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KINETICS OF OXIDATION OF PHENANTHRENE BY ACIDIC HEXACYANOFERRATE(III)

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Under kinetically controlled conditions, phenanthrene is converted to 9-hydroxyphenanthrene by acid hexacyanoferrate(III) in 90% aqueous acetic acid. The φ value of –4.0 indicates that the reaction proceeds via the formation of a cation radical intermediate.

При кинетически контроллируемых условиях фенантрен с помощью гексацианоферрата(III) превращается в 9-гидроксифенантрен в водной 90%-ой уксусной кислоте. Величина $\rho = -4{,}00$, что указывает на протекание реакции через образование промежуточного радикал-катиона.

INTRODUCTION

Oxidation of phenanthrene by various oxidants usually yields either phenathroquinones or phenanthroic acid as product /1–9/. Our kinetic investigations on the oxidation of polynuclear aromatic hydrocarbons by acidic hexacyanoferrate(III) have yielded unusual products. For example, the oxidation of naphthalene had yielded α-naphthol in approximately 35–45% conversion /10/. This paper reports the results of a kinetically controlled conversion of phenanthrene to 9-hydroxyphenanthrene by acidic hexacyanoferrate(III), using acetic acid (90%, v/v) as solvent, under a nitrogen atmosphere at 45 °C.

EXPERIMENTAL

Materials and methods

Phenanthrene (mp 102 °C) was a BDH sample, and its purity was checked by UV analysis (in ethanol, absorption bands at 250 nm, 293 nm and 346 nm). Perchloric acid was a "Baker analyzed" sample. All other materials were of E. Merck grade. The solutions of phenanthrene in acetic acid and water, and potassium hexacyanoferrate(III) in acetic acid, perchloric acid and water, were separately thermostated at 45 °C for 3 h, under ntirogen, and then mixed in equal volumes. The progress of the reaction was followed by observing the disappearance of $[Fe(CN)_6^{3-}]$ at 420 nm spectrophotometrically, as described in an earlier communication /11/. All values of rate constants were the average of two or more experiments, with agreement being ±1.5% or better.

Product analysis

Stoichiometric amounts of substrate (1 mol) and oxidant (2 mol) were mixed at 45 °C, and maintained under a nitrogen atmosphere for 24 h. The reaction mixture was neutralized with $NaHCO_3$, extracted with chloroform, washed with water, dried over anhydrous $MgSO_4$, and concentrated. TLC analysis of the residue showed two spots. The crude product was chromatographed on a neutral alumina column, using hexane and benzene in varying proportions (100 : 0 to 70 : 30, v/v) for elution. The product obtained with increasing proportions of benzene was found to be 9-hydroxyphenanthrene. The product was recrystallized from benzene-cyclohexane, and characterized by mp (156–157 °C), the benzoyl derivative (mp 98–99 °C), the picrate derivative (mp 182–184 °C), and by IR /12/ and UV /13/ analyses. There was approximately 25–30% conversion of phenanthrene to 9-hydroxyphenanthrene. The second product was the starting phenanthrene (~ 70%), indicating that the actual yield of the product was higher than the percent of conversion.

RESULTS AND DISCUSSION

Kinetic results

The reaction obeyed the rate equation:

$$\text{Rate} = -\frac{d[Fe(CN)_6^{3-}]}{dt} = k_{obs}\,[\text{Substrate}]\,[HFe(CH)_6^{2-}] \qquad (1)$$

where $[HFe(CN)_6^{2-}] = K\,[Fe(CN)_6^{3-}]\,[H^+]$. The value of K, the first protonation constant of $Fe(CH)_6^{3-}$, has been reported /14/ to be 10. The pseudo first order rate constant, k_{obs}, was determined by keeping the concentrations of two out of the three reactants (substrate, oxidant and acid) constant, and was calculated /15/

from Eq. (2):

$$k_{obs} = \frac{2.303}{t} \log \frac{D_0}{D_t} \qquad (2)$$

where D_0 was the initial optical absorbance of the reaction mixture, and D_t that at time t. The rate data are given in Table 1. The activation parameters have been calculated as: $E = 28.8 \pm 1.2$ kJ/mol; $\Delta H^{\neq} = 26.2 \pm 0.9$ kJ/mol; $\Delta S^{\neq} = -226.0 \pm 12.0$ JK^{-1} mol^{-1}.

