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Oxidation of Alkyl Derivatives of Aromatic Hydrocarbons by Transition Metal Salts

I.P.Beletskaya and D.I.Makhon'kov

The oxidation reactions of aromatic compounds and their alkyl derivatives under the influence of salts of variable-valence transition metals are examined.
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I. INTRODUCTION

Reactions involving the oxidation of aromatic compounds by transition metal salts have attracted much attention in recent years. These reactions, which have come to be called "stoichiometric oxidation", make it possible to obtain in many instances mainly one of the oxidation products, i.e. to "functionalise" aromatic compounds selectively[1].

Substituted benzenes and condensed aromatic systems without substituents capable of being oxidised have always given rise to products with functional groups, which are linked directly to the aromatic nucleus. Another important class of substrates are alkyl derivatives of aromatic compounds, which yield, on oxidation, the products of monosubstitution in the α-position of the side chain as well as the corresponding oxo- and carboxy- derivatives, apart from the compounds of the type mentioned above.

There is an extensive literature on problems of liquid-phase and stoichiometric oxidation and the number of original publications in this field continues to increase rapidly. This review summarises data on the oxidation of aromatic compounds and their alkyl derivatives by variable valence metal ions (the literature up to the middle of 1979 is included). We shall not consider oxygen-containing metal compounds in the highest oxidation states (such as the salts of chromic and manganic acids), which have been used for a long time and which have been fairly thoroughly investigated, as well as substrates which exhibit specific features in oxidation processes (phenols, aromatic alcohols, amines, etc.), with the exception of those cases where the oxidation involves only the aromatic system and (or) alkyl substituents in these compounds.

II. GENERAL MECHANISMS OF OXIDATION BY METAL SALTS

Silver(II), copper(II), palladium(II), cobalt(III), manganese(II), iron(III), thallium(III), lead(IV), and cerium(IV) compounds used as oxidants can be divided into two groups: one-electron and two-electron oxidants; their standard electrode potentials vary within wide limits [the values of E^0 (V) are listed below]:

Ag^{2+}/Ag^{+} 1.91	$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ 0.36
Co^{3+}/Co^{2+} 1.808	Cu^{2+}/Cu^{+} 0.167
Ce^{4+}/Ce^{3+} 1.61	Pb^{4+}/Pb^{2+} 1.694
Mn^{3+}/Mn^{2+} 1.509	Tl^{3+}/Tl^{+} 1.252
Fe^{3+}/Fe^{2+} 0.771	Pd^{2+}/Pd^{0} 0.987

One should note that a characteristic feature of variable-valence metal compounds is the occurrence in solutions of complex equilibria involving hydrolytic and complex formation reactions and the formation of dimers and polymers, which alter the oxidation-reduction potentials and the activities of the above compounds. Depending on the structural characteristics of the salt, the specific features of the metal and its ligand environment, the type of aromatic compound, and the conditions (for example, temperature, and the nature of the solvent), the oxidant and the substrate can interact via several different mechanisms.

1. Electron transfer from the π-electron system of the substrate to the metal atom with formation of a radical-cation of the aromatic compound. This process can proceed after the inclusion of the substrate molecule in the coordination sphere of the metal (inner-sphere transfer, *a*) or without the breakdown of this sphere (outer sphere transfer, *b*):

$$CH_3ArH + M^{n+} \begin{cases} \xrightarrow{a} [CH_3ArH\ldots M^{n+}] \rightarrow [(CH_3ArH^{\cdot+})\ldots M^{(n-1)+}] \\ \xrightarrow{b} CH_3ArH^{\cdot+} + M^{(n-1)+} \end{cases} \quad (1)$$

2. Homolytic decomposition of the substrate–oxidant complex with simultaneous transfer of an electron and a ligand and the formation of a benzyl type radical (2*a*) or the product of radical addition to the substrate (2*b*):

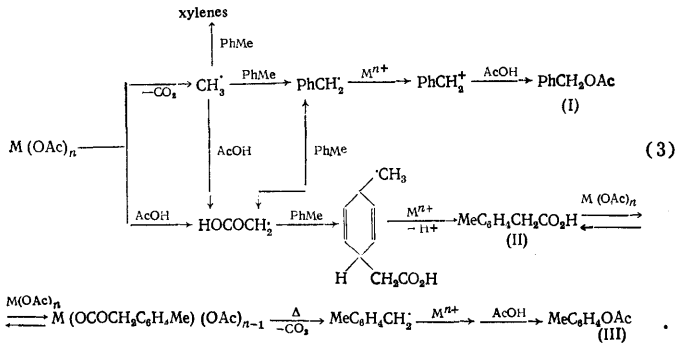
$$HArCH_3 + M^{n+}X^- \begin{cases} \xrightarrow{a} HArCH_2^{\cdot} + HX + M^{(n-1)+} \\ \xrightarrow{b} H_3CAr\overset{\cdot}{\underset{X}{\overset{H}{<}}} + M^{(n-1)+} \end{cases} \quad (2)$$

Processes of this kind appear, in particular, in oxidation by complex cerium(IV) salts, copper(II) and iron(III) halides, etc. (see below).

