

Kinetics of oxidation of fluorene by alkaline hexacyanoferrate(III)

M KRISHNA PILLAY* and N NAGASUNDARAM

Department of Chemistry, Bharathidasan University, Tiruchirappalli 620023, India

MS received 3 April 1984; revised 21 May 1985

Abstract. The kinetics of oxidation of fluorene by alkaline hexacyanoferrate(III) is followed under pseudo-first-order conditions in 50% aqueous acetonitrile. The reaction is first-order both in the oxidant and substrate. The rate dependence on $[\text{NaOH}]$ is unity. Hexacyanoferrate(II) retards the reaction. The product of oxidation is fluorenone and the stoichiometry between the substrate and the oxidation is 1:4. A large positive salt effect and specific cation effect are observed. A tentative mechanism accounting for all the observations is envisaged.

Keywords. Fluorene; oxidation; hexacyanoferrate(III); kinetics.

1. Introduction

Even though hexacyanoferrate(III) is a weak oxidant, a number of organic substrates were oxidised by it under proper conditions and the kinetics of these reactions were rigorously investigated by several workers (Speakman and Waters 1955; Mahapatra and Radhakrishnamurti 1976b; Hamilton and McDonald 1973; Chatterji *et al* 1976). In all these cases the important step is conceived to be the abstraction of an electron by the one-electron oxidant hexacyanoferrate(III) (Thyagarajan 1958; Wilson 1966). Sluggish oxidation reactions were found to be catalyzed by metal ions like Os(VIII) (Singh *et al* 1975, 1977b; Radhakrishnamurti 1979), Ru(III) (Singh and Singh 1978; Radhakrishnamurti and Sahu 1979a, b) and Cu(II) (Bridgart *et al* 1973a, b; Mathur and Srivastava 1977; Bansal and Singh 1979). A unique instance of the oxidation of an alkyl function, activated by a nitro group, with alkaline hexacyanoferrate(III) was reported recently by Mahapatra and Radhakrishnamurti (1976b). This prompted us to take up the study of the oxidation of fluorene (Fl), which contains a reactive methylene function at the 9-position. The literature survey revealed that the kinetics of the oxidation of fluorenes by hypobromite (Kozuka *et al* 1975), ceric ammonium nitrate (Narasimhan and Venkatasubramanian 1977a), phenyliodosyl acetate (Panda and Radhakrishnamurti 1979), lead tetraacetate and V(V) (Mahapatra and Radhakrishnamurti 1976a; Narasimhan and Venkatasubramanian 1979b) only have been studied. The present investigation deals with the oxidation of fluorene by alkaline hexacyanoferrate(III) under different conditions. As far as we know this is the first report of the oxidation of an aromatic hydrocarbon by alkaline hexacyanoferrate(III). However, recently there is a report on the oxidation of naphthalene by hexacyanoferrate(III) in acetic acid-perchloric acid medium (Bhattacharjee and Mahanti 1983).

* To whom all correspondence should be addressed.

2. Experimental

Potassium hexacyanoferrate(III), sodium hydroxide, potassium chloride, sodium chloride and potassium hexacyanoferrate(II) were of AnalaR grade and used as received. Technical grade fluorene (Koch-Light) was purified by chromatography followed by crystallization from ethanol (m.p. 113°). Acetonitrile was distilled before use. Carbon dioxide-free sodium hydroxide solution was prepared by the standard procedure (Vogel 1961). Double distilled water was used throughout for preparing reaction mixtures. The kinetic studies were carried out in 50% aqueous acetonitrile under pseudo-first-order conditions with hexacyanoferrate(III) as the limiting reagent. The progress of the reaction was followed by estimating the unreacted hexacyanoferrate(III) iodometrically. For reasons of maintaining considerably high ionic strength of the reaction medium low concentrations of sodium hydroxide, fluorene and hexacyanoferrate(III) (5×10^{-4} M) had to be used allowing greater solubility of potassium chloride. In such cases the spectrophotometric method was adopted using a Carl-Zeiss Specord UV-vis Spectrophotometer. Equal volumes of solutions of appropriate concentrations of the reactants were mixed after allowing them to attain equilibrium temperature in a constant temperature water bath ($\pm 0.1^\circ$). The reaction was conducted in a vessel wrapped with black cloth. Since hexacyanoferrate(III) is the limiting reagent the rate, v , is given by

