Radiation-Induced Homolytic Aromatic Substitution. V. Effect of Metal Ions on the Hydroxylation of Toluene

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Publication costs assisted by the Puerto Rico Nuclear Center

The radiation-induced hydroxylation of toluene was investigated in presence of $K_2Cr_2O_7$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, $Fe(ClO_4)_3$, $Fe(NH_4)(SO_4)_2$, $CuSO_4$, $Cu(ClO_4)_2$, and $Cu(OCOCH_3)_2$. With $K_2Cr_2O_7$, $K_3Fe(CN)_6$, and the Cu^{2+} salts high conversions of the OH radicals to cresols were obtained. In all these cases the isomer distribution obtained at the highest concentration investigated (5 × 10⁻² M) was the same (49–52% ortho, 22–24% meta, and 26–28% para). With the exception of $K_3Fe(CN)_6$ the percentage of G(m-cresol) increased with increasing concentration of metal salt. The pH had a marked effect on the formation of cresols due to the competing acid-catalyzed elimination of water from the initially formed hydroxymethylcy-clohexadienyl radicals to give benzyl radicals. No reduction of the hydroxymethylcyclohexadienyl radicals the following sequence was established: $Fe(CN)_6^{3-} > Cu^{2+} > Fe^{3+}$.

Introduction

In the radiation-induced hydroxylation of aromatic compounds usually only a small fraction of the .OH radicals are converted to phenols.^{2,3} The radiation-induced hydroxylation of toluene has been studied previously by Christensen and Gustafsson,⁴ and by Eberhardt and Yoshida.³ Low vields of cresols were observed by both groups. Christensen and Gustafsson studied the effect of $Fe(ClO_4)_3$. They found no increase in G(cresols), but rather a decrease, however, they observed a large amount of dibenzyl which they showed to arise via an acid-catalyzed water elimination from the initially formed hydroxymethylcyclohexadienyl radicals. In a recent publication⁵ we have reported on the hydroxylation of nitrobenzene in presence of a variety of metal salts and we observed a quantitative conversion of •OH radicals to nitrophenols. In the present paper we wish to report on the effect of metal salts on the hydroxylation of toluene.

Experimental Section

Materials. All solutions were prepared using water which was doubly distilled from an all glass still. Then it was further distilled over alkaline permanganate, acidic dichromate, and one final distillation. Toluene was reagent grade and was redistilled. All metal salts were of reagent grade quality. The aqueous solutions were deoxygenated by bubbling argon through 1 l. of the solution for 1 hr. The saturation was enhanced by frequent shaking.

Irradiations. Irradiations were carried out with a 60 Co source at a dose rate of 2.44 $\times 10^{16}$ eV/g min and a total dose of 1.46 $\times 10^{18}$ eV/g (determined by Fricke dosimetry with $G(\text{Fe}^{3+}) = 15.5$). The dosimetry was carried out by using the same bottles and volume as the irradiated solutions.

Analytical Procedure. Immediately after the irradiation the pH of the solution (1 l.) was adjusted to about 4-4.5 and then extracted once with 200 ml of ether and four times with 100 ml of ether. The ether extract was dried over 80 g of Na₂SO₄ for about 24 hr, and was then concentrated to 10 ml and analyzed by vapor phase chromatography using a hydrogen flame detector. The column was a 6-ft DEGS (diethyleneglycol succinate 5% liquid phase on Chromosorb W-AW-DMCS (100-120 mesh)) column at 170° and a flow of about 25 ml of He/min. The products appeared in the following sequence: benzyl alcohol (2.15 min), o-cresol (2.60 min), m- and p-cresol (3.35 min), dibenzyl (3.80 min). Dimethyldiphenyls had somewhat longer retention times than dibenzyl. The m- and p-cresol were separated on a 12-ft column (xylenylphosphate 5% liquid phase on Chromosorb W-AW-DMCS (100-120 mesh)) at 150° and a flow of about 25 ml of He/min. The following retention times were observed: benzyl alcohol (13.6 min), ocresol (27.2 min), p-cresol (34.0 min), m-cresol (36.5 min). Standard aqueous cresol and benzyl alcohol solutions were prepared containing amounts of cresol and benzyl alcohol which were very close to the amounts present in the irradiated solutions and worked up in the same way. The G(dibenzyl) was determined from standard ether solutions of dibenzyl. All experiments were carried out in duplicate and triplicate and were found to be reproducible within the limits of the analytical technique $(\pm 5\%)$. The smaller G values for benzyl alcohol (<0.5) are somewhat less accurate (±10%).

