A Study of the Kinetics and Mechanism of Oxidation of Fluorene by Alkaline Hexacyanoferrate(III)

Ahmed Fawzy[1, 2, *], Rabab S. Jassas[1], Saleh A. Ahmed[1, 2], Hazim M. Ali[2, 3], Nermeen S. Abbas[4, 5], Ishaq A. Zaafarany[1]

[1]Chemistry Department, Faculty of Applied Science, Umm Al-Qura University, Makkah, Saudi Arabia

[2]Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

[3]Chemistry Department, Faculty of Science, Aljouf University, Aljouf, Saudi Arabia

[4]Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt

[5]Chemistry Department, Faculty of Science, Taibah University, Al Madinah, Saudi Arabia

Email address:

afsaad13@yahoo.com (A. Fawzy), rabab-j@hotmail.com (R. S. Jassas), saleh_63@hotmail.com (S. A. Ahmed),
hmali@ju.edu.as (H. M. Ali), nermeen_gomaa@yahoo.com (N. S. Abbas), iazaafarany@uqu.edu.sa (I. A. Zaafarany).
[*]Corresponding author

Abstract: Kinetics of hexacyanoferrate (III) (HCF) oxidation of fluorene (Fl) in organic alkaline medium has been studied by spectrophotometric technique at a constant ionic strength of 0.15 mol dm^{-3} and at a temperature of 25°C. The reaction showed a first order kinetics with respect to [HCF] and fractional-first order dependences on both [Fl] and [OH$^-$]. The oxidation rate was increased with the increase in the ionic strength of the reaction medium. The oxidation mechanism was suggested which involves formation of a 1:1 intermediate complex between fluorene and HCF species in a pre-equilibrium step. The final oxidation product of fluorene was identified by spectroscopic and chemical tools as 9H-fluorenone. The appropriate rate law expression was deduced and the reaction constants involved in the mechanism were evaluated. The activation parameters of the rate constant of the slow step along with the thermodynamic quantities of the equilibrium constants were evaluated and discussed.

Keywords: Fluorene, Kinetics, Mechanism, Oxidation, Hexacyanoferrate (III)

1. Introduction

Fluorene is a polycyclic aromatic hydrocarbon (PAHs) that exists in fossil fuels [1, 2]. Fluorene and its derivatives have a large list of significant applications [3-10] as dye-sensitized solar cells, polymer light-emitting diodes and electroemitting materials. Moreover, fluorene is considered as effective and pronounced precursor for synthesis of photochromic di and tetrahydroindolizines [11-14]. On the other hand, oxidation of organic compounds by hexacyanoferrate (III) has been a subject of much interest especially in alkaline media [15-26] because hexacyanoferrate (III) has a high stability, water solubility and moderate reduction potential [27]. A literature survey revealed no work has been reported about the kinetics of oxidation of fluorene by any oxidant. Hence, the title reaction was investigated to establish the factors affecting oxidation of fluorene to arrive at a plausible oxidation mechanism.

2. Experimental

2.1. Materials

The chemicals used in this work were of reagent grade and doubly distilled water was used in all preparations. Fluorene was prepared according to the procedures described earlier [28, 29]. The synthesized fluorene was confirmed by both spectroscopic and analytical tools. A solution of hexacyanoferrate (III) was prepared by

dissolving potassium hexacyanoferrate (III) (BDH) in doubly distilled water and its concentration was determined spectrophotometrically.

2.2. Kinetic Measurements

Kinetic measurements were carried out under pseudo-first order conditions where [fluorine] $\gg$ [HCF]. The ionic strength, I, of the reaction mixture was adjusted to 0.15 mol dm^{-3} using $NaClO_4$ and the reaction temperature (25°C) was controlled within $\pm$ 0.1°C. The progress of the oxidation reaction was followed by measuring the decrease of its absorption spectrophotometrically at λ_{max} = 420 nm, its absorption maximum. NMR analysis was recorded on a Bruker Advance 400 MHz where GC-Mass spectra were recorded on a Shimadzu GCMS-QP1000 EX mass spectrometer at 70 eV. The kinetic measurements were performed on a temperature-controlled Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. First order plots of ln (absorbance) against time were good straight lines for more than 70% of the reaction completion and the observed-first order rate constant values were calculated as the slopes of these plots and average values of at least two independent kinetic runs of the rate constant were taken for the analysis. The rate constants were reproducible to within 2-3%. The orders of the reaction with respect to the reactants were determined from the plots of log k_{obs} versus log (concentration).

