Acid-catalysed Electron-transfer Reactions of Lead Tetra-acetate: Stable Cation-radicals from Carbazole Derivatives

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LEAD tetra-acetate is a versatile oxidising agent for organic molecules: several different reaction mechanisms are possible depending on the oxidisable substrate.[1] Recently Allara, Gilbert, and Norman[2] showed that boron trifluoride etherate acts as a catalyst for one-electron transfer reactions involving lead tetra-acetate. Aylward[3] has extended the original observations[2] and has discussed the mechanism of oxidative coupling of aromatic molecules induced by BF_3–Pb^{IV} systems.

We have carried out a detailed investigation of the oxidation of carbazole derivatives using many oxidising systems, including BF_3–Pb^{IV}, and now report that electron-transfer reactions involving $Pb(OAc)_4$ in glacial acetic acid are strongly catalysed by the addition of perchloric (70% w/w aqueous solution) or fluoroboric (42% w/w aqueous solution) acids. Toluene-*p*-sulphonic and trichloracetic acids have a much weaker catalytic effect.

The one-electron nature of these oxidations is apparent from the instantaneous and quantitative reactions involving ferrocene and tri-*p*-tolylamine, at room temperature:

$$(C_5H_5)_2Fe + \tfrac{1}{2}Pb(OAc)_4 \xrightarrow{HClO_4,\ HOAc} \underset{(\lambda_{max}620\ m\mu)}{(C_5H_5)_2Fe^+} + \tfrac{1}{2}Pb(OAc)_2 + OAc^-$$

$$(p\text{-tolyl})_3N + \tfrac{1}{2}Pb(OAc)_4 \xrightarrow{HClO_4,\ HOAc} \underset{(\lambda_{max}\ 660m\mu)}{(p\text{-tolyl})_3N^{\cdot+}} + \tfrac{1}{2}Pb(OAc)_2 + OAc^-$$

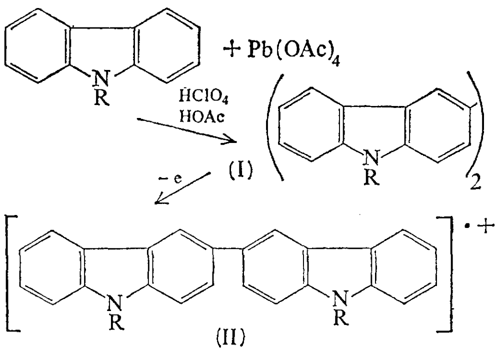
In both cases the one-electron deficient products, ferricinium ion[4] and tri-*p*-tolylammonio cation-radical[5] can be recognised by their characteristic visible absorption spectra.

A very efficient oxidative coupling was observed when either $HClO_4$–Pb^{IV} or BF_3–Pb^{IV} oxidants were treated with carbazole derivatives. In these cases the yields of coupled product are essentially quantitative (at room temperature) and the oxidation does not stop at the neutral 3,3′-dicarbazolyl derivative (I) but proceeds further to give extremely stable cation-radicals (II).

From *N*-ethylcarbazole the deep green cation-radical (IIa; R = Et) was readily prepared as the BF_4^- or ClO_4^- salt (λ_{max} = 390, 800 mμ). E.s.r. spectroscopy of dilute solutions in HOAc or CH_2Cl_2 showed a strong signal with a *g* value of 2·0048 which has not yet been resolved into its fine structure. The cation radical (IIa) was unaffected by air or water, but was readily reduced by $Fe(CN)_6{}^{4-}$ or dithionite ion to the neutral 3,3′-dicarbazolyl (Ia; R = Et), identical with a sample prepared independently.[6] Similar derivatives were prepared from *N*-methyl-, *N*-isopropyl-, and *N*-phenyl-carbazoles. The formation of blue-green products is a very common reaction of carbazole derivatives, especially under acidic conditions[7] but the cation radicals (II) have not previously been characterised.

Strong protonic acids such as perchloric and fluoroboric acids are known to promote the one-electron oxidising power of organomercuric acetates,[8] *via* formation of organomercuric cations:

$$\begin{tikzcd} PhHgOAc \arrow[r, "HClO_4", "HOAc"'] & PhHg^+ \arrow[d, "-e"] & \\ & (PhHg) \arrow[r] & Ph\cdot + Hg^0 \end{tikzcd}$$



By analogy, acid-catalysed oxidations with lead tetra-acetate may involve catalysed formation of the triacetoxyplumbic cation originally proposed by Criegee[9] as the active species in reaction of $Pb(OAc)_4$, *i.e.*

$$Pb(OAc)_4 + HClO_4 \rightleftharpoons (AcO)_3Pb^+ClO_4^- + HOAc$$

Catalysis by BF_3 would then be expected to involve similar intermediates such as $(AcO)_3Pb^+$-$[BF_3OAc]^-$.

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