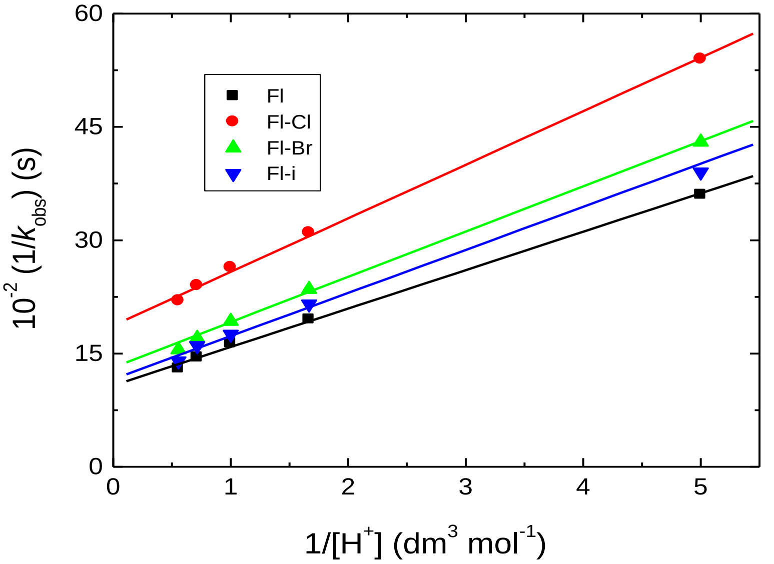


Figure 5 Plots of $1/k_{obs}$ versus 1/[H^+] at constant [F] in the oxidation of fluorene derivatives by chromium(VI) in perchlorate solutions. [Cr(VI)] = 5.0 x 10^{-4}, [F] = 6.0 x 10^{-3} and I = 2.0 mol dm^{-3} at 25 °C.

Conclusion

Oxidation of fluorene derivatives by chromium(VI) wasstudied spectrophotometricallyin perchlorate solutions. The order of the oxidation rates of such derivatives was: Fl > Fl-I > Fl-Br > Fl-Cl.The oxidation products were characterized as 9H-fluorenone derivatives.

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