3. Results and Discussion

### 3.1. Reaction Stoichiometry and Product Identification

The stoichiometry of the oxidation reaction was determined spectrophotometrically which indicates that one mole of fluorene consumed two moles of hexacyanoferrate (III) to yield the oxidation products as illustrated in the following equation,
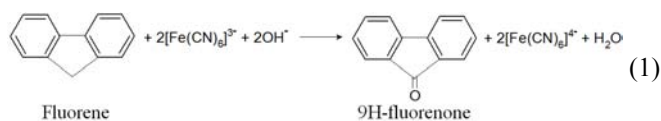
This equation is in good agreement with the results of products analyses as confirmed by both GC/MS and chemical tools [30, 31].

3.2. Spectral Changes

The spectral scans throughout oxidation of fluorene by HCF in organic alkaline medium are shown in Figure 1. The scanned spectra shows that there is a continuous decrease in HCF absorbance at 420 nm, due to its reduction to $[Fe(CN)_6]^{4-}$ by fluorene. A hyposchromic shift in the HCF band of about 18 nm from 420 to 402 nm as well as two isosbestic points located at 380 and 438 nm are also observed in the spectra.
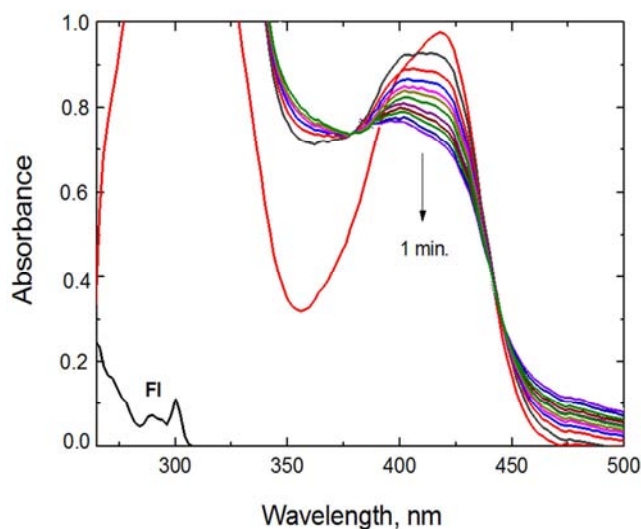
Figure 1. *Spectral changes during the oxidation of fluorene by HCF in alkaline medium.*

[HCF] = $7.0x10^{-4}$, [Fl] = $6.0 x 10^{-3}$, [OH⁻] = 0.05 and I = 0.15 mol dm^{-3} at 25°C

3.3. Dependence of [HCF]

The effect of hexacyanoferrate (III) oxidant on the oxidation rate was investigated by varying its concentration in the range (3.0 – 13.0) $x10^{-4}$ mol dm^{-3} at constant concentrations of other reagents. The ln (absorbance) versus time plots were linear for more than 70% of the reaction completion. Also, the first order rate constant, k_{obs}, was independent of the initial concentration of HCF as listed in Table 1. These results suggest that the reaction exhibited a first order dependence on [HCF].
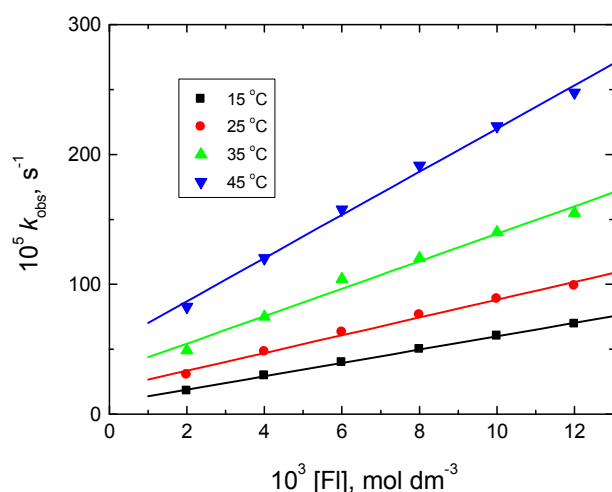
3.4. Dependence of [Fl]

The reaction rate was measured at different concentrations of the reductant fluorene (Fl) with keeping other reactant concentrations constant. The plots of k_{obs} versus [Fl], at different temperatures, were found to be linear with positive intercepts (Figure 2) indicating that the reaction order with respect to [Fl] was found to be less than unity.