$$v = k_{\text{obs}} [\text{Fe}(\text{CN})_6^{3-}]$$

where k_{obs} is the observed pseudo-first-order rate constant obtained as the slope of a line resulting from a plot of log of the volume of the titrant versus time. The slopes for all the runs were obtained by the method of least squares and the correlation coefficients for all the runs were excellent. All the runs were carried out after removing air by passing nitrogen through solutions of the reactants before mixing.

2.1 Product analysis

The reaction mixture was analyzed to identify the product after keeping it for two days for completion. The acetonitrile was removed and the aqueous layer extracted with benzene. The benzene layer was dried with anhydrous magnesium sulphate. The residue obtained after the evaporation of benzene was subjected to column chromatography using alumina. Petroleum ether and petroleum ether-benzene eluates gave unreacted fluorene. The benzene eluate yielded a yellow compound which melted at 80–81° after crystallization from petroleum ether. It was confirmed to be fluorenone by determining the mixed melting point with an authentic sample of fluorenone and by spectroscopic analysis.

2.2 Stoichiometry

The stoichiometry of the reaction was determined by allowing an excess of hexacyanoferrate(III) to react with fluorene under alkaline conditions and estimating the unreacted hexacyanoferrate(III) in an acid condition after the completion of the reaction. The stoichiometry of the reaction was 1:4 between the substrate and oxidant. The expected stoichiometry for the fluorenone formation is the same as above



3. Results and discussion

3.1 Effect of varying [fluorene]

The order of the reaction with respect to fluorene was determined by varying [F1] and keeping other experimental variables constant. The results are presented in table 1. The pseudo-first-order rate constants vary proportionally with the initial [F1]. The second-order rate constants k_2 ($k_2 = k_{\text{obs}}/[\text{F1}]$) remain constant for all the runs performed. This confirms the unit dependence of the rate of oxidation on [F1].

3.2 Effect of varying [hexacyanoferrate(III)]

The reaction is first order in hexacyanoferrate(III) as shown by the good correlation ($r = 0.994$) for the plot of log of concentration of hexacyanoferrate(III) versus time for 70% completion of the reaction. But, contrary to the expectation, the k_{obs} value changes with the change in the initial concentration of hexacyanoferrate(III) (table 2). Though for any one kinetic run there is a first-order dependence on hexacyanoferrate(III), the rate decreases with the increase in the initial concentration of hexacyanoferrate(III). Such an observation is not uncommon and many workers have come across the anomalous behaviour in the different oxidation studies (Hinshelwood and Shorter 1950; Kansal *et al* 1979; Bakore *et al* 1971; Bhagawat and Yadav 1964; Acharya *et al* 1976; Venkatasubramanian and Srinivasan 1970; Krishna Pillay and

Table 1. Effect of [F1].

[F1] $\times 10^3$ (M)	$k_{\text{obs}} \times 10^4$ (sec ⁻¹)	$k_2 \times 10^2$ (l mol ⁻¹ sec ⁻¹)
7.0	1.84	2.62
8.0	2.07	2.59
9.0	2.27	2.52
10.0	2.52	2.52

$[\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-3}$ M; $[\text{NaOH}] = 2 \times 10^{-1}$ M;
 $[\text{KCl}] = 2.5 \times 10^{-2}$ M; solvent = 50% aqueous CH_3CN ;
 temperature = 35°.

Table 2. Effect of $[\text{K}_3\text{Fe}(\text{CN})_6]$.

$[\text{K}_3\text{Fe}(\text{CN})_6] \times 10^4$ (M)	$k_{\text{obs}} \times 10^4$ (sec ⁻¹)	$k_2 \times 10^2$ (l mol ⁻¹ sec ⁻¹)
2.5	4.78	4.78
5.0	3.85	3.85
7.5	3.39	3.39
10.0	2.52	2.52

[F1] = 1×10^{-2} M; $[\text{NaOH}] = 2 \times 10^{-1}$ M; $[\text{KCl}] = 2.5 \times 10^{-2}$ M; solvent = 50% aqueous CH_3CN ; temperature = 35°.