In presence of $K_3Fe(CN)_6$ at low pH (see experiments 23-26) much smaller G values were observed than in neutral solutions. In order to show that this effect is partly due to secondary oxidations of the cresols we proceeded as follows: 1 l. solutions of 2.7 mg of o-cresol, 1.35 mg of m-cresol, and 1.35 mg of p-cresol and $5 \times 10^{-4} M K_3Fe(CN)_6$ at pH 1.6 in one experiment and $5 \times 10^{-2} M K_3Fe(CN)_6$ in a second experiment were left standing at room temperature for 1 hr (same time as the irradiation time) and then worked up in the usual manner. The results show that there is a slight preference for ortho-para oxidation.

Results and Discussion

The results in Table I show that at the higher metal salt concentration $(5 \times 10^{-2} M)$ we observe a high conversion of •OH radicals $(G(\cdot OH) = 2.74)^6$ to cresols. We, therefore, feel confident that the dose was low enough to render sec-

Ernt		(D b		G(cresols)				~~~	~	~~~
no.	Conditions	G(Ph- CH ₂ OH)	$G(Ph-CH_2)_2$	Ortho	Meta	Para	G(total cresols)	% ortho	% meta	% para
1	$Cu(OCOCH_3)_2 5 \times 10^{-4}M$	0.1		1.05	0.18	0.56	1.79	58.7	10.1	31.3
2	$Cu(OCOCH_3)_2$ 10 ⁻³ M	Trace		1.22	0.43	0.67	2.32	52.6	18.5	28.9
3	$Cu(OCOCH_3)_2 5 \times 10^{-3} M$	Trace		1.20	0.58	0.67	2.45	49.0	23.7	27.3
4	$CuSO_4$ 5 $ imes$ 10 ⁻⁴ M	0.21		0.86	0.14	0.42	1.42	60.6	9.9	29.6
5	$CuSO_4 \ 10^{-3} \ M$	0.18		1.12	0.22	0.53	1.87	59.9	11.8	28.3
6	$CuSO_4$ 5 \times 10 ⁻³ M	0.15		1.37	0.43	0.69	2.49	55.0	17.3	27.7
7	$CuSO_4 5 \times 10^{-2} M$	Trace		1.28	0.55	0.72	2.55	50.2	21.6	28.2
8	$Cu(ClO_4)_2$ 5 × 10 ⁻⁴ M	0.2		0.83	0.14	0.40	1.37	60.6	10.2	29.2
9	$Cu(ClO_4)_2 \ 10^{-3} M$	0.2		1.08	0.23	0.53	1.84	58.7	12.5	28.8
10	Cu(ClO ₄) ₂ $5 \times 10^{-3} M$ nat. pH 5.0	0.12		1.20	0.36	0.58	2.14	56.1	16.8	27.1
11	Cu(ClO ₄) ₂ $5 \times 10^{-2} M$ nat. pH 4.4	Trace		1.14	0.49	0.61	2.24	50.9	21.9	27.2
12	$Cu(ClO_4)_2 5 \times 10^{-3} M$ + HClO ₄ ~ 10 ⁻³ M nH 2.6	0.52		0.78	0.14	0.32	1.24	63.0	11.2	25.8
13	$Cu(ClO_4)_2 5 \times 10^{-3} M$ + HClO ₂ ~ 5 × 10 ⁻² M pH 2.0	1.65		Trace	Trace	Trace				
14	$K_{\rm Cr.O.} 5 \times 10^{-4} M$	0.34		1 42	0.41	0 49	9 39	61.0	177	21 1
15	$K_2 Cr_2 O_7 = 0 \land 10 $ M	0.01		1 44	0.49	0.40	2.02	58.5	19.5	22.1
16	$K_2 C r_2 O_7 T C = M^2$ K ₂ C $r_2 O_7 T C = M^2$	0.00		1 44	0.55	0.67	2,40	54 1	20.7	25.2
17	$K_2 C r_2 O_7 = 5 \times 10^{-2} M$	0.1		1 54	0.64	0.01	2.98	51 7	21.5	26.8
18	$K_{2}EP(CN)_{2} = 5 \times 10^{-4} M$	0.1		1.08	0.51	0.57	2.00	50.0	23.6	26.4
19	$K_{3}Fe(CN)_{a} = 10^{-3} M$			1.15	0.55	0.60	2.30	50.0	23.9	26.1
20	$K_{s}Fe(CN)_{c} = 5 \times 10^{-3} M$			1.12	0.54	0.60	2.26	49.6	23.9	26.5
21	$K_{3}Fe(CN)_{6} = 5 \times 10^{-2} M$			1.15	0.56	0.61	2.32	49.6	24.1	26.3
22	$K_{0}Fe(CN)_{0} 5 \times 10^{-4} M$			0.94	0.46	0.49	1.89	49.8	24.3	25.9
	$+ K_{4} Fe(CN)_{a} 5 \times 10^{-4} M$			0.01	0.10	0110	1.00			
23	$K_{a}Fe(CN)_{c} 5 \times 10^{-4} M \text{ pH } 1.6^{b}$	Trace		0.96	0.12	0.53	1.61	59.6	7.5	32.9
24	$K_{0}Fe(CN)_{c} 10^{-3} M pH 1.6^{b}$	Trace		1.14	0.17	0.63	1.94	58.8	8.8	32.4
25	$K_{0}Fe(CN)_{c} 5 \times 10^{-3} M \text{ pH } 1.6^{b}$			0.88	0.39	0.45	1.72	51.2	22.7	26.2
26	$K_{0}Fe(CN)_{c} 5 \times 10^{-2} M \text{ pH } 1.6^{b}$			0.36	0.30	0.21	0.87	41.4	34.5	24.1
27	$K_3 Fe(CN)_6 10^{-3} M + K_4 Fe(CN)_6$ 5 × 10 ⁻⁴ M pH 1 6 ^b			1.06	0.16	0.60	1.82	58.2	8.8	33.0
28	$Fe(ClO_4)_3 5 \times 10^{-4} M$	0.14	1.07	Trace	Trace	Trace	Trace			
29	Fe(ClO ₄) ₃ 5 × 10 ⁻³ M	2.0	0.1	0.26		0.20	0.46	56.5	0	43.5
30	Fe(ClO ₄) ₃ 5 × 10 ⁻² M	1.60		0.74		0.60	1.34	55.3	0	44.7
31	nat. pH 2.0 Fe(NH ₄)(SO ₄) ₂ 5 × 10 ⁻⁴ M		1.08	Trace						
32	nat. pH 3.0 No additives°	0.02	0.02	0.22	0.09	0.14	0.45	48.9	20.0	31.1

