

KINETICS AND MECHANISM OF OXIDATION OF QUINOL BY ALKALINE HEXACYANOFERRATE(III)

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Received April 7, 1982

Accepted August 5, 1982

The reaction between quinol and alkaline hexacyanoferrate(III) at constant ionic strength gives p-benzoquinone. The rate of the reaction was first order in the concentrations of substrate, oxidant and alkali. The slow step of the reaction involves the formation of the p-benzosemiquinone radical, which was detected by esr spectroscopy as a five-line spectrum with peak intensity ratios of 1 : 4 : 6 : 4 : 1.

Реакция между хинолом и щелочным гексацианоферратом(III) при постоянной ионной силе дает п-бензохинон. Скорость реакции зависит от субстрата, окислителя и щелочи в первой степени. Медленная ступень реакции включает в себя образование п-бензосемихинонного радикала, который был детектирован с помощью ЭПР, давая квинтет с отношением интенсивностей 1 : 4 : 6 : 4 : 1.

INTRODUCTION

The aerial oxidation of quinol results in coupled products /1/, whereas the photo-oxidation of quinol yields dimers /2/. The oxidation of quinol in perchloric acid medium has been carried out by a variety of oxidants such as Fe(III) /3/, Cr(VI) /4/, Co(III) /5, 6/, Ce(IV) /7/ and Mn(III) /8/, to give p-benzoquinone. In the case of oxidations by Co(III), Ce(IV) and Mn(III), intermediate complexes were observed. These complexes were rapidly decomposed to give the semiquinone radical (or its anion), which was then further oxidized to the quinone. The oxidation of quinol by V(V) is rapid /9/, and the variation of the rate with changes in acidity was explained in terms of the decomposition of the various complexes formed as intermediates. Np(VI) has also been used to oxidize quinol /10/, but there was no evidence for the formation of a semiquinone intermediate. Thallium(III) trifluoroacetate, taken in either trifluoroacetic acid or in CCl₄ as solvent, has been observed to rapidly oxidize quinol to p-quinone in nearly 70% yield /11, 12/.

EXPERIMENTAL

(a) *Materials*

Quinol was a BDH analar sample; its melting point was 173 °C. The purity of the quinol was checked by infrared and uv analyses. The solvent methanol was an E. Merck sample and was distilled before use. Sodium hydroxide, potassium hexacyanoferrate(III) and potassium hexacyanoferrate(II) were IDPL samples. Sodium perchlorate was prepared by neutralizing 70% perchloric acid (E. Merck) with sodium hydroxide. The solution was concentrated, when crystals of sodium perchlorate were obtained. The crystals were filtered, recrystallized from water, and dried over silica gel under vacuum. This sample of sodium perchlorate was used for the preparation of the stock solution of 1 M NaClO₄, and for maintaining a constant ionic strength.

(b) *Methods*

The substrate was weighed and the solution was prepared in aqueous methanol. Potassium hexacyanoferrate(III) was weighed and dissolved in a small volume of water. Sodium hydroxide of known strength was added, the requisite amount of sodium perchlorate solution was introduced, and the solution was made up in methanol and water. The solutions were thermostated at 30 °C for 3 h under nitrogen and then mixed in equal volumes. The reaction was followed by observing the disappearance of hexacyanoferrate(III), by monitoring the absorption band at 420 nm /13/, as a function of time, using a spectrophotometer (Systronics, MK II model).

All infrared spectra were recorded on an IR-297 (Perkin-Elmer) spectrophotometer. All uv spectra were recorded on an UV-26 (Beckman) spectrophotometer. All esr spectra were recorded on a Varian (E-4) ESR spectrometer.

(c) *Product analysis*

Using the same experimental conditions that were used for the kinetic determinations quinol and hexacyanoferrate(III), in a mole ratio of 1 : 2 were allowed to react at 30 °C for 24 h. The mixture was filtered. The filtrate was taken up in ether, the ether layer was separated, washed with water, and then evaporated at room temperature. The solid residue was analysed for the product as follows:

(i) The melting point of the sample was 116 °C.

(ii) On treatment with an alkaline solution of ethylenediamine, a deep yellow colored solution was obtained, characteristic of p-benzoquinone /14/.

(iii) Infrared analysis gave two sharp bands at 1670 cm⁻¹ and 1655 cm⁻¹, corresponding to the presence of two carbonyl groups in the same ring, charac-

teristic of p-benzoquinone /15, 16/. Pronounced shoulders on the lower frequency side of the main band have been observed between 1640 and 1650 cm^{-1} . This spectrum was compared with that of an authentic sample of p-benzoquinone, and found to be identical /15, 16/.

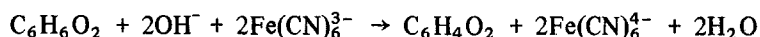
(iv) The uv spectrum of the product sample in CCl_4 gave three bands. The first band of greatest intensity was at 245 nm, the second band of medium intensity was at 288 nm, and the third band of weak intensity was observed in the visible region at 440 nm. These absorptions were attributed to singlet-singlet $\pi-\pi^*$, $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively, characteristic of p-benzoquinone /17, 18/. No absorption band was observed at 420 nm, indicating that the product did not interfere with the kinetic measurements carried out at 420 nm.