Thirunavukkarasu 1981) including the oxidation by alkaline hexacyanoferrate(III) (Radhakrishnamurti *et al* 1975; Bakore and Narain 1964; Singh *et al* 1977a).

3.3 Effect of varying [sodium hydroxide]

The reaction is base-catalyzed as shown by the results in table 3. A plot of log pseudo-first-order rate constants against [NaOH] gives a straight line ($r = 0.999$) with slope = 1.29. This indicates the first-order dependence of the rate on sodium hydroxide concentration.

3.4 Effect of ionic strength

With the concentrations of the oxidant, substrate and sodium hydroxide given in table 4, we have been unable to vary the concentration of potassium chloride very widely for practical reasons. Small changes in ionic strength did not have much influence on the rate of the reaction as shown in table 4. To have wide variation in the concentration of potassium chloride, the concentrations of other components were greatly decreased and the change of concentration of hexacyanoferrate(III) was followed spectrophotometrically. The results (table 5) show that the pseudo-first-order rate constant increases with increasing ionic strength indicating a positive salt effect. The reaction was found to show specific cation catalysis. For example, for the same

Table 3. Effect of [NaOH].

[NaOH] × 10 (M)	$k_{\text{obs}} \times 10^4$ (sec ⁻¹)	$k' \times 10^4 = k_{\text{obs}}/[\text{NaOH}]$ (l mol ⁻¹ sec ⁻¹)
0.50	0.61	1.22
1.25	1.60	1.28
1.75	2.28	1.30
2.00	2.52	1.26

[F] = 1×10^{-2} M; $[\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-3}$ M; [KCl] = 2.5×10^{-2} M; solvent = 50% aqueous CH₃CN; temperature 35°.

Table 4. Effect of [KCl]

[KCl] × 10 ² (M)	$k_{\text{obs}} \times 10^4$ (sec ⁻¹)	$k_2 \times 10^2$ (l mol ⁻¹ sec ⁻¹)
0.00	2.50	2.50
1.25	2.61	2.61
2.50	2.52	2.52
5.00	2.47	2.47
7.50	2.49	2.49

[F] = 1×10^{-2} M; $[\text{K}_3\text{Fe}(\text{CN})_6] = 1 \times 10^{-3}$ M; [NaOH] = 2×10^{-1} M; solvent = 50% aqueous CH₃CN; temperature 35°.

Table 5. Effect of [KCl].

[KCl] × 10 (M)	$k_{\text{obs}} \times 10^5$ (sec ⁻¹)	$k_2 \times 10^2$ (l mol ⁻¹ sec ⁻¹)
0.0	2.55	0.51
2.0	3.95	0.79
3.0	8.42	1.68

[Fl] = 5×10^{-3} M; [K₃Fe(CN)₆] = 5×10^{-4} M;
[NaOH] = 5×10^{-2} M; solvent = 50% aqueous
CH₃CN; temperature = 35°.

Table 6. Effect of [K₄Fe(CN)₆].

[K ₄ Fe(CN) ₆] × 10 ³ (M)	[KCl] × 10 (M)	$k_{\text{obs}} \times 10^5$ (sec ⁻¹)	$k_2 \times 10^2$ (l mol ⁻¹ sec ⁻¹)
0.0	3.00	8.42	1.68
0.5	2.98	5.67	1.13
1.0	2.96	5.35	1.07
5.0	2.80	4.64	0.93

[Fl] = 5×10^{-3} M; [K₃Fe(CN)₆] = 5×10^{-4} M; [NaOH] = 5×10^{-2} M;
solvent = 50% aqueous CH₃CN; temperature 35°.

concentration of K⁺ and Na⁺ (3×10^{-1} M) with the other variables constant, the k_2 values are 7.30×10^{-3} and 3.26×10^{-3} l mol⁻¹ sec⁻¹, respectively. The specific cation effect suggests the interaction to be between negatively charged ions (Olson and Simonson 1949).

