KINETICS OF OXIDATIVE COUPLING OF PHENOLS. OXIDATION OF PYROGALLOL BY ALKALINE HEXACYANOFERRATE(III)

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The reaction of pyrogallol with alkaline hexacyanoferrate(III) at constant ionic strength gave 3,3',5,5'-tetrahydroxy-4,4'-diphenoquinone in a yield of 80%. The rate is dependent on the first powers of the concentrations of substrate, oxidant and alkali. The reaction pathway could be visualized as proceeding via a radical intermediate formed in the rate determining step. This radical was detected by ESR spectroscopy as two triplets with the intensity ratios of (1,2,1), (1,2,1), and showed absorptions at 655 nm, and at 1560 cm^{-1} in the infrared region.

Взаимодействие пирогаллола со щелочным гексацианоферратом(III) при постоянной ионной силе с 80%-ым выходом дает 3,3',5,5'-тетрагидрокси-4,4'-дифенохинон. Скорость реакции зависит от концентраций субстрата, окислителя и щелочи в первой степени. Реакция протекает с радикальным промежуточным продуктом, образующимся на ступени, лимитирующей скорость реакции. Этот радикал был детектирован с помощью ЭПР, спектр которого представляет два триплета с отношением интенсивностей 1:2:1 и 1:2:1. В его ИК спектре наблюдается абсорбция при 655 нм и 1560 см$^{-1}$.

## INTRODUCTION

Aerial oxidation of pyrogallol in the presence of Ba(OH)$_2$ has yielded coupled products /1, 2/ while aerial oxidation in alkaline medium has yielded trimeric products /3/. Substituted pyrogallols gave trimeric products when oxidized by peroxysulfate /4/, molecular iodine /5/, or when aerial oxidations were performed in presence of ammonia /6–8/, NaHCO$_3$ /8, 9/, Ba(OH)$_2$ /9, 10/, or some enzyme /11/. In continuation of our work on the oxidative coupling of phenols by K$_3$Fe(CN)$_6$ in alkaline medium /12/, we now report the kinetic features of the oxidation of a trihydric phenol(pyrogallol) by alkaline K$_3$Fe(CN)$_6$ at constant ionic strength under a nitrogen atmosphere.

EXPERIMENTAL

(a) *Materials, methods and stoichiometry*

Pyrogallol (BDH) was recrystallized before use (mp 133 °C), and its purity checked by UV analysis (in methanol, absorption at 267 nm). The other materials used have been described earlier /13/. 1 ml aliquots of substrate and oxidant solutions were injected into the spectrophotometric cell, and the reaction was monitored for the disappearance of $Fe(CN)_6^{3-}$ at 420 nm, spectrophotometrically (UV-26, Beckman) at the required temperature. The reaction was followed up to 60% conversion, the relation between $\log k_{obs}$ and t being linear in this range. The stoichiometry of the reaction was determined /13/ to be:

$$2C_6H_6O_3 + 4Fe(CN)_6^{3-} + OH^- \rightarrow C_{12}H_8O_6 + 4Fe(CN)_6^{4-} + H_2O + 3H^+$$
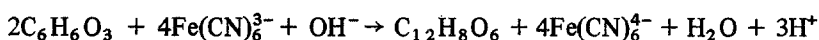
(b) *Product analysis*

Pyrogallol (2.0 g) in 70% methanol (v/v) was mixed with 11.0 g of $K_3Fe(CN)_6$ containing NaOH (0.05 M), 70% methanol (v/v), and $NaClO_4$ (0.5 M), and the mixture refluxed for 3 h under nitrogen. After cooling and filtration, the solvent was removed to give a red residue (0.065 g). The insoluble portion of the mixture was washed with chloroform, and after removal of the chloroform, a red residue (1.585 g) was obtained. The mp of both these residues was 240 °C. IR analysis of both residues in chloroform showed them to be identical with 3,3', 5,5'-tetrahydroxy-4,4'diphenoquinone, I. A sharp band at 1640 cm^{-1} corresponding to the carbonyl stretching of the C=O groups in two rings of an extended quinonoid structure was obtained /14/. The NMR spectrum of the product sample in chloroform (internal standard: TMS, sweep width: 10 ppm) gave the OH peak at 3.90 τ, and four doublets in the vinylic proton region at 3.19 τ, 3.10 τ, 2.31 τ and 2.20 τ. The structure of the product was confirmed to be *I*.

RESULTS AND DISCUSSION

Kinetic results

The rate of the reaction showed a first order dependence on the concentrations of substrate, oxidant and alkali (Table 1). Under the present experimental conditions, the rate law could be expressed as:

$$\text{Rate} = -\frac{d[Fe(CN)_6^{3-}]}{dt} = k_{obs}[\text{Pyrogallol}]\,[Fe(CN)_6^{3-}]\,[OH^-]$$

where k_{obs}, the pseudo first order rate constant, was determined by keeping the concentrations of two out of the three reactants (substrate, oxidant and alkali) constant, and was calculated from the equation given earlier /15/.

