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Kinetic Evidence for Radical Anions in the Oxidation of p-Nitrotoluene & 2,4-Dinitrotoluene by Alkaline Hexacyanoferrate(III) in Aqueous Dimethyl Sulphoxide
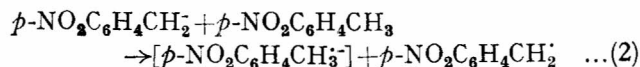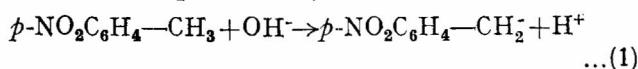
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Stoichiometry in the oxidation of p-nitrotoluene by alkaline ferricyanide in aqueous DMSO is 1:3 under excess or low base concentration whereas in the case of 2,4-dinitrotoluene the stoichiometry is 1:1 in deficient base which becomes 1:2 in excess base. This has been rationalized on the basis of formation of radical ion in the case of p-nitrotoluene at all [base] whereas in the case of 2,4-dinitrotoluene only feeble [base] generates the radical ion.

RECENTLY we have reported the kinetics of oxidation of p-nitrotoluene in aqueous DMSO by alkaline ferricyanide[1]. We had explained the oxidation process as involving a rate determining abstraction of an electron from the carbanion formed in a fast step from p-nitrotoluene and the base. A thorough study of these reactions showed that the stoichiometry was 1:3 and not 1:6 (p-nitrotoluene: ferricyanide) as it should have been in the presence of excess oxidant.

This is a pointer to the fact that, in addition to the oxidation process which uses the carbanion that is formed, there is a parallel reaction of radical ion formation (Eqs. 1 and 2).

$$p\text{-}NO_2C_6H_4\text{—}CH_3 + OH^- \rightarrow p\text{-}NO_2C_6H_4\text{—}CH_2^- + H^+ \quad \ldots(1)$$

$$p\text{-}NO_2C_6H_4CH_2^- + p\text{-}NO_2C_6H_4CH_3 \rightarrow [p\text{-}NO_2C_6H_4CH_3^{\cdot-}] + p\text{-}NO_2C_6H_4CH_2^{\cdot} \quad \ldots(2)$$

Due to this parallel reaction, the p-nitrotoluene species that is used for oxidation is about half that of the total concentration and the rest half being used for radical ion formation, whose concentration becomes constant after certain period.

Hence the overall stoichiometry of 1:3 is actually 1:6 when the used up concentration of p-nitrotoluene for oxidation is taken into account for stoichiometric computation. This is quite in conformity with the nature of ferricyanide as a one-electron oxidant.

Evidences for radical ion formation in basic systems have been well summarized by Russel and

Janzen[2]. The important point noted in the present investigation is even though an oxidant is present to react firmly with the carbanion there exists a parallel reaction of spontaneous breakdown of the carbanion into radical ion.

Another important point is that radical ions are stable in partially aqueous system for nitroaromatics even though the base is not so strong as in a non-aqueous system like t-butanol or t-butanol-DMSO.

According to Russel and Janzen[2] in the spontaneous disproportionation of p-nitrotoluene in basic solution, 50% of the initial p-nitrotoluene is recovered. This checks remarkably well with our finding that actually 50% of initial [p-nitrotoluene] is available for oxidation by ferricyanide while the rest is converted into radical anion.

We have confirmed the above reasoning by further experiments with 2,4-dinitrotoluene. The rate constants for 2,4-dinitrotoluenes at varying [substrate] and [base] are given in Tables 1 and 2. For purposes of comparison the rate constants reported for p-nitrotoluene oxidation are also included. The reactivity order is 2,4-dinitrotoluene > p-nitrotoluene which is quite plausible on the basis of acidity considerations. The reaction of 2,4-dinitrotoluene with ferricyanide is first order each in the substrate and in the oxidant. Dependence on [OH⁻] is unity. The stoichiometry with excess oxidant is 1:1 and the product is 2,4-dinitrobenzyl alcohol unlike p-nitrobenzoic acid in p-nitrotoluene oxidation. The stoichiometry for the single step of oxidation is 1:1, in consonance with our earlier work that the effective concentration of 2,4-dinitrotoluene for oxidation is just half the total concentration of 2,4-dinitrotoluene and the other half is converted

TABLE 1 — SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF 2,4-DINITROTOLUENE BY FERRICYANIDE

{Solvent: aq. DMSO (50%, v/v); [ferricyanide] = $0.0011M$; [KCl] = $0.025M$; [NaOH] = $0.002M$; temp. = 35°}

[Substrate] M	k_2 litre mole⁻¹ sec⁻¹
0.001267	0.1714
0.002417	0.1586
0.003297	0.1675
0.004548	0.1694

TABLE 2 — DEPENDENCE ON [OH⁻] IN THE OXIDATION OF 2,4-DINITROTOLUENE BY FERRICYANIDE

{Solvent: aq. DMSO (50%, v/v); [ferricyanide] = $0.0011M$; [substrate] = $0.0012M$; [KCl] = $0.025M$; temp. = 35°}

[NaOH] M	k_2 litre mole⁻¹ sec⁻¹
0.002	0.167
0.005	0.432
0.007	0.731
0.011	1.210

k_2 for the p-nitrotoluene oxidation by ferricyanide in 50% aq. DMSO, $0.1M$ NaOH at 45°C is 0.03834 litre mole⁻¹ sec⁻¹ (loc. cit.).

into radical anions in a parallel reaction. As stated earlier the stoichiometry 1:1 is actually 1:2 when the effective concentration of the hydrocarbon is used for computation.

