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Kinetics of Oxidative Coupling of Phenols. Oxidation of Guaiacol by Alkaline Hexacyanoferrate(III)

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Synopsis. The reaction between guaiacol and alkaline hexacyanoferrate(III), at constant ionic strength, gave a coupled product, 3:3′-dimethoxydiphenoquinone. The rate of the reaction was dependent on the first orders of the concentrations of substrate, oxidant, and alkali. The rate determining step involved the formation of a radical intermediate, which was detected by ESR spectroscopy.

Kinetic studies on the oxidation of phenols by hexacyanoferrate(III) in alkaline medium have not received much attention.[1,2] The oxidation of phenols gives rise to radicals, which can yield coupled products. Guaiacol has been chosen for purposes of oxidation by alkaline hexacyanoferrate(III). A survey of the literature revealed that the oxidation of guaiacol had yielded coupled products.[3–5]

Experimental

IR spectra were recorded on an IR-297(Perkin-Elmer) spectrophotometer; NMR spectra on an EM-390(Varian) 90 MHz NMR spectrometer; ESR spectra on an E-4(Varian) EPR spectrometer.

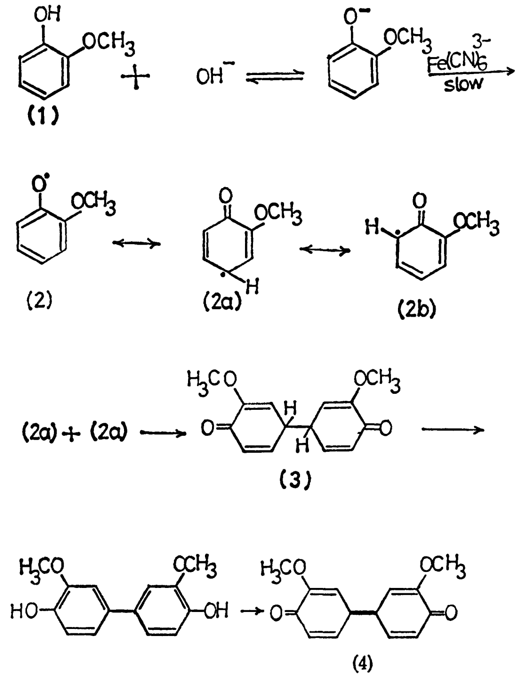
Materials. Guaiacol(SISCO) was distilled before use (bp 204 °C), and its purity confirmed by IR analysis.[6] Methanol (E. Merck) was distilled before use. $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and NaOH were IDPL samples. $HClO_4$ (E. Merck, 70%) was neutralized with NaOH; the solution was concentrated, and the crystals of $NaClO_4$ obtained were filtered, recrystallized from water, and dried over silica gel under vacuum. The ionic strength of the medium was maintained by the addition of the requisite amount of $NaClO_4$.

Methods. Solutions of guaiacol in aqueous methanol, and $K_3Fe(CN)_6$ in methanol, NaOH, $NaClO_4$, and water were separately thermostated at 30 °C for 3 h under nitrogen, and then mixed in equal volumes. The progress of the reaction was followed by monitoring the disappearance of $[Fe(CN)_6]^{3-}$, spectrophotometrically.[7]

Stoichiometry. Reaction mixtures containing an excess of oxidant were allowed to react to completion, and the $[Fe(CN)_6]^{3-}$ which was left was analyzed, spectrophotometrically. The results gave a ratio of substrate to oxidant according to the equation:

$$2C_7H_8O_2 + 4[Fe(CN)_6]^{3-} + OH^- \longrightarrow C_{14}H_{12}O_4 + 4[Fe(CN)_6]^{4-} + H_2O + 3H^+.$$

Product Analysis. Guaiacol (2.0 g) in 70% methanol (v/v) was mixed with 11.0 g of $K_3Fe(CN)_6$ containing NaOH (0.05 M†) and 70% methanol(v/v), and the mixture refluxed at 60 °C for 3 h under nitrogen. After cooling and filtration, removal of the solvent gave a red residue (0.072 g). The insoluble portion of the mixture was washed with $CHCl_3$, and after removal of $CHCl_3$, a red residue (1.615 g) was obtained. The mp of both these residues was 245 °C. IR analysis of both these residues, in $CHCl_3$, showed them to be identical with 3:3′-dimethoxydiphenoquinone, **4**. A sharp band at 1640 cm^{-1} was obtained, corresponding to the carbonyl stretching of the C=O groups in two rings of an extended quinonoid structure.[8] The $\nu(OCH_3)$ band at 1020 cm^{-1} was also present in the IR spectrum of **4**, indicating that the OCH_3 group was unaffected by the oxidation. The NMR spectrum of **4**, in $CHCl_3$, (internal standard TMS, sweep width 10 ppm), gave a peak at 6.1 τ (OCH_3), and four doublets in the vinylic proton region at 3.20 τ, 3.10 τ, 2.30 τ, and 2.20 τ.



Scheme 1.

Results and Discussion

Kinetic Results. The rate data are shown in Table 1. Under the present experimental conditions, the rate law can be expressed as:

$$\text{Rate} = -\frac{d[Fe(CN)_6]^{3-}}{dt} = k_{obsd}[\text{Guaiacol}][Fe(CN)_6{}^{3-}][OH^-]. \qquad (1)$$

The pseudo first order rate constant, k_{obsd}, was determined by keeping the concentrations of two of the three reactants constant, and was calculated from the equation:[9]

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

The effect of temperature was studied (Table 1) and the activation parameters evaluated: $E = 23.0 \pm 0.8$ kJ mol^{-1}; $A = 9.5 \pm 0.5$ s^{-1}; $\Delta H^{\neq} = 20.4 \pm 0.8$ kJ mol^{-1}; $\Delta S^{\neq} = -28.0 \pm 1.2$ J K^{-1} mol^{-1}.

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† 1 M = 1 mol dm^{-3}.

Table 1. Rate data for the oxidation of guaiacol

[Guaiacol] / 10^3 M	[$K_3Fe(CN)_6$] / 10^4 M	[NaOH] / 10^2 M	Temp/°C (±0.1 °C)	$10^3 \times k_{obsd}$ / s^{-1}
5.0	10.0	5.0	30.0	1.05
10.0	10.0	5.0	30.0	2.09
20.0	10.0	5.0	30.0	4.20
25.0	10.0	5.0	30.0	5.24
5.0	2.5	5.0	30.0	1.06
5.0	5.0	5.0	30.0	1.10
5.0	7.5	5.0	30.0	1.05
5.0	10.0	2.5	30.0	0.52
5.0	10.0	7.5	30.0	1.57
5.0	10.0	10.0	30.0	2.10
5.0	10.0	5.0	35.0	1.43
5.0	10.0	5.0	40.0	1.86
5.0	10.0	5.0	45.0	2.05
5.0	10.0	5.0	50.0	2.68

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

The variation of the ionic strength (0.10 M to 0.50 M $NaClO_4$) and the addition of $K_4Fe(CN)_6$ in the concentration range 1.0×10^{-4} M to 1.0×10^{-3} M, did not have any effect on the rate of the reaction.

Increasing proportions of methanol from 60% to 75% (v/v) decreased the rate constant $10^3 \times k_{obsd}/s^{-1}$ from 1.41 to 0.90 at [guaiacol] $= 5 \times 10^{-3}$ M, [$K_3Fe(CN)_6$] $= 1 \times 10^{-3}$ M, [NaOH] $= 5 \times 10^{-2}$ M, $\mu = 0.50$ M and temp = 30 °C. From the linear plot of $\log k_{obsd}$ *versus* $1/D$, the value of r, the distance of approach between the ions, was calculated from the Scatchard equation[10] to be 3.1 Å, which was of the right order of magnitude.

Radical Intermediate. Phenols are known to give rise to stable radicals, which have been detected and characterized.[11,12] In this investigation, the ESR spectrum of the radical obtained from the oxidation of guaiacol was a spectrum consisting of 9 lines, which were rather broad. This spectrum was interpreted in a manner similar to that in an earlier investigation.[13] For the present, it can be concluded that the rate determining step of the reaction involved the formation of a radical intermediate, which could be stabilized by resonance. It was further observed that this radical intermediate showed a typical absorption band at 1560 cm^{-1} in the IR spectrum. In general, phenoxyl radicals have been characterized by their electronic spectra.[14,15]

Mechanism. Pummerer *et al.*[16,17] had postulated a free phenoxyl radical as the first intermediate in the reactions of phenol coupling. The observed coupling positions, ortho and para, show that a free phenoxyl radical would be reactive only on the oxygen and on the ortho and para carbon atoms of guaiacol. The resonance structures for the radical would symbolize a high density of the unpaired electron at these positions. Guaiacol can be oxidized to the corresponding phenoxyl radical, **2**↔**2a**↔**2b**. Combination of **2a** + **2a** would result in the formation of the dimer, **3**, which would undergo tautomerization rapidly in methanol, and would be oxidized further to yield the extended quinone, **4**. No other intermediate product(s) could be recovered. The mechanism is shown in Scheme 1.

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