3. Oxidation initiated by free radicals arising in the decomposition (photochemical or thermal) of the oxidant molecule (usually the metal carboxylate).

Depending on the nature of the metal, the structure of the carboxylate ion, and the solvent used, such decomposition is accompanied by decarboxylation leading to alkyl or aryl radicals and (or) the formation of carboxyalkyl radicals. Both types of radicals initiate the process, giving rise to alkylation, carboxyalkylation, acyloxyalkylation, etc. products in proportions determined by the specific characteristics of the intermediates, which can be illustrated by the general mechanism of the oxidation of toluene in AcOH by

lead(IV), manganese(III), and cerium(IV) acetates (for further details, see the appropriate sections of the review):



(3)

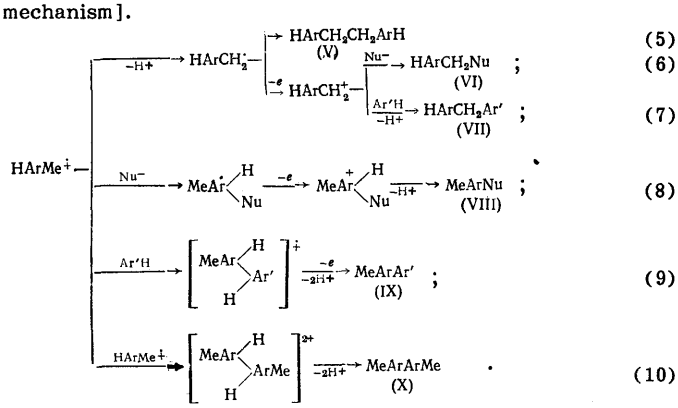
4. Metallation of the aromatic substrate with a metal salt and subsequent decomposition of the organometallic compound with formation of an aryl radical or an aryl cation:

$$ArH + MX_n \xrightarrow{-HX} \underset{(IV)}{ArMX_{(n-1)}} \begin{cases} \rightarrow Ar^+ + MX_{n-2} + X^- \\ \rightarrow Ar^{\cdot} + MX_{n-2} + X^{\cdot} \end{cases} \quad (4)$$

Processes of this type are characteristic of lead(IV), palladium(II), and particularly thallium(III) salts (see below).

Thus the first stage of the reaction of the aromatic substrate with a metal complex leads to the formation of a radical, cation, or a radical-cation, depending on the mechanism. The transformations of radicals on interaction with the metal compounds have been discussed in detail in reviews[2,3]. They are usually terminated either by oxidation via a ligand transfer mechanism [analogous to mechanism (2)] or by oxidation to a cation, which subsequently reacts with a suitable nucleophile (see below).

The fate of the radical-cation formed via mechanism (1) merits a more detailed investigation. In the presence of an alkyl (particularly methyl) group in the molecule, the radical-cation usually loses a proton with formation of a radical of the benzyl type, which is then oxidised to a cation, reacting with an anion or a solvent molecule to form a product of substitution in the α-position of the side chain [mechanism (6)]. When the stability of this radical is high, 1,2-diarylethanes of type (V) are also formed. In a weakly nucleophilic medium (in the presence of strong acids or in the heterophase oxidation in an excess of the substrate) the cation formed attacks a second substrate molecule with formation of diarylmethanes via mechanism (7) [in principle the formation of compound (VII) is also possible as a result of the oxidation of the radical adduct comprising $HArCH_2^{\cdot}$ and $HArCH_3$, but the available literature data concerning the high regioselectivity of reaction (7) are inconsistent with this mechanism].