TABLE I: Yields of Cresols, Benzyl Alcohol, and Dibenzyl in the Radiolysis of Aqueous Toluene Solutions^a

^a All solutions were deoxygenated solutions (5 × 10⁻³ M toluene) irradiated at a dose rate of 2.44 × 10¹⁶ eV/g min, and a total dose of 1.46 × 10¹⁸ eV/g. ^b The pH was adjusted with H₂SO₄. ^c Results taken from ref 4.

TABLE II: Dose Dependence of $G(Cresols)$ at Low Cu ²⁺	Salt Concentration (5×10^{-4}	$M)^a$
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Conditions	Total dose, eV/l.	G(ortho $)$	G(meta)	G(para)	Total G(cresols)	% ortho	% meta	% para	
Cu(OCOCH ₃) ₂	4.9×10^{20}	1.28	0.22	0.68	2.18	58.6	10.2	31.2	
Cu(OCOCH ₃),	$1.46 imes 10^{21}$	1.05	0.18	0.56	1.79	58.6	10.1	31.3	
CuSO	$4.9 imes 10^{20}$	1.24	0.19	0.58	2.01	61.8	9.3	28.9	
CuSO	$1.46 imes 10^{21}$	0.86	0.14	0.42	1.42	60.5	9.9	29.6	
$Cu(ClO_1)$	$4.9 imes10^{20}$	1.08	0.17	0.49	1.74	62.0	9.8	28.2	
$Cu(ClO_1)_2$	$1.46 imes 10^{21}$	0.83	0.14	0.40	1.37	60.7	10.1	29.2	

^a All solutions were deoxygenated solutions (5 \times 10⁻³ M toluene) irradiated at a dose rate of 2.44 \times 10¹⁶ eV/g min.