Another interesting point observed is that the stoichiometry changes over to 1:2 in the case of 2,4-dinitrotoluene if the [base] $\gg$ [substrate]. At 0·2M NaOH in 50% aq. DMSO (v/v) with 2,4-dinitrotoluene (0·0012M) and ferricyanide (0·0024M) there was no residual ferricyanide in a stoichiometric run. This shows that there is no parallel reaction of radical anion formation in the case of 2,4-dinitrotoluene and the rapidly formed carbanions are converted into the oxidation product. Thus it is clear that only feeble [base] generates radical anions in the case of 2,4-dinitrotoluene. However, irrespective of the [base], there is radical ion formation in the oxidation of p-nitrotoluene.

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Polarographic Behaviour of Picoline Complexes of Cu(II)

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Polarographic reduction of an aqueous solution of Cu(4-picoline)$_4$(NO$_3$)$_2$ and Cu(3-picoline)$_4$(NO$_3$)$_2$ in the presence of gelatin gives diffusion-controlled one-step irreversible reduction waves (Cu^{II} → Cu^0). The processes have been characterized by measuring rate constant (k_r) and activation energy of diffusion (E_a) at a reference potential −0·16 V. 4-Picoline complex having more negative value of $aE_{\frac{1}{2}}$ is more stable than the 3-picoline complex which is more easily reduced at the d.m.e. This is in conformity with the order of basicity of the ligands.

THE polarographic behaviour of Cu(3-pic)$_4^{2+}$ ion and Cu(4-pic)$_4^{2+}$ ion (where 3-pic = 3-picoline and 4-pic = 4-picoline) have been studied in different media to get useful information on the electrode reduction of these complex ions at the d.m.e. under comparable conditions.

To a clear ethanolic solution of Cu(NO$_3$)$_2$.6H$_2$O (AR) pure ligand was added in slight excess and the solution was crystallized to get pure blue crystals of Cu(pic)$_4$(NO$_3$)$_2$. The crystals were separated under suction, washed with ethanolic solution of respective picoline (2%), dried and analysed by standard methods.

Distilled water redistilled in an all-glass still with the addition of little KMnO$_4$ and KOH was used to prepare all the solutions.

Freshly prepared solution of gelatin was used as the maxima suppressor.

The polarograms of the deaerated, thermostated ($\pm 0·1°$) solutions were recorded on a polarograph provided with automatic recording device (Hungarian make, type OH 101/1). SCE was used as the reference electrode. Sensitivity of the current measurement could be selected out of 28 variable steps between 1×10^{-9} and 8×10^{-6} a/mm. A potential range of 0·5 V could be applied at the indicator electrode and the recorder pen travelled 200 mm on the chart paper for the applied e.m.f. By knowing the initial potential reading it was possible to evaluate $E_{\frac{1}{2}}$ and values of i and i_d at different potentials. An external SCE was used which was connected to the experimental solution in the polarographic cell through appropriate agar-salt bridge. The unit was calibrated as usual.

A conductivity bridge (Toshniwal) was used for conductance measurements for evaluating diffusion coefficients as required.

It has been found that in the absence of 'free' ligand in solution the main polarographic wave of each complex ion in the presence of KNO$_3$ is preceded by a very small prewave the height of which is independent of the height of mercury column. For the main wave of each complex

$$i_{\text{lim}}/h_{\text{eff}}^{\frac{1}{2}}\left(h_{\text{eff}} = h - \frac{3·1}{(mt)^{\frac{1}{2}}}\right)$$

is constant indicating that limiting current is diffusion-controlled. Thus, with two different heights of mercury reservoir, namely 79·8 and 70·0 cm, the ratio $i_{\text{lim}}/h_{\text{eff}}^{\frac{1}{2}}$ gave the values 0·80 and 0·82 for 4-picoline complex and 0·69 and 0·70 for 3-picoline complex.

As the electro-reduction process is irreversible, Ilkovic equation ($i_{\text{lim}} = 607\ nD^{1/2}\ \text{cm}^{2/3}\ t^{1/6}$) was not used to evaluate the value of n, the number of electrons involved in the electrode process. The value of diffusion coefficient (D) for each complex ion was obtained from the value of equivalent conductance of the corresponding complex salts at infinite dilution from the well-known relation $D = (RT/ZF^2)\ \lambda_0$.

The usual plot of $-E$ vs log ($i/i_{\text{lim}}-i$) was used for the evaluation of $E_{\frac{1}{2}}$. The slope of the log plots indicated irreversible nature of the waves. The $E_{\frac{1}{2}}$ values in different supporting electrolytes are given in Table 1.

TABLE 1 — HALF-WAVE POTENTIAL OF PICOLINE COMPLEXES OF Cu(II) IN DIFFERENT MEDIA

[Temp.= 25° $\pm$ 0·1°, complex conc. = 1 × 10^{-3}M; gelatin = 0·005%, h = 79·8 cm, m = 0·77 mg sec^{-1}, t = 3·25 sec^{-1}]

Medium	$E_{\frac{1}{2}}$ (vs SCE), V	
	Cu(3-pic)$_4^{2+}$	Cu(4-pic)$_4^{2+}$
0·1M KNO$_3$	−0·036	−0·049
1·0M KNO$_3$	−0·038	−0·050
0·1M KCl	−0·079	−0·110
0·1M NH$_4$Cl	−0·069	−0·106

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