Hence, the product of the oxidation reaction was confirmed to be p-benzoquinone (yield $\sim 80\%$).

RESULTS AND DISCUSSION

Stoichiometry

Reaction mixtures containing an excess of hexacyanoferrate(III) were allowed to react to completion and the mixture was analyzed spectrophotometrically for unreacted hexacyanoferrate(III). The results gave a substrate: oxidant ratio of 1 : 2 according to the equation:



Kinetic results

The rate of the reaction depends on the first power of the concentrations of quinol, hexacyanoferrate(III) and alkali (Table 1). Under the present experimental conditions, the following rate law is valid:

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

where k_{obs} , the pseudo first order rate constant, was determined by keeping the concentrations of two of the three reactants (substrate, oxidant and alkali) constant, and was calculated from the equation /19/:

$$k_{\text{obs}} = \frac{2.303}{t} \log \frac{D_0}{D_t}$$

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 Table 1
 Rate data for the oxidation of quinol

[Quinol] (10 ³ M)	[K ₃ Fe(CN) ₆] (10 ⁴ M)	[NaOH] (10 ² M)	Temp. (±0.1 °C)	10 ⁴ × k _{obs} (s ⁻¹)
10.0	1.0	5.0	30.0	10.8
10.0	5.0	5.0	30.0	10.7
10.0	7.5	5.0	30.0	10.8
10.0	10.0	5.0	30.0	10.8
20.0	10.0	5.0	30.0	21.6
50.0	10.0	5.0	30.0	54.2
100.0	10.0	5.0	30.0	109.0
10.0	10.0	10.0	30.0	21.7
10.0	10.0	15.0	30.0	32.0
10.0	10.0	20.0	30.0	43.8
10.0	10.0	5.0	35.0	12.1
10.0	10.0	5.0	40.0	13.6
10.0	10.0	5.0	45.0	14.8

Methanol = 70% (v/v); μ = 0.50 M;

All rate constants are the averages of two or more experiments with-
in ±1.5% or better.

where D₀ was the initial optical density of the reaction mixture, and D_t was the optical density at time t.

The activation parameters of the reaction are:

$$E = 17.6 \pm 0.4 \text{ kJ mol}^{-1}; \quad A = 1.1 \text{ s}^{-1}; \quad \Delta H^\ddagger = 14.9 \pm 0.6 \text{ kJ mol}^{-1};$$

$$\Delta S^\ddagger = -27.3 \pm 1.0 \text{ JK}^{-1} \text{ mol}^{-1}.$$

Variation of the ionic strength using NaClO₄ (0.10 M to 0.50 M) did not affect the rate of the reaction. Added hexacyanoferrate(II) (5.0 × 10⁻⁴ M to 1.0 × 10⁻³ M) had no effect on the rate of the reaction.

Radical intermediate

The esr spectrum exhibited five equally spaced lines with the intensity ratio of 1 : 4 : 6 : 4 : 1. This pattern is caused by the coupling of the unpaired electron to four equivalent protons (hyperfine splitting). Four such protons in a non-overlapping spectrum would produce a splitting into five lines with peak intensity ratios of 1 : 4 : 6 : 4 : 1. This radical intermediate has also been detected and iden-

tified by esr during the two-step oxidation of quinol catalyzed by enzymes such as peroxidase /20/ and laccase /21/.

This radical intermediate showed an absorption in the visible region at 650 nm.

During the course of the reaction, the reaction mixture became colored, in contrast to the colorless starting phenol. This indicated the formation of a radical intermediate, which showed a typical absorption band at 1560 cm^{-1} in the infrared spectrum. Indeed, phenoxy radicals have been characterized by their electronic spectra /24–28/.

Mechanism

The alkali dependence of the oxidation process indicated that the reaction proceeded via an intermediate anion of the reducing substrate formed with hydroxide ions. For the formation of the dianion of quinol, the pK values for the two steps have been reported /29/ as 9.85 and 11.4. Hexacyanoferrate(III) would react with this dianion to yield the p-benzosemiquinone radical. This radical intermediate, detected by esr spectroscopy, showed a five line spectrum with peak intensities of 1 : 4 : 6 : 4 : 1. The reaction of the radical, with more oxidant, would be rapid, yielding the product, which has been characterized as p-benzoquinone. Redox equilibrium data /30/ indicate that the potential for the removal of the second electron is so low that quinones are formed quite rapidly. The mechanism is shown in the Scheme.

Acknowledgements. We thank the technical staff of the Regional Sophisticated Instrumentation Centre, IIT, Madras, for recording the esr spectra. Financial assistance to one of us (MB) from the CSIR, Government of India, is gratefully acknowledged.

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