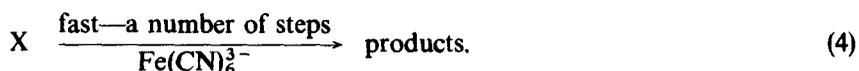
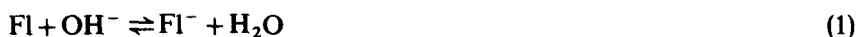
3.5 Effect of varying [hexacyanoferrate(II)]

The effect of change of [hexacyanoferrate(II)] on the rate of oxidation was studied under constant ionic strength by adjusting the concentration of potassium chloride suitably (see table 6). Addition of hexacyanoferrate(II) to the reaction mixture decreases the rate indicating that it is involved in an equilibrium step prior to the rate-limiting step.

4. Mechanism

The oxidation reaction is first-order both with respect to substrate and oxidant. The rate dependence on concentration of hydroxide is unity and the reaction is retarded by hexacyanoferrate(II). A positive salt effect and the specific cation effect indicate that negatively charged ions interact. Since a ketone (fluorenone) is the product of oxidation starting from a hydrocarbon containing a reactive methylene function (9-position of fluorene) we anticipated that the corresponding alcohol, *viz.* 9-fluorenol might be the intermediate. An authentic sample of 9-fluorenol was prepared and rate of oxidation was followed. The rate of oxidation of 9-fluorenol ($k_2 = 8.92 \times 10^{-3}$ l mol⁻¹ sec⁻¹)

was found to be about three times slower than that of fluorene ($k_2 = 2.52 \times 10^{-2} \text{ l mol}^{-1} \text{ sec}^{-1}$), hence, 9-fluorenol is not the intermediate in this reaction. A similar observation is made in the oxidation of fluorene by hypobromite in which the product of oxidation is fluorenone whereas the intermediate is not found to be the alcohol (Kozuka *et al* 1975). A tentative mechanism which is compatible with the experimental observations is given below:



Since the hydrogen atoms of the 9-position are sufficiently acidic owing to the activation by the two coplanar phenyl rings a proton is abstracted from the 9-position by the hydroxide ion in an initial equilibrium step. From the resulting carbanion an electron is removed by hexacyanoferrate(III) in an equilibrium step leading to the formation of the 9-fluorenyl radical (step 2). This intermediate radical gets converted into an intermediate whose nature we are not able to identify from the available experimental data and observations. However, we are forced to believe step (2) to be reversible and step (3) to be the slow step in order to account for all the experimental facts. The step in which a free radical changes over to another free radical is assumed to be the rate-determining one in the oxidative coupling reaction of 2,3,4-trihydroxybenzophenone by alkaline hexacyanoferrate(III) (Hamilton and McDonald 1973). The intermediate X reacts to form fluorenone probably through a number of fast steps. The involvement of hexacyanoferrate(II) in a prior equilibrium explains its retardation effect. Acrylamide was found to increase the rate of reaction by one and half times. This indicates that a free radical is involved in a slow step. Moreover the first-order dependence on hexacyanoferrate(III) concentration also implies a free radical intermediate (Hamilton and McDonald 1973). According to the above mechanism the following expressions may be obtained

$$\text{rate} = k'_2 [\text{Fl}^\cdot]. \quad (5)$$

Applying steady-state approximation

$$k_1 [\text{Fl}^-] [\text{Fe}(\text{CN})_6^{3-}] = k_{-1} [\text{Fl}^\cdot] [\text{Fe}(\text{CN})_6^{4-}] + k'_2 [\text{Fl}^\cdot]$$

Therefore

$$[\text{Fl}^\cdot] = \frac{k_1 [\text{Fl}^-] [\text{Fe}(\text{CN})_6^{3-}]}{k_{-1} [\text{Fe}(\text{CN})_6^{4-}] + k'_2}. \quad (6)$$

Substitution for $[\text{Fl}^-]$ from the equilibrium (1) and further substitution in (5) gives

$$\text{rate} = \frac{k_1 k'_2 K [\text{Fl}] [\text{OH}^-] [\text{Fe}(\text{CN})_6^{3-}]}{[\text{H}_2\text{O}] k_{-1} [\text{Fe}(\text{CN})_6^{4-}] + k'_2}. \quad (7)$$

This rate expression accounts for the experimental observations.