(5) (6) (7) (8) (9) (10)

An alternative reaction pathway involves direct attack by an anion or a solvent molecule on the radical-cation and the formation of the ring-substituted product (VIII) via mechanism (8). In the absence of alkyl substituents from the substrate molecule or when factors (for example, steric factors) hindering the formation of a benzyl radical operate, this reaction pathway becomes dominant in highly nucleophilic media. The dimerisation of the radical-cation or its interaction with another molecule of the aromatic compound leads to the formation of biphenyl derivatives via mechanisms (9) and (10). The oxidative dehydrodimerisation pathway, leading to products of types (VII), (IX), (X), depends on the structure and on the distribution of the positive charge (in a substituted or unsubstituted position of the aromatic ring) of the initial radical-cation. Reactions of this type are frequently accompanied by polymerisation and disproportionation.

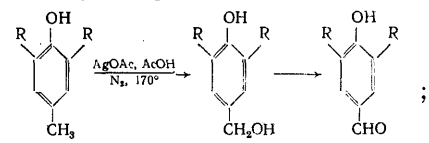
Reactions (5)–(10) frequently take place simultaneously, but the choice of conditions (variation of the temperature parameters and solvents, the introduction of nucleophilic additives, strong acids, complex-forming agents, etc.) makes it possible to drive the process in the required direction and to obtain a product with a high selectivity.

The specific features of such processes are considered below in relation to various types of oxidants in conformity with the classification adopted for the latter (see above) in order of their decreasing oxidation-reduction potentials.

III. VARIABLE-VALENCE METAL IONS AS OXIDANTS FOR ALKYLARENES

1. Silver(I), Silver(II), and Silver(III)

The use of silver(I) salts and Ag_2O for the oxidation of hydroquinones and aldehydes is well known, but the stepwise oxidation of the methyl group of 2,6-dialkyl-*p*-cresols is apparently the only example of reactions of this kind†.



R = t-Bu or Me.

Silver(II) compounds are strong oxidants, but their use in organic syntheses is fairly limited[6].

Many oxidation processes take place successfully in the $Ag^+–S_2O_8^{2-}$ system, but do not occur in the absence of silver ions. As suggested previously, the role of the latter is not exhausted by the formation of $SO_4^{\cdot-}$ radical-anions. The latest studies[7,9] have shown that Ag^{2+} ions make an appreciable contribution to the oxidation of the substrate. The process involves a series of oxidation-reduction reactions:

$$S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{2-} + SO_4^{\cdot-} + Ag^{2+} ;$$
$$SO_4^{\cdot-} + RH \rightarrow SO_4^{2-} + R^{\cdot} + H^+ ;$$
$$SO_4^{\cdot-} + Ag^+ \rightarrow SO_4^{2-} + Ag^{2+} ;$$
$$Ag^{2+} + RH \rightarrow Ag^+ + RH^{+\cdot} .$$

†There exist also patent data[5] concerning the oxidation of toluene to benzyl alcohol by passing oxygen through a solution in acetic anhydride containing catalytic amounts of silver acetate.

The Ag^{2+} and $SO_4^{\cdot-}$ species act in these reactions as oxidants with different selectivities[8] and the contribution of the oxidation by Ag^{2+} ions increases with increasing Ag(II)/substrate ratio.

The stability of organic silver(II) complexes increases appreciably with increasing acidity of the medium and in the presence of nitrogen-containing ligands[6,7]. Thus bis(2,2-bipyridyl)silver(II) peroxydisulphate in acetic acid acetoxylates alkylarenes in the ring and (or) in the α-position of the side chain[7,8] via mechanism (11) in ~300% yield with respect to silver(II) (two oxidants are involved in the reaction):

$$3ArH + 2Ag(II) + 2S_2O_8^{2-} + 3AcO^- \rightarrow 3ArOAc + 2Ag(I) + 4SO_4^{2-} + 3H^+ \quad (11)$$

In addition, methylbenzenes give rise to small amounts of benzaldehydes. Silver(II) salts without the $S_2O_8^{2-}$ anion react analogously[10]. Silver(II) picolinate (pyridine-2-carboxylate) $Ag(pic)_2$ and bis(2,2-bipyridyl)silver(II) trifluoromethanesulphonate $Ag(bipy)_2(CF_3SO_3)_2$ oxidise *p*-methylanisole to a mixture of the corresponding alcohol and aldehyde (3:1) in quantitative yields. The rate of oxidation increases greatly in the presence of potassium acetate, which has been attributed[10] to the buffer effect of the acetate ion [see mechanism (11)] and (to a greater extent) to the increased solubility of the silver(II) complexes in the presence of potassium acetate.

The results of the competitive oxidation of *p*-substituted toluenes yield $\rho = -3.4$ and the kinetic isotope effect, which is absent in the acetoxylation of the ring, amounts to 5.9 for α, α, α-d_3-*p*-methoxytoluene. Thus, in the absence of the peroