

KINETICS OF OXIDATION OF METHOXYTOLUENES BY ACIDIC HEXACYANOFERRATE(III)

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Methoxytoluenes react with acidic $K_3Fe(CN)_6$ giving aldehyde as major product. The rate depends on the first powers of the concentrations of substrate, oxidant and acid. A radical pathway is indicated by $\varphi^* = -0.50$ and $k_H/k_D = 6.0$. The ESR spectrum of this radical intermediate gave 15 lines.

В качестве главного продукта реакции метокситолуолов с гексацианоферратом(III) в кислой среде получается альдегид. Реакция первого порядка по субстрату, оксиданту и кислоте. Величины $\varphi^* = -0,50$ и $k_H/k_D = 6,0$ говорят о радикальном пути реакции. Спектр ЭПР промежуточного радикала имеет пятнадцать линий.

INTRODUCTION

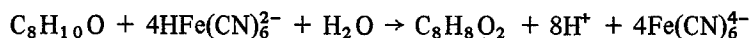
Methoxytoluenes have been oxidized by aqueous sodium dichromate giving the acid /1/, by Mn(II) acetate giving anisyl acetate /2/, by LTA giving methoxybenzyl acetate /3/, by chromyl chloride /4/ and by ceric ions /5-7/ giving the aldehyde. We report here the kinetic features of the oxidation of methoxytoluenes by acidic $K_3Fe(CN)_6$ under a nitrogen atmosphere.

EXPERIMENTAL

(a) *Materials, methods and stoichiometry*

Methoxytoluenes were prepared by the known method /8/, and the purity of each isomer was checked by UV analysis (in ethanol: 224 nm for the para, 227 nm for the ortho, 222 nm for the meta isomers). Perchloric acid was a 'Baker analysed' sample. All other materials were of E. Merck grade. The deuterated compounds,

ArCD_3 , were obtained from Isotopes Inc., and the NMR spectrum of each of the samples did not show any peaks for methyl protons. The kinetic method employed has been described earlier /9/. The stoichiometry of the reaction was determined /9/ to be:



(b) *Product analysis*

Stoichiometric amounts of substrate (1 mol) and oxidant (4 mol) were mixed at 40 °C, and maintained under nitrogen for 24 h. The reaction mixture was neutralized with NaHCO_3 , extracted with CH_2Cl_2 , washed with water, dried over anhydrous MgSO_4 , and concentrated. TLC analysis of the residue showed two spots. Separation was carried out on a silica gel column using varying proportions (100 : 0 to 70 : 30, v/v) of hexane and chloroform for elution. The product obtained with the lesser proportions of chloroform was tested for the aldehyde by TLC. One spot was obtained when the chromatogram was sprayed with 2,4-DNP. An aliquot (5 ml) was pipetted into 50 ml of 2N HCl saturated at 0 °C with 2,4-DNP. The aldehyde was converted to 2,4-dinitrophenylhydrazone, which was filtered, washed, dried and weighed. The yields were calculated from the amounts of 2,4-dinitrophenylhydrazone formed (80–85% yields for the three isomers), and the melting points determined after recrystallization from ether (para = 254 °C; meta = 244 °C; ortho = 249 °C). The presence of the aldehyde was confirmed by isolating the aldehyde using the standard method /10/. IR analysis gave a sharp

Table 1
Rate data for oxidation of methoxytoluenes

[Substrate] ($10^2 \times \text{M}$)	[$\text{K}_3\text{Fe}(\text{CN})_6$] ($10^3 \times \text{M}$)	[HClO_4] (M)	$10^5 \times k_{\text{obs}} (\text{s}^{-1})$		
			Para	Meta	Ortho
2.5	1.0	0.5	9.1	6.8	5.3
5.0	1.0	0.5	18.0	13.3	10.4
10.0	1.0	0.5	36.5	27.1	21.0
5.0	2.5	0.5	18.3	13.7	10.5
5.0	5.0	0.5	18.4	13.4	10.2
5.0	1.0	0.25	9.0	6.6	5.2
5.0	1.0	1.0	36.3	26.7	21.0

HOAc = 80% (v/v); Temp. = 40.0 ± 0.1 °C; all values of rate constants were the average of two or more experiments, with agreement being ± 1.5% or better

band at 1700 cm^{-1} , characteristic of C=O stretching for an aldehyde group attached to an aryl ring. Two weak bands at 2850 cm^{-1} and 2750 cm^{-1} indicated C-H stretching. The second product was a polymeric material, and was not characterized.