The formation of $HFe(CH)_6^{2-}$ was inferred by the spectral shift from 420 nm to 435 nm. Moreover, if $HFe(CH)_6^{2-}$ is the reacting species in the rate determing step, then k_{obs} should depend linearly on $[HFe(CH)_6^{2-}]$. This has been observed to be so.

The effect of substituents on the rate of the reaction was studied under the conditions $[\text{substrate}]_0 = 0.01$ M; $[K_3Fe(CN)_6]_0 = 1 \times 10^{-3}$ M; $[HClO_4]_0 = 0.1$ M; HOAc = 90% and temperature = 45 °C. While electron-releasing substituents like 9-methyl and 9-methoxy groups increased the rate constant ($10^4 \times k_{obs}$, s^{-1}) from 9.6 (for the unsubstituted) to 25.0 and 260.0, respectively, electron-withdrawing group like 9-nitro, decreased the value to 1.8. A Hammett-type plot with σ gave a φ value of −4.0 (correlation coefficient = 0.99).

Increasing proportions of acetic acid from 80% to 95% (v/v) increased the rate constant ($10^5 \times k_{obs}$, s^{-1}) from 29.4 to 285.0 at $[\text{substrate}]_0 = 0.01$ M; $[K_3Fe(CN)_6]_0 = 1 \times 10^{-3}$ M; $[HClO_4]_0 = 0.1$ M and temperature = 45 °C This was probably due to lowering the dielectric constant of the medium. A plot of log k_{obs} against the reciprocal of the dielectric constant was linear, suggesting an ion-dipole interaction.

Table 1

Rate data for the oxidation of phenanthrene in 90% HOAc (v/v)

[Phenanthrene] ($M \times 10^3$)	$[K_3Fe(CN)_6]$ ($M \times 10^3$)	$[HClO_4]$ (M)	Temp. (±0.1 °C)	10^4 k_{obs} (s^{-1})
10.0	1.0	0.1	45.0	9.6
25.0	1.0	0.1	45.0	24.2
50.0	1.0	0.1	45.0	48.5
10.0	0.5	0.1	45.0	9.4
10.0	0.1	0.1	45.0	9.7
10.0	1.0	0.3	45.0	29.0
10.0	1.0	0.5	45.0	48.0
10.0	1.0	0.1	30.0	5.5
10.0	1.0	0.1	35.0	6.5
10.0	1.0	0.1	40.0	7.8

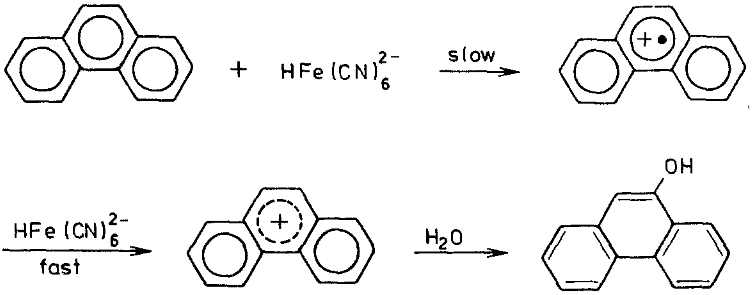
Mechanism

The oxidant species, HFe(CH)$_6^{2-}$, would react with the substrate to give an aromatic cation radical. Under the present experimental conditions, faint ESR signals were obtained, indicating the formation of a cation radical in the rate determining step of the reaction.

The effect of substituents yielding a φ value of –4.0 would suggest that the organic moiety had acquired some positive charge in the transition state.

The reaction sequence is shown in the Scheme:

SCHEME



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