5. Conclusion

The oxidation of fluorene by alkaline hexacyanoferrate(III) gives fluorenone; it takes place *via* free radicals and not through 9-fluorenol.

Acknowledgement

The authors thank the University Grants Commission for the award of a Fellowship to one of them (NN).

References

- Acharya R C, Nanda C N, Mohanty S B and Rout M K 1976 *Indian J. Chem.* **A14** 42
Bakore G V, Banerji K K and Tandon S K 1971 *Indian J. Chem.* **9** 677
Bakore G V and Narain S 1964 *Z. Phys. Chem. (Leipzig)* **8** 227
Bansal O P and Singh M 1979 *J. Indian Chem. Soc.* **56** 673
Bhagawat W V and Yadav R L 1964 *J. Indian Chem. Soc.* **41** 389
Bhattacharjee A K and Mahanti M K 1983 *Indian J. Chem.* **B22** 74
Bridgart G J, Fuller M W and Wilson I R 1973a *J. Chem. Soc. Dalton Trans.* 1274
Bridgart G J, Waters W A and Wilson I R 1973b *J. Chem. Soc. Dalton Trans.* 1582
Chatterji H R, Gupta S S, Sarkar K K and Sen Gupta 1976 *Indian J. Chem.* **A14** 583
Hamilton G A and McDonald P D 1973 *J. Am. Chem. Soc.* **95** 7752
Hinshelwood C N and Shorter J 1950 *J. Chem. Soc.* 3277
Kansal B D, Singh H and Singh N 1979 *J. Indian Chem. Soc.* **56** 579
Kozuka M, Nagura K and Ogata Y 1975 *J. Org. Chem.* **40** 615
Krishna Pillay M and Thirunavukkarasu A 1981 *Indian J. Chem.* **B20** 583
Mahapatra S N and Radhakrishnamurti P S 1976a *Indian J. Chem.* **A14** 478
Mahapatra S N and Radhakrishnamurti P S 1976b *Indian J. Chem.* **A14** 613 (and references cited therein)
Mathur P C and Srivastava S S 1977 *Indian J. Chem.* **A15** 788
Narasimhan S and Venkatasubramanian N 1977 *Indian J. Chem.* **A15** 353
Narasimhan S and Venkatasubramanian N 1979a *Indian J. Chem.* **B17** 143
Narasimhan S and Venkatasubramanian N 1979b *Int. J. Chem. Kinet.* **11** 883
Olson A R and Simonson T R 1949 *J. Chem. Phys.* **17** 1167
Panda H P and Radhakrishnamurti P S 1979 *Indian J. Chem.* **A18** 419
Radhakrishnamurti P S and Sahu S 1979a *Indian J. Chem.* **A17** 93
Radhakrishnamurti P S and Sahu S 1979b *Indian J. Chem.* **A17** 95
Singh A K, Singh B, Singh H S, Singh M P and Sisodia A K 1975 *Indian J. Chem.* **13** 489
Singh H S and Singh R N 1978 *Indian J. Chem.* **A16** 145
Singh H S, Singh V P, Singh J M and Srivastava P N 1977a *Indian J. Chem.* **A15** 517
Singh J M, Singh H S, Singh V P and Srivastava P N 1977b *Indian J. Chem.* **A15** 520
Speakman P T and Waters W A 1955 *J. Chem. Soc.* 40
Thyagarajan B S 1958 *Chem. Rev.* **58** 439
Wilson I R 1966 *Rev. Pure Appl. Chem.* **16** 103
Venkatasubramanian N and Srinivasan V S 1970 *Indian J. Chem.* **8** 57
Vogel A I 1961 *A text book of quantitative inorganic analysis* (London: ELBS and Longman) 23