The Journal of Physical Chemistry, Vol. 79, No. 18, 1975

Scheme I



ondary reactions insignificant. At the lowest Cu²⁺ concentration $(5 \times 10^{-4} M)$ we have investigated a lower dose $(4.98 \times 10^{17} \text{ eV/g})$ and we found an increase in G(total cresols) but the percentage composition of the cresols did not change (see Table II). The high G(cresols) at the higher metal salt concentrations confirms previous conclusions⁷ that the initial step in the reaction of •OH radicals with toluene is addition at the ring positions rather than abstraction from the methyl group (Scheme I). The fate of the metal ions was not investigated quantitatively, but in the case of Cu^{2+} salts the formation of metallic copper was observed. The oxidation of the hydroxymethylcyclohexadienyl radicals I-III competes with the acid-catalyzed dehydration and the radical shifts (II \rightarrow I and II \rightarrow III). The acid-catalyzed formation of benzyl radicals from hydroxymethylcyclohexadienyl radicals was first reported by Norman and coworkers⁸ in the hydroxylation of toluene by Fenton's reagent. Subsequently, the kinetics of this reaction was studied by pulse radiolysis⁷ and it was shown that the rate of benzyl radical formation is proportional to the proton concentration, and the pseudo-first-order rate constant was found to be $1.1 \pm 0.04 \times 10^6 M^{-1} \text{ sec}^{-1}$. One may speculate that the mechanism of this water elimination proceeds via protonation of the hydroxyl and formation of a radical cation, followed by a rapid deprotonation from the methyl group:



The elimination of water and the deprotonation may proceed synchronously as was suggested by Norman and co-

workers.⁸ Recently Walling and Johnson⁹ have postulated the radical cation as a distinct intermediate. The above shown water elimination is particularly favorable from the meta hydroxyl radical adduct since the developing positive charge is stabilized by the hyperconjugating methyl group. The competition between oxidation and dehydration can be seen from the result with $Fe(ClO_4)_3$. With increasing $Fe(ClO_4)_3$ concentration the ratio Fe^{3+}/H^+ is increasing and so is the yield of cresols while the yields of benzyl radical derived products is decreasing. The same effect was observed with $Cu(ClO_4)_2$ (experiments 10, 12, 13). The cresol isomer distributions in our experiments with $Fe(ClO_4)_3$ are in excellent agreement with the isomer distribution obtained recently by Walling and Johnson⁹ in the hydroxylyation with Fenton's reagent. However we observe a quantitative conversion of OH radicals to products.

While the pH has a marked effect on the product distribution if $Fe(ClO_4)_3$, $Fe(NH_4)(SO_4)_2$, or $Cu(ClO_4)_2$ are used as oxidizing agents, the pH effect is rather small at the lower concentrations of $K_3Fe(CN)_6$. The G(o-cresol) and G(p-cresol) does not change much, whereas the G(m-cresol) is decreasing substantially. (Compare experiments 18 and 19 with 23 and 24.) This decrease in G(meta) at low pH can be due to several factors: (1) a selective oxidation of m-cresol; (2) a selective reduction of the meta adduct (II) by $Fe(CN)_6^{4-}$; (3) a slower rate of oxidation of the meta adduct (II); (4) a faster rate of dehydration of the meta adduct (II). We studied the reaction of $K_3 Fe(CN)_6$ (5 × 10⁻⁴ M) in acidic solutions (pH 1.6) with cresols $(5 \times 10^{-4} M)$ and we find no selective oxidation of m-cresol, but rather a slight preference for ortho-para oxidation. (See Experimental Section.) The experiments in presence of $K_4Fe(CN)_6$ at pH 1.6 and neutral solutions (experiments 27 and 22) show that there is no reduction of any of the isomeric hydroxymethylcyclohexadienyl radicals. A slower rate of oxidation of the *m*-hydroxymethylcyclohexadienyl radical at low pH compared to neutral solution appears unlikely in view of previous results⁵ on the hydroxylation of nitrobenzene with $K_3Fe(CN)_6$ at low pH. A faster rate of acid-catalyzed dehydration from the meta adduct (II) compared to the ortho and para adducts (I and III) appears a reasonable assumption considering the arguments concerning the mechanism presented above.

The considerable difference in isomer distribution between the Cu^{2+} and Fe^{3+} experiments was explained by Walling and Johnson⁹ on the basis of the different oxidation mechanisms by these two metal ions. The oxidation with Fe³⁺ involves the formation of a carbonium ion intermediate which can undergo 1,2 hydroxyl anion shifts to produce mainly o- and p-cresol. Norman and coworkers⁸ on the other hand have concluded that the electron transfer and the deprotonation proceed synchronously. The percentage of *m*-cresol increases with increasing metal ion concentration with the exception of $K_3Fe(CN)_6$. This increase in G(meta) with increasing metal salt concentration was observed previously in the hydroxylation of nitrobenzene⁵ and benzoic acid.¹⁰ Radical rearrangements have been suggested as explanation for this observation. In the case of hydroxymethylcyclohexadienyl radicals analogous rearrangements may take place to give the more stable ortho and para hydroxyl radical adducts³ (II \rightarrow I, and II \rightarrow III). In the case of the hydroxymethylcyclohexadienyl radicals the rearrangement may proceed via a reversible water elimination. Strong evidence for this reaction was presented by Walling and Camaioni¹¹ in the hydroxylation of benzene and toluene by SO_4 . This reversible water elimination however was not observed in the hydroxylation of phenol, chlorobenzene, and nitrobenzene.12 The increase in G(meta) with increasing metal salt concentration, may, however be solely due to a competition between oxidation and dehydration, assuming a greater rate constant for dehydration of the meta radical (II) than of the ortho and para isomer (I and III).

