

Kinetics of Oxidative Coupling of Phenols: Oxidation of Phloroglucinol by Alkaline Hexacyanoferrate(III)

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The reaction of phloroglucinol with alkaline hexacyano-
ferrate(III) at constant ionic strength gives a carbon-oxygen coupled
product(I) in 80-85% yield. A radical intermediate is formed in the
rate-determining step, as revealed by ESR spectroscopy (1:3:3:1
quartet) and IR band at 1560 cm⁻¹.

Kinetic studies on the oxidation of phenols by
hexacyanoferrate(III) have received very little
attention^{1,2}. We report herein the kinetics of oxidation
of phloroglucinol by alkaline hexacyanoferrate(III) at
constant ionic strength, under nitrogen atmosphere.

The reaction was followed by observing the
disappearance of Fe(CN)₆³⁻ at 420 nm, spectropho-
tometrically³. The reaction obeyed the rate Eq. (1)

$$\text{Rate} = -\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} \\ = k_{\text{obs}}[\text{substrate}][\text{Fe}(\text{CN})_6^{3-}][\text{OH}^-] \quad \dots (1)$$

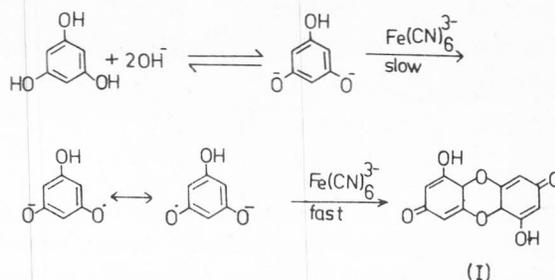
The rate data are given in Table 1. The activation
parameters were evaluated: $E_a = 28.2 \pm 0.8 \text{ kJmol}^{-1}$;

Table 1—Rate Data for Oxidation of Phloroglucinol

[Solvent: 70%(v/v) aq. methanol; $\mu = 0.5 \text{ mol dm}^{-3}$ temp = 30°]

10 ³ × [Substrate] (mol dm ⁻³)	10 ³ × [K ₃ Fe(CN) ₆] (mol dm ⁻³)	10 ² × [NaOH] (mol dm ⁻³)	10 ² × k _{obs} (s ⁻¹)
10.0	1.0	5.0	4.8
25.0	1.0	5.0	12.0
50.0	1.0	5.0	24.2
100.0	1.0	5.0	48.8
10.0	0.2	5.0	4.7
10.0	0.5	5.0	4.9
10.0	0.7	5.0	4.8
10.0	1.0	2.0	2.0
10.0	1.0	7.0	7.2
10.0	1.0	10.0	10.1
10.0	1.0	5.0	5.7*
10.0	1.0	5.0	6.8†
10.0	1.0	5.0	8.3‡

Temp: *35°; †40°; ‡45°



$A = (1.3 \pm 0.2) \times 10^4 \text{ s}^{-1}$; $\Delta H^\ddagger = 25.6 \pm 0.8 \text{ kJmol}^{-1}$;
and $\Delta S^\ddagger = -174.0 \pm 1.6 \text{ JK}^{-1} \text{ mol}^{-1}$.

For the isolation of the products, stoichiometric
amounts of substrate (2mol) and oxidant (4 mol) were
mixed at 30°, and maintained under N₂ atmosphere for
24 hr. The reaction mixture was cooled, filtered and
concentrated. The residue was extracted with ether,
and the ether extract concentrated after drying over
anhyd. Na₂SO₄. TLC analysis of the residue, using
benzene as the developer, gave two spots. Separation
on a silica gel column, using mixtures of hexane and
chloroform in varying proportions (100:0 to 70:30, v/v)
as eluents, gave two products. The first product,
obtained in 80-85% yield, was characterized by m.p.
(250°), IR data [2960, 2910 (νOH; H-bonded); 1640,
1620 (νC=O); 1480, 1380, 1210 (νC-O); 1130 (vas
for six-membered rings as in 1, 4-dioxan); 1030 and 920
(νC-O) cm⁻¹], and PMR data [τ2.5(OH) and 5.0
(tertiary protons)]. It was assigned structure(I) based
on these data (see Scheme 1). This product(I) provides
an example of C-O coupling, as has been observed, *in*
vivo, in the formation of dehydrodigallic and valonic
acids⁴. The second product was a polymeric material,
and was not analyzed.

Increasing proportions of methanol from 70% to
85%(v/v) decreased the rate constant: 10³k_{obs}(s⁻¹) from
48.0 to 37.3 at [substrate] = 1 × 10⁻² mol dm⁻³,
[K₃Fe(CN)₆] = 1 × 10⁻³ mol dm⁻³, [NaOH] = 5 ×
10⁻² mol dm⁻³, $\mu = 0.5 \text{ mol dm}^{-3}$, temp. = 30.0 ±
0.1°C. From the linear plot of log k_{obs} against 1/D, the
value of *r* was calculated from the Scatchard equation⁵
to be 5.6 Å.

The ESR spectrum of the radical generated during
the oxidation of phloroglucinol by alkaline
K₃Fe(CN)₆ exhibited a 1:3:3:1 quartet, due to the three
equivalent protons at positions 2, 4 and 6. The IR
spectrum of the reaction mixture, scanned rapidly at
two-minute intervals, exhibited a stable band at
1560 cm⁻¹. These data suggested the formation of a
radical intermediate in the rate-limiting step.

The alkali dependence of the oxidation process indicated that the reaction proceeded via an intermediate anion of the reducing substrate formed with hydroxyl ions. Hexacyanoferrate(III) reacts with this anion to yield the radical in the rate-determining step, which then undergoes rapid coupling to give the product (Scheme 1). One of us (MB) gratefully acknowledges the award of a junior research fellowship by the CSIR, Government of India.

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