Ru(III) inhibition on the oxidation of anilines with HOOSO$_3^-$

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Ligation to metal centre does inhibit aniline oxidation with HOOSO$_3^-$ in the presence of Ru(III).
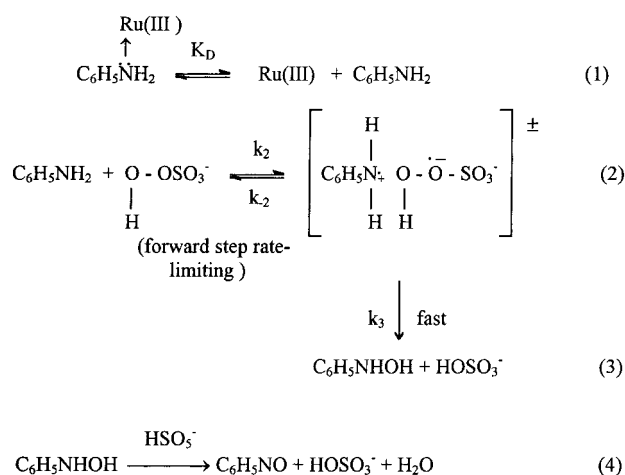
Johnson and Nickerson[6] have examined the oxidation by HOOSO$_3^-$ of a series of thiols coordinated to Ru(III) and Co(III). Ligation to metal centre does not inhibit oxidation. Recently Pd(II) inhibition[7] on the hexacyanoferrate(III) oxidation of sugars has been reported. Certain ligands like diethylene triamine pentaacetic acid inhibit the Ti^{III} – H$_2$O$_2$ reaction.[8] In the present study, detailed kinetic investigations have been carried out on the Ru(III) inhibited oxidation of some *20 meta-, para-* and *ortho-* substituted anilines with HOOSO$_3^-$. Based on the kinetic data, structure–reactivity relationships are ascertained.

Pseudo-first-order conditions were maintained by keeping a large excess of anilines over potassium peroxomonosulfate. Control experiments ruled out the decomposition of the oxidant under the experimental conditions maintained. The reactions were carried out in 50% aqueous acetic acid (v/v) medium. All the solutions were kept in a thermostat at constant temperature which was controlled using a Gallenkemp thermostat to an accuracy of ± 0.1° and the measurements were made between 298 and 318 K. The required volume of these solutions for each run were mixed and 2 ml aliquots of the reaction mixture were pipetted out at convenient time intervals and quenched in 10 ml 2% potassium iodide solution and the liberated iodine was titrated against standard thiosulfate to a starch end point. Stoichiometric studies reveal that 2 mol of the oxidant is consumed by 1 mol of the reductant. Product analysis indicates the presence of nitroso products in the reaction mixture, confirmed by TLC.

The reaction exhibits first-order dependence each on oxidant and reductant. Ru(III) retards the reactivity of anilines significantly. The linear plot of log k_{obs} *versus* D^{-1} ($r = 0.999$, $s = 0.009$) very much suggests that there is an involvement of a negative ion in the rate-limiting step. The effect of substituents on the reactivity has been investigated by employing some *20 meta-*, *para-* and *ortho-* substituents. Interestingly, the rates of all the substituted anilines are higher than for the parent (Table 4). Substituent effects are small in the case of electron-donating substituents. In spite of obvious imperfections, a nonlinear concave upward Hammett plot can be observed, rather than a random scatter of points (Fig.4). These results can be described by a rate-limiting one-electron transfer from nucleophile to electrophile resulting in a radical-cation-like transition state which can be stabilized by both electron-donating and withdrawing substituents.[11,15]

Substituent effects in this reaction system are composite since they represent the combination of effects on the oxidation rate constant and on Ru(III) complex dissociation constant. A treatment with the Yukawa–Tsuno equation is successful only to a limited extent. The linear relation between $\Delta H^{\#}$ and $\Delta S^{\#}$ suggests the operation of a similar mechanism in all the anilines. Exner plots further confirm the above view.

A facile oxidation process with the *ortho-* substituents provides information about the importance of anchimeric assistance. Except for *o*-NO$_2$C$_6$H$_4$NH$_2$, in all the other *ortho-*

* To receive any correspondence.

$$C_6H_5\overset{\uparrow}{N}H_2 \quad \overset{Ru(III)}{\underset{K_D}{\rightleftarrows}} \quad Ru(III) + C_6H_5NH_2 \qquad (1)$$

$$C_6H_5NH_2 + O\text{-}OSO_3^- \quad \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \quad \left[C_6H_5\overset{H}{\underset{H}{\overset{|}{N}}}{\overset{.}{\underset{H}{\overset{|}{O}}}}\text{-}O\text{-}SO_3^- \right]^{\pm} \qquad (2)$$

(forward step rate-limiting)

$$\downarrow k_3 \quad \text{fast}$$

$$C_6H_5NHOH + HOSO_3^- \qquad (3)$$

$$C_6H_5NHOH \quad \xrightarrow{HSO_5^-} \quad C_6H_5NO + HOSO_3^- + H_2O \qquad (4)$$

substituents the ratio of rate constants of *ortho-* and *para-* substituted anilines is > 1 (Table 6). It appears that in these conversions the steric hindrance is slightly overcompensated by an effective anchimeric assistance. The relative rate of *ca* 0.36 obtained for *o*-NO$_2$ substituent reflects not too large steric effects in these reactions. Further, the activation energy values of the *o*-isomers are lower than for the *para-* analogues. This supports the intramolecular participation of the *o*-isomer in the transition state.