Table 1

Rate data for the oxidation of pyrogallol

| [Pyrogallol] (10^3 M)	[K_3Fe(CN)$_6$] (10^3 M)	[NaOH] (M)	Temp. (±0.1 °C)	$10^2 \times k_{obs}$ (s^{-1})
6.0	1.0	0.1	40.0	24.1
10.0	1.0	0.1	40.0	40.0
20.0	1.0	0.1	40.0	80.7
50.0	1.0	0.1	40.0	203.0
10.0	0.5	0.1	40.0	39.6
10.0	0.25	0.1	40.0	40.6
10.0	0.1	0.1	40.0	40.3
10.0	1.0	0.25	40.0	101.0
10.0	1.0	0.5	40.0	204.0
10.0	1.0	0.1	35.0	31.7
10.0	1.0	0.1	45.0	53.0
10.0	1.0	0.1	50.0	65.0

Methanol = 70% (v/v); μ = 0.50 M; all values of rate constants were the average of two or more experiments, with agreement being ±1.5% or better

The effect of temperature was studied (Table 1), and the activation parameters evaluated: E = 38.3 ±0.8 kJ mol^{-1}; A = 3.2 × 10^2 s^{-1}; $\Delta H^{\neq}$ = 35.6±0.7 kJ mol^{-1}; $\Delta S^{\neq}$ = −163.0±2.0 JK^{-1} mol^{-1}. Ionic strength variations using NaClO$_4$ (0.1 OM to 0.5 OM), and addition of K$_4$Fe(CN)$_6$ in the range 1.0 × 10^{-4} M to 1.0 × 10^{-3} M, did not affect the rate of the reaction.

Radical intermediate

The ESR spectrum of the radical gave two groups of three lines each, resulting from hyperfine interaction of protons on the ring with the unpaired electron spin. The resonance forms of this semiquinone structure would make protons at positions 4 and 6 equivalent. The observed splitting of the line follows from doubling due to the proton at position 5, followed by tripling of each of these two lines by the remaining equivalent protons at positions 4 and 6. The intensity ratios were (1, 2, 1), (1, 2, 1). This radical intermediate showed an absorption in the visible region at 655 nm, and gave an absorption band at 1560 cm^{-1} in the IR spectrum. In general, phenoxy radicals have been characterized by their electronic spectra /16, 17/.

SCHEME
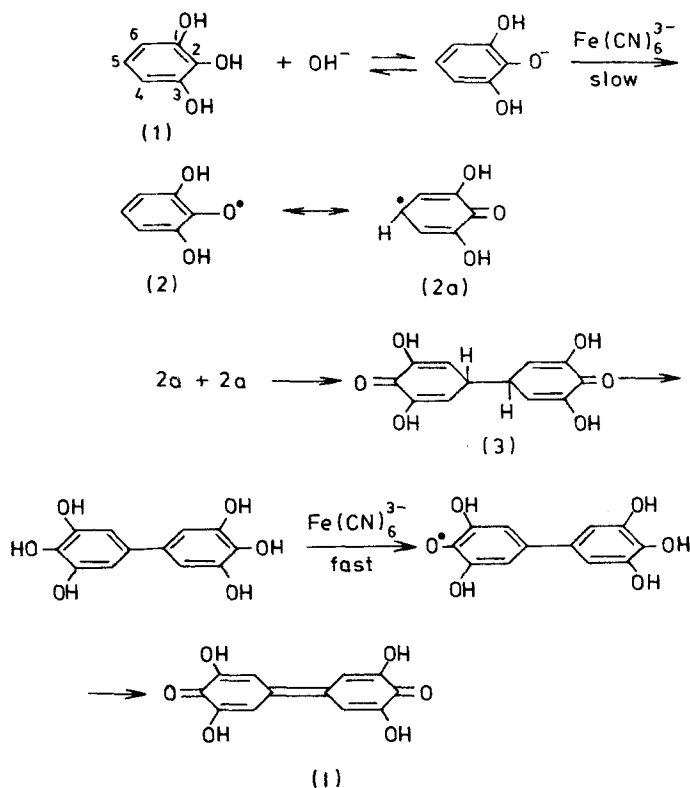
Mechanism

Pummerer et al. /18, 19/ had postulated a free phenoxyl radical as the first intermediate in the reactions of phenol coupling. This radical would be reactive oxygen and in the 5 position of pyrogallol. Pyrogallol, *1*, can be oxidized to the radical, *2⇔2a*. Combination of *2a + 2a* would give a dimer, *3*, which would undergo tautomerization in methanol rapidly, and would be oxidized further to yield the extended quinone, *I* (Scheme). No other intermediate(s) could be observed.

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