RESULTS AND DISCUSSION

Kinetic results

The rate of the reaction was dependent on the first powers of the concentrations of substrate, oxidant and acid (Table 1). The reactions were studied over the temperature range 35° – 50°C , and activation parameters were evaluated (Table 2).

Table 2
Activation parameters for methoxytoluenes

Parameter	Para	Meta	Ortho
$E(\text{kJ mol}^{-1})$	47.8 ± 0.8	61.4 ± 1.1	71.0 ± 1.3
$A(\text{s}^{-1})$	1.3×10^4	2.3×10^6	7.5×10^7
$\Delta H^{\ddagger}(\text{kJ mol}^{-1})$	45.3 ± 0.6	58.7 ± 1.0	68.3 ± 1.2
$\Delta S^{\ddagger}(\text{JK}^{-1}\text{ mol}^{-1})$	-19.0 ± 1.0	-14.0 ± 1.0	-12.0 ± 1.0

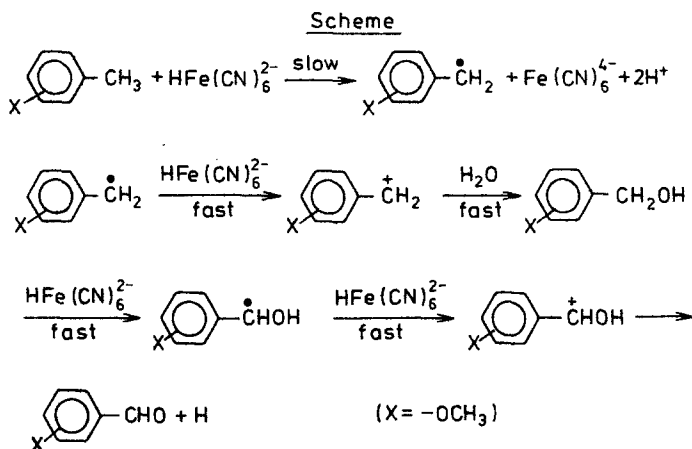
Using the σ^+ values (para = -0.78 , meta = $+0.05$), and the σ_0 value for ortho isomers /11/, the Hammett plot gave a ρ^+ value of -0.50 (correlation coefficient = 0.99). This showed that the rate determining step involved the abstraction of a hydrogen atom giving a benzylic radical intermediate. Reactions having ρ values of -0.50 have been reported to proceed via radical intermediates.

A kinetic isotope effect, $k_H/k_D = 6.0$, was observed, supporting the assumption of a cleavage of the C-H bond to give a radical intermediate. In the oxidation of some organic substrates, similar k_H/k_D values had indicated cleavage of the C-H bond giving a radical /13–16/. The ESR spectrum of this radical exhibits 15 lines; such spectra were analyzed earlier /17/.

Fe(III) is an effective oxidizer of radical species /18/, and could combine with the radical to yield the carbocation (R^+) and Fe(II). This carbocation would be formed presumably in a rapid step, and no evidence could be obtained for its formation. It could be envisaged that the radical undergoes rapid conversion to the product. No intermediate product(s) could be isolated from the reaction mixture. Efforts to isolate the intermediate, methoxybenzyl alcohols, were not

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successful. Independent kinetic experiments yielded values of rate constants at 40 °C as follows: $10^2 \times k_{\text{obs}}$, (s^{-1}) = 5.5 (para), 4.0 (meta), 3.1 (ortho) at [substrate] = 0.1 M, $[\text{K}_3\text{Fe}(\text{CN})_6] = 0.001$ M (cf. rate data in Table 1), establishing that methoxybenzyl alcohols, when formed as intermediates in the oxidation of methoxytoluenes by acidic $\text{K}_3\text{Fe}(\text{CN})_6$, would be rapidly oxidized to the product. The reaction sequence is shown in the Scheme.



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