Contrary to the hydroxynitrocyclohexadienyl radicals where the ortho and para isomers are selectively reduced by Fe(CN)₆⁴⁻ no reduction of the three isomeric hydroxymethylcyclohexadienyl radicals by Fe(CN)₆⁴⁻ was observed (experiments 21 and 27). Only those radicals which have an electron-withdrawing substituent α to the radical site undergo reduction. This observation is in agreement with results of Walling and coworkers¹³ on the redox reactions of α -hydroxyalkyl radicals with Fe³⁺-Fe²⁺.

With $K_3Fe(CN)_6$ in neutral solutions we do not find any change in G(cresols) nor in the isomer distribution with increasing concentration (experiments 18-21). This observation together with the minor change at low pH indicates that the oxidation by $K_3Fe(CN)_6$ must be a fast process. This fast oxidation by $K_3Fe(CN)_6$ was also observed in the hydroxylation of nitrobenzene at low pH. We, therefore, suggest that the cresol isomer distribution obtained with $K_3Fe(CN)_6$ represents the relative reactivity of $\cdot OH$ radicals toward the different positions in the toluene molecule. At the higher metal ion concentration $(5 \times 10^{-2} M)$ of the Cu^{2+} salts and $K_2Cr_2O_7$ we observed almost the same isomer distribution as with $K_3Fe(CN)_6$. From these results the

relative reactivity appears to be approximately 2:1:1. This preference for ortho-para substitution is to be expected on the basis of the well-known electrophilic character of the •OH radical.^{3,14} From the results in Table I we can see that $Cu(ClO_4)_2$ at a concentration of $5 \times 10^{-3} M$ and a pH of 2.6 gives more G(cresols) and less G(benzyl alcohol) than $Fe(ClO_4)_3$ at the same concentration and pH. From this we conclude that Cu²⁺ oxidizes the hydroxymethylcyclohexadienyl radicals faster than does Fe³⁺. We have, therefore, the following reactivity sequence for oxidation: $Fe(CN)_6^{3}$ $> Cu^{2+} > Fe^{3+}$.

References and Notes

- (1) This paper was prepared in connection with work under Contract No. AT(40-1)-1833 with The U.S. Atomic Energy Commission.
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Kinetics and Mechanism of the Osmium Tetroxide Catalyzed Oxidation of 2-Propanol and 1-Propanol by the Hexacyanoferrate(III) Ion in Aqueous Alkaline Medium

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A study is reported of the hexacyanoferrate(III) oxidations of 2-propanol and 1-propanol in the presence of osmium tetroxide as catalyst. The kinetic data suggest that the oxidation of these alcohols proceeds via the formation of an activated complex between the alcohol molecule and osmium tetroxide which rapidly decomposes to an intermediate product and osmium(VI) species. The osmium(VI) thus produced is rapidly oxidized to osmium(VIII) with hexacyanoferrate(III) ion. The oxidation products are determined and a possible set of reactions for their formation is presented.

Introduction

Sussela¹ and Solymosi² have studied, from an analytical point of view, the oxidation of a number of organic compounds with hexacyanoferrate(III) in aqueous alkaline medium using osmium tetroxide as a homogeneous catalyst. We were the first to examine the kinetic features of the osmium tetroxide catalyzed oxidation of methanol and ethanol³ by hexacyanoferrate(III) ion in aqueous alkaline medium. Recently, we have also studied the kinetic features of osmium tetroxide catalyzed oxidation of ketones,⁴ aldehydes,⁵ α -hydroxy acids,⁶ and diols⁷ with hexacyanoferrate(III) in aqueous alkaline medium. However, the mechanism of oxidation of monohydric alcohols has yet not been studied and in the present study we have carried out the oxidation of 2-propanol and 1-propanol by aqueous alkaline hexacyanoferrate(III) ion using osmium tetroxide as a