3.5. Dependence of [OH]

The effect of hydroxide ion concentration on the reaction rate was studied by changing the concentration of NaOH in the range 2.0 to 12.0 x 10^{-2} mol dm^{-3} at constant [Fl], [HCF] and ionic strength. An increase in alkali concentration decreased the oxidation rate (Table 1) indicating that the oxidation process was base-catalyzed. The plots of k_{obs} versus [OH⁺], at different temperatures, were also found to be linear with positive intercepts on k_{obs} axes suggesting that the reaction order was fractional-first as shown in Figure 3.

Table 1. *Effect of [HCF], [Fl], [OH⁻] and ionic strength (I) on the observed first order rate constant k_{obs} in the oxidation of fluorene by HCF in alkaline medium at 25°C.*

10^4 [HCF] (mol dm^{-3})	10^3 [Fl] (mol dm^{-3})	[OH⁻] (mol dm^{-3})	I (mol dm^{-3})	10^4 k_{obs} (s^{-1})
3.0	6.0	0.05	0.15	63.4
5.0	6.0	0.05	0.15	66.1
7.0	6.0	0.05	0.15	64.8
9.0	6.0	0.05	0.15	65.7
11.0	6.0	0.05	0.15	62.9
13.0	6.0	0.05	0.15	63.0
7.0	2.0	0.05	0.15	33.0
7.0	4.0	0.05	0.15	47.1
7.0	6.0	0.05	0.15	63.8
7.0	8.0	0.05	0.15	74.0
7.0	10.0	0.05	0.15	88.6
7.0	12.0	0.05	0.15	99.7
7.0	6.0	0.01	0.15	22.7
7.0	6.0	0.03	0.15	45.0
7.0	6.0	0.05	0.15	63.8
7.0	6.0	0.07	0.15	77.8
7.0	6.0	0.09	0.15	93.9
7.0	6.0	0.11	0.15	104.1
7.0	6.0	0.05	0.15	63.8
7.0	6.0	0.05	0.20	67.1
7.0	6.0	0.05	0.25	74.2
7.0	6.0	0.05	0.30	79.2
7.0	6.0	0.05	0.35	86.0
7.0	6.0	0.05	0.40	91.9

Experimental error ± 3%

Figure 2. *Effect of fluorene concentration on the rate of oxidation of fluorene by HCF in alkaline medium.*

[HCF] = 7.0 x 10^{-4}, [OH⁻] = 0.05 and I = 0.15 mol dm^{-3} at different temperatures.

3.6. Dependence of Ionic Strength

The ionic strength was varied from 0.15 to 0.40 mol dm^{-3} using sodium perchlorate at constant concentrations of fluorene and HCF and at constant pH and temperature. Increasing the ionic strength increased the oxidation rate (Table 1). The Debye-Huckel plot was found to linear with a positive intercept, Figure 4.
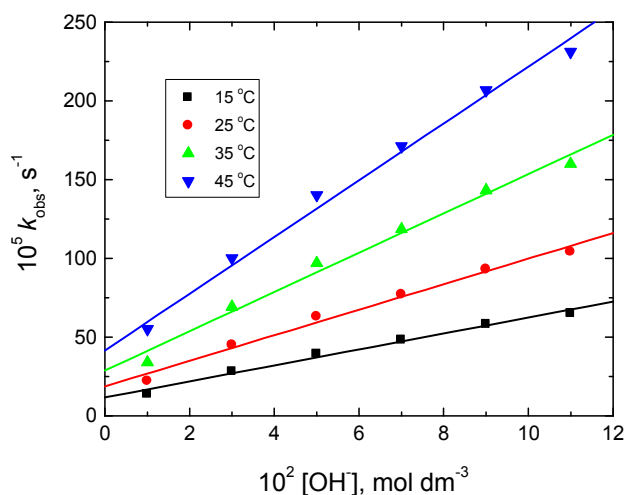
Figure 3. *Effect of alkali concentration on the rate of oxidation of fluorene by HCF in alkaline medium.*

[HCF] = 7.0 x 10^{-4}, [Fl] = 6.0 x 10^{-3} and I = 0.15 mol dm^{-3} at different temperatures

3.7. Dependence of [HCF(II)]

The effect of addition of hexacyanoferrate(II) as a reduction product of HCF(III) was investigated in the concentration range (2.0 - 10.0) x 10^{-4} mol dm^{-3} at fixed concentrations of the oxidant, reductant and alkali. It was found that HCF(II) did not have any significant effect on the oxidation rate.
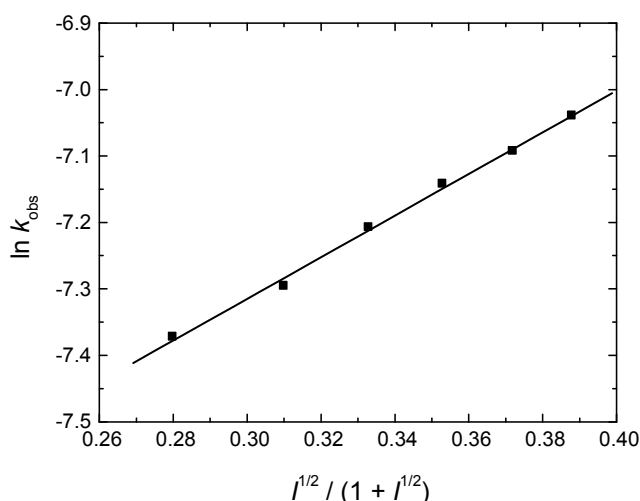
[HCF] = 7.0 x10^{-4}, [Fl] = 6.0 x 10^{-3} and [OH$^-$] = 0.05 mol dm^{-3} at 25°C

Figure 4. *Debye-Huckel plot in the oxidation of fluorene by HCF in alkaline medium.*

3.8. Dependence of Temperature

The reaction was investigated at different temperatures ranging between 15 to 45°C with varying both fluorene and alkali concentrations while other conditions were kept constant. The obtained results indicate increasing oxidation rate with raising temperature. The activation parameters of the rate constant of the slow step along with the thermodynamic quantities of the equilibrium constants were evaluated and were listed in Tables 2 and 3, respectively.

### 3.9. Test for Free Radical Intermediate

The intervention of free radicals in the oxidation reaction was investigated by a polymerization test where a known quantity of acrylonitrile was added to the reaction mixture in an inert atmosphere, with the result of formation of a white precipitate in the reaction mixture indicating presence of free radical during reaction. When the experiment was repeated in the absence of fluorene under similar conditions, the test was negative indicating that the reaction proceeded through a free radical path.

3.10. Reaction Mechanism

The reaction between fluorene reductant and hexacyanoferrate (III) oxidant in alkaline medium had a stoichiometry of 1:2, i.e., one mole of fluorene consumed two moles of hexacyanoferrate (III). The reaction showed a first order kinetics with respect to [HCF] and less than unit orders with respect to both [Fl] and [OH$^-$]. The less than unit order dependence in [OH$^-$] suggests deprotonation of fluorene substrate by alkali prior to the equilibrium step to form a more reactive species of the reductant. The rate was not significantly affected by HCF(II) confirming absence of a fast equilibrium with the products in the rate-determining step. The later should be irreversible [32] and the oxidation reaction proceeded through intervention of a free radical as experimentally obtained. Also, the oxidation rate was found to increase with

increasing both ionic strength and dielectric constant suggesting that the reaction occurs between two similarly charged ions [33, 34] i.e. between negatively charged deprotonated fluorene and HCF. On the other hand, the less than unit with respect to fluorene concentration may be due to formation of a complex (C) between HCF and deprotonated fluorene species prior to the equilibrium step. The complex formation was kinetically proved by the non-zero intercept of the $1/k_{obs}$ versus 1/[Fl] plot (Figure 5) in favor of possible formation of an intermediate complex between the oxidant and substrate [35]. The formed complex (C) was slowly decomposed in the rate-determining step giving substrate radical (Fl.) and HCF(II). The substrate radical reacts with another HCF species in a subsequent fast step to yield fluorene cation intermediate. In a further fast step, such intermediate product is rapidly hydrolyzed to give the final oxidation product of fluorene, 9H-fluorenone, as illustrated in Scheme 1.

The obtained large negative values of $\Delta S^{\neq}$ (Table 2) suggests that the more plausible mechanism is one-electron transfer of inner-sphere nature [36-38]. Also, the large negative values of $\Delta S^{\neq}$ indicate that there is a randomness decrease during the oxidation reaction which leads to formation of a compacted intermediate complex. On the other hand, the positive value of $\Delta H^{\neq}$ indicates that the complex formation is endothermic. Also, the large positive value of $\Delta G^{\neq}$ suggests enhanced formation of the intermediate with increasing temperature as well as to the non-spontaneity of the complex formation.
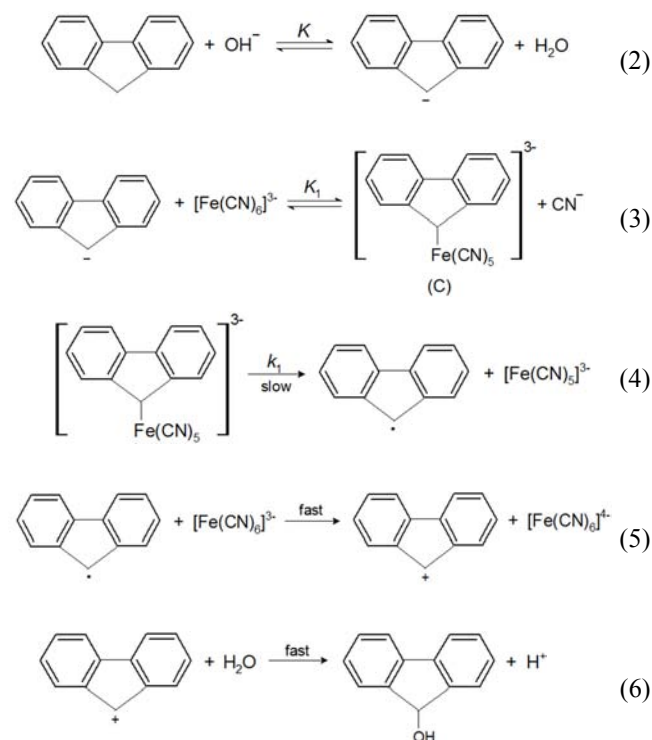
Scheme 1. *Mechanism of oxidation of fluorene by HCF in alkaline medium.*

The rate-law expression describing the dependence of the

reaction rate on the substrate, oxidant and alkali concentrations has been deduced (see Appendix A) to give the following equation,

$$\text{Rate} = \frac{k_1 KK_1[\text{Fl}][\text{HCF}][\text{OH}^-]}{1 + K[\text{OH}^-] + KK_1[\text{Fl}][\text{OH}^-]} \quad (7)$$

Under pseudo-first order condition,

$$\text{Rate} = \frac{-d[\text{HCF}]}{dt} = k_{obs}[\text{HCF}] \quad (8)$$

Comparing Eqs. (7) and (8), the following equation is obtained,

$$k_{obs} = \frac{k_1 KK_1[\text{Fl}][\text{OH}^-]}{1 + K[\text{OH}^-] + KK_1[\text{Fl}][\text{OH}^-]} \quad (9)$$

Equation (9) can be verified by rearranging to Eqs. (10) and (11),

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 KK_1[\text{OH}^-]} + \frac{1}{k_1 K_1} \right) \frac{1}{[\text{Fl}]} + \frac{1}{k_1} \quad (10)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 KK_1[\text{Fl}]} \right) \frac{1}{[\text{OH}^-]} + \frac{1}{k_1 K_1[\text{Fl}]} + \frac{1}{k_1} \quad (11)$$

Equations (10) and (11) required that the plots of $1/k_{obs}$ versus $1/[\text{Fl}]$ at constant $[\text{OH}^-]$, and $1/k_{obs}$ versus $1/[\text{OH}^-]$ at constant $[\text{Fl}]$ to be linear with positive intercepts and are found to be so as shown in Figures 5 and 6, respectively. The values of the rate constant of the slow step (k_1) at different temperatures obtained as reciprocal of the intercepts of $1/k_{obs}$ versus $1/[\text{Fl}]$ plots along with the activation parameters of k_1 which calculated from the Eyring and Arrhenius plots (Figures not shown) and are listed in Table 2. Values of the equilibrium constants associated with the mechanistic scheme (K and K_1) at different temperatures are also calculated from the slopes and intercepts of such plots and are inserted in Table 3. The thermodynamic parameters of K and K_1 are evaluated from van't Hoff plot (Figure not shown) and are also inserted in Table 3.

