Oxidation of Substituted Toluenes by Manganese(III) Acetate

By J. R. GILMORE and J. M. MELLOR*

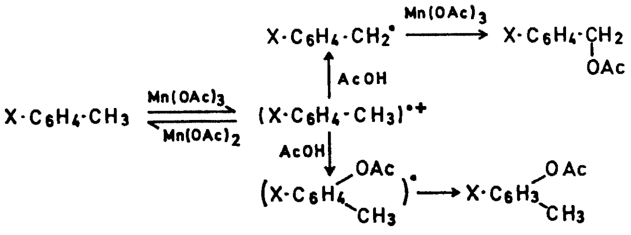
(*Chemistry Department, Southampton University, Southampton* SO9 5NH)

Summary Toluenes give benzyl acetates with manganese(III) acetate by a radical process involving potassium bromide as catalyst, but without catalyst oxidation is by one-electron transfer.

LITTLE is known concerning the formation and subsequent decomposition of cation radicals derived from simple aromatic compounds. To examine the role of cation radicals as intermediates in these oxidations—a problem of increased interest in view of the suggestion that the formation of cation radicals may be the initial step in chemical carcinogenesis by polycyclic aromatic hydrocarbons[1]—we have studied the reaction of a series of substituted toluenes with $Mn(OAc)_3$.

Kinetic evidence suggested that oxidation of *p*-methoxytoluene to the acetate of *p*-methoxybenzyl alcohol by

$Mn(OAc)_3$ in acetic acid at 70° proceeds by an initial one-electron transfer to the intermediate cation radical[2] (Scheme 1). At higher temperatures, the one-electron transfer oxidation is less important and oxidation proceeds by homolytic decomposition of $Mn(OAc)_3$. Catalysis by potassium bromide has been observed.[4] With the more powerful $Co(OAc)_3$ substituted toluenes are oxidized by one-electron transfer and the intermediate cation radicals have been detected spectroscopically; and the catalysis of the reaction by lithium chloride has been attributed to the formation of a cobalt(III) complex of higher oxidation potential.[5] No Hammett σ–ρ correlation has been examined for one-electron transfer oxidations of $Mn(OAc)_3$ but with $Co(OAc)_3$ a correlation with σ^+ yielded a ρ value of $-2{\cdot}4$ for the non-catalysed reaction and a ρ value of $-1{\cdot}35$ for the lithium chloride catalysed oxidation.[5]



SCHEME 1

We have examined the reactivities of 18 substituted toluenes with $Mn(OAc)_3$ at 70° in acetic acid and compared the reactivities with the corresponding halfwave oxidation potentials ($E_{\frac{1}{2}}$) measured in acetonitrile at a platinum electrode. Initial rates were measured spectroscopically at 510 nm after mixing carefully deoxygenated solutions of the substituted toluene (8×10^{-2}M) and $Mn(OAc)_3$ (5×10^{-3}M) in acetic acid. The relative reactivities of 6 substituted toluenes in the potassium bromide catalysed oxidation with $Mn(OAc)_3$ were measured by competitive experiments in which the products at low percentage conversion were analysed by g.l.c. Relative reactivities were also determined for the competitive photochemical bromination of the same 6 toluenes in acetic acid using molecular bromine.

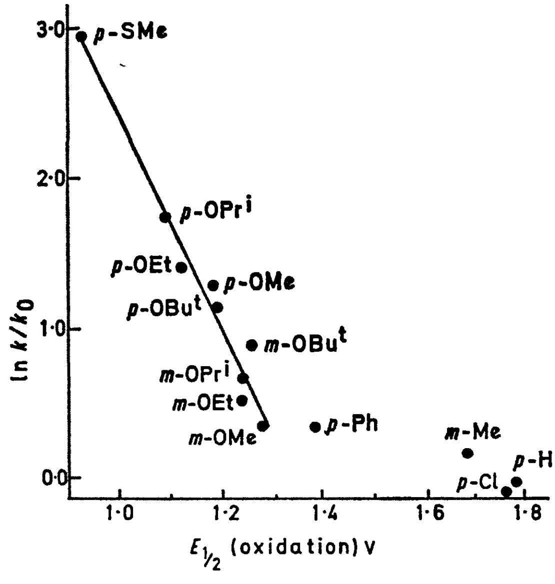
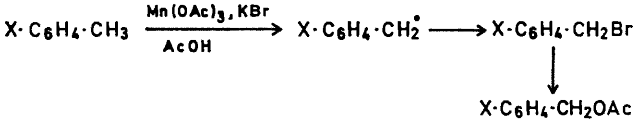


FIGURE. *Reactivity of substituted toluenes with* $Mn(OAc)_3$ *at* 70° *in acetic acid plotted against* $E_{\frac{1}{2}}$ *determined in acetonitrile at a platinum electrode against* $Ag^+/0{\cdot}01N\text{-}Ag^+$.

We observe a non-linear Hammett correlation for the non-catalysed reaction, but find a good linear correlation of ln k/k_0 with $E_{\frac{1}{2}}$ for the more reactive toluenes and conclude that reaction is by an initial one-electron transfer (Scheme 1). In such an oxidation the ionisation potential or $E_{\frac{1}{2}}$ value is a much better criterion of reactivity than σ^- (see Figure). The relative rates of *p*-methylthioanisole ($\sigma_{p\text{-SMe}}$ $-0{\cdot}60$) and *p*-methoxytoluene ($\sigma^+_{p\text{-OMe}}$ $-0{\cdot}78$) and of *m*-methoxytoluene ($\sigma^+_{m\text{-OMe}}$ $+0{\cdot}05$) and *p*-methoxytoluene illustrate this point. The toluenes of low reactivity are probably oxidized by a different mechanism.

We conclude that in contrast to the oxidation of toluenes by $Co(OAc)_3$ which is catalysed by lithium chloride,[5] and is interpreted as an electron transfer process, the potassium bromide catalysed oxidation using $Mn(OAc)_3$ proceeds *via* radical intermediates (see Scheme 2). This is shown by the following observations:



SCHEME 2.

(i) correlation of σ^+ yields a ρ value of $-1{\cdot}81$ for the catalysed oxidation and a value of $-1{\cdot}82$ for the photochemical bromination; (ii) isopropylbenzene reacts much faster than toluene in the catalysed oxidation, with a rate difference similar to that found in the photochemical bromination; and (iii) intermediate bromides are initially formed, which subsequently acetolyse under the reaction conditions. Potassium chloride is a poor catalyst.

In the catalysed reaction high yields (>90%) of benzyl acetates may be obtained with the more reactive toluenes. In the non-catalysed reaction *p*-substituted toluenes give mainly substituted benzyl acetates (>90%) but *m*-substituted toluenes give nuclear acetates in addition to benzyl acetates thus indicating nucleophilic substitution of the cation radical in addition to elimination (see Scheme 1).

We thank the British Empire Cancer Campaign for support and the S.R.C. for a maintenance grant (to J.R.G.)

(*Received, February* 17*th*, 1970; *Com.* 231.)

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