Free aniline facilitating the oxidation, as proposed in the reaction scheme, is well supported by the observation that the rate constant increases with increasing pH, as at higher pH there is a greater concentration of free aniline. The involvement of free radical intermediates in this oxidation system is well characterized by very low reaction constant values.

Techniques used: TLC, IR, NMR, titrimetry

References: 31

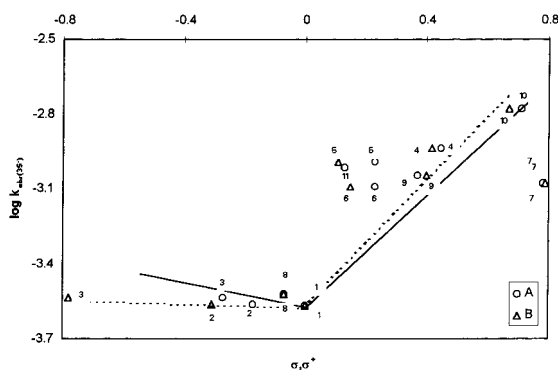Table 1: Dependence of the oxidation rate on [oxidant], [substrate] and [Ru(III)] at 308 K

Fig. 4   A Non-linear Hammett plot (Numbered as in Table 4)
A - σ B - σ⁺
(solid line represents σ plot)
(dashed line represents σ⁺ plot)

Table 4   Rate constants and activation parameters for the oxidation of *meta*- and *para*- substituted anilines with PMS in presence of Ru(III) ; [PMS] = 1.00 x 10^{-3} mol/dm^{-3}, [Ru(III)] = 1.20 × 10^{-5} mol/dm^3 , [S] = 5.27 × 10^{-2} mol/dm^3; AcOH: Water = 50 : 50 (v/v)

No.	Substrate	$k_{obs} \times 10^4$/ s^{-1}			$\Delta H^{\#}$ kJ/mol	$-\Delta S^{\#}$ J/K/mol	$\Delta G^{\#}$ kJ/mol
		25°	35°	45°			
1	H	1.21	2.69	5.85	60.39	117.61	96.61
2	*p*-CH$_3$	1.32	2.73	6.92	63.14	108.15	96.42
3	*p*-OCH$_3$	1.45	2.89	6.44	56.55	129.17	96.33
4	*p*-COOH	7.46	11.50	20.28	37.13	180.67	92.77
5	*p*-Cl	3.81	10.20	18.41	58.91	112.44	93.54
6	*p*-Br	3.68	8.08	16.68	57.19	119.10	93.84
7	*p*-NO$_2$	4.33	8.33	13.10	43.11	171.34	93.88
8	*m*-CH$_3$	1.54	3.00	8.13	63.49	105.72	96.05
9	*m*-Cl	5.60	9.00	16.20	39.53	174.97	93.42
10	*m*-NO$_2$	10.01	16.56	32.94	41.13	164.24	91.71
11	*m*-OH	4.98	9.65	17.57	47.29	149.67	93.38
12	*o*-CH$_3$	1.81	3.78	8.02	56.37	127.78	95.73
13	*o*-OCH$_3$	2.43	4.65	8.11	45.10	162.95	95.28
14	*o*-Cl	8.46	14.62	23.41	37.67	177.50	95.34
15	*o*-Br	7.76	15.47	28.77	49.23	139.49	92.19
16	*o*-F	5.62	11.11	20.24	48.12	145.90	93.05
17	*o*-I	13.47	22.84	38.87	39.38	168.01	91.12
18	*o*-NO$_2$	1.97	3.05	6.02	41.79	176.28	96.08
19	*o*-COOH	9.33	15.31	24.44	36.17	181.82	92.17
20	*o*-COCH$_3$	8.51	16.57	28.47	45.16	152.28	92.06

Table 6   Ratio of rate constants of oxidation for the *ortho*- and *para*- substituted anilines at 308 K ; [PMS] = 1.00 × 10^{-3} mol/ dm^3, [Ru(III)] = 1.20 × 10^{-5} mol/dm^3 [S] = 5.27 × 10^{-2} mol/dm^3

Substituent	$k_{ortho} \times 10^4$ / s^{-1}	$k_{para} \times 10^4$ /s^{-1}	k_{ortho}/ k_{para}
CH$_3$	3.78	2.73	1.38
OCH$_3$	4.65	2.89	1.61
Cl	14.62	10.20	1.43
Br	15.47	8.08	1.91
NO$_2$	3.05	8.33	0.36
COOH	16.57	11.50	1.33

Table 2: Effect of pH and solvent composition on reaction rate

Table 3: Dependence of the reaction rate at 308 K on ionic strength and acrylonitrile

Table 5: The reaction constant values for ρσ and ρσ$^+$ correlations

Table 7: Comparison of energy of activation values for *ortho*- and *para*-substituted anilines

Figures: 7

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