Table 2. *Values of the rate constant of the slow step (k_1) and its associated activation parameters in the oxidation of fluorene by HCF in alkaline medium.*

Rate Constant (s^{-1})	Temperature (K)				Activation parameters			
	288	298	308	318	$\Delta S^{\neq}$ (Jmol^{-1}K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}_{298}$ (kJ mol^{-1})	$E_a^{\neq}$ (kJ mol^{-1})
$10^4 k_1$	13.34	17.01	24.93	35.74	-137.2	23.09	63.92	25.77

Experimental error ±3%

Table 3. *Values of the equilibrium constants (K and K_1) and their thermodynamic quantities in the oxidation of fluorene by HCF in alkaline medium.*

Equilibrium Constant (dm^3 mol^{-1})	Temperature (K)				Thermodynamic parameters		
	288	298	308	318	ΔH^o (kJ mol^{-1})	ΔG^o_{298} (kJ mol^{-1})	ΔS^o (J mol^{-1}K^{-1})
K	7.31	5.42	4.40	2.89	-22.69	-3.96	-62.85
K_1	277.05	473.12	630.45	929.31	29.93	-15.26	151.64

Experimental error ± 4%
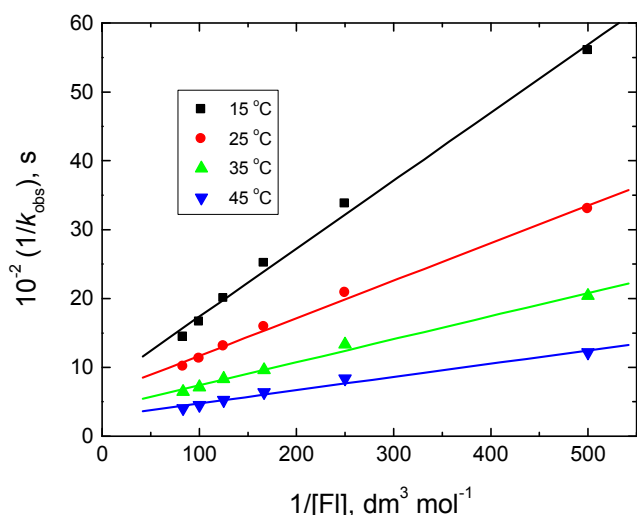
Figure 5. *Plots of $1/k_{obs}$ versus $1/[\text{Fl}]$ for the oxidation of fluorene by HCF in alkaline medium at different temperatures.*

[HCF] = 7.0 x10^{-4}, [OH$^-$] = 0.05 and I = 0.15 mol dm^{-3}
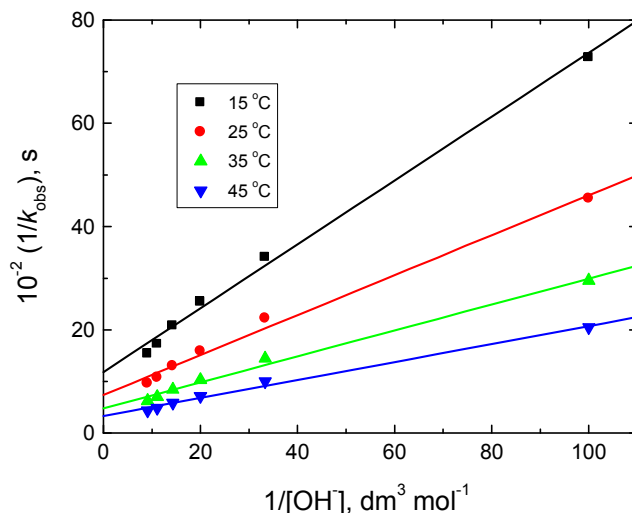
Figure 6. *Plots of $1/k_{obs}$ versus $1/[\text{OH}^-]$ for the oxidation of fluorene by HCF in alkaline medium at different temperatures.*

[HCF] = 7.0 x10^{-4}, [Fl] = 6.0 x 10^{-3} and I = 0.15 mol dm^{-3}

4. Conclusions

Kinetics of hexacyanoferrate(III) oxidation of fluorene in organic alkaline medium was studied spectrophotometrically. The final oxidation product of fluorene was identified by spectroscopic and chemical tools as 9H-fluorenone. The activation parameters of the rate constant of the slow step along with the thermodynamic quantities of the equilibrium constants were evaluated and discussed.

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