

### Oxidation of Acetonaphthones by Hexacyanoferrate(III)

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Kinetics of oxidation of a number of 4-substituted 1-acetonaphthones and of 2-acetonaphthone by hexacyanoferrate(III) in aq. ethanol at 35° have been studied. An increase in ethanol content of the solvent decreases the kinetic rate while increase in concentration of either alkali or a neutral salt increases the rate. This may provide evidence for the oxidation to proceed through the enolate anion intermediate. Hammett equation is found to be valid in the presently studied system.

ALTHOUGH far more attention has been paid to correlate the reactivities of *meta*- and *para*-substituted benzene derivatives in a large number of reactions<sup>1</sup>, relatively very few systematic studies of similar type are available in naphthalene system<sup>2,3</sup>. The kinetics of oxidation of a number of 4-substituted 1-acetonaphthones by hexacyanoferrate(III) in aq. ethanol at constant ionic strength and constant temperature have been investigated and the results are reported in this note.

All the ketones used were prepared by the literature method<sup>3</sup>. The procedure for the determination of rate constants was similar to that followed for acetophenones<sup>4</sup>. Rate constants have been determined using second order rate equation for the reactants present in equal concentration. The kinetic data are given in Tables 1-3. It has been shown<sup>4,5</sup> that the oxidation of acetophenones by hexacyanoferrate(III) proceeds through the enolate anion.

TABLE 1 — EFFECT OF VARYING [KCl] ON THE REACTION RATE  
 {[1-Acetonaphthone]=[K<sub>3</sub>Fe(CN)<sub>6</sub>]=1.014 × 10<sup>-3</sup> M; [NaOH]=0.05 M; solvent=15% ethanol; temp.=35°C}

[KCl] M	√μ	k, litre mole <sup>-1</sup> min <sup>-1</sup>
0.250	0.5533	3.22
0.1875	0.4935	2.63
0.1250	0.4255	2.48
0.0764	0.3641	1.81
0.0371	0.3054	1.36

TABLE 2 — EFFECT OF VARYING SOLVENT COMPOSITION AND [NaOH] ON THE REACTION RATE

{[1-Acetonaphthone]=[K<sub>3</sub>Fe(CN)<sub>6</sub>]=1.014 × 10<sup>-3</sup> M; [KCl]=0.25 M; temp.=35°C}

Ethanol % (v/v)	k, litre mole <sup>-1</sup> min <sup>-1</sup>	[NaOH] M	k, litre mole <sup>-1</sup> min <sup>-1</sup>
[NaOH]=0.05 M		Ethanol, 15% (v/v)	
15	3.22	0.010	0.88
20	2.39	0.025	1.80
25	2.19	0.050	3.22
		0.075	5.12

TABLE 3 — SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF KETONES IN 15% (v/v) ETHANOL AT 35°

{[Ketone]=[K<sub>3</sub>Fe(CN)<sub>6</sub>]=0.001014 M; [KCl]=0.25 M; [NaOH]=0.05 M}

Ketones	k litre mole <sup>-1</sup> min <sup>-1</sup>
Acetophenone	1.54
2-Acetonaphthone	3.07
1-Acetonaphthone	3.22
4-Fluoro-1-acetonaphthone	3.42
4-Chloro-1-acetonaphthone	7.51
4-Bromo-1-acetonaphthone	9.53
4-Methyl-1-acetonaphthone	2.60
4-Methoxy-1-acetonaphthone	1.52

With a view to finding whether a similar mechanism holds good for acetonaphthones, the oxidation of 1-acetonaphthone was carried out at different ionic strengths. The rate (Table 1) was found to increase with increasing ionic strength. A plot of log k versus √μ was linear. Also the rate was found to decrease with increasing ethanol content of the solvent medium (Table 2). These determinations point out to an ion-ion type of reaction which proceeds through the formation of enolate anion.

It is seen from the data in Table 3 that electron attracting groups in the naphthalene ring facilitate oxidation whereas electron releasing groups retard the oxidation. If the oxidation proceeds through the enolate anion, the rate of oxidation will depend on the stability and percentage of the enol content. In the presence of electron attracting groups the keto form will be more unstable than the enolic form. The results on the effect of various substituents and those in Table 2 of varying [alkali] provide evidence in favour of the oxidation taking place through the enolate anion. However, it is difficult to decide about the exact nature of enolate in the absence of any product analysis.

A plot of log k/k<sub>0</sub> against the σ constants of the 4-substituents is linear at 35° (ρ = 1.3; r = 0.942) showing that the Hammett equation applies satisfactorily in the oxidation of 4-substituted 1-acetonaphthones.

It is evident that 1-acetonaphthone reacts faster than acetophenone. This is due to the electron attracting nature of the 2,3-benzo substituent which has a σ value<sup>6</sup> of 0.5. Oxidation of 2-acetonaphthone proceeds at a slower rate than 1-acetonaphthone. This may be due to the lower σ value (0.04) of the 3,4-benzo substituent<sup>6</sup> compared to that of the 2,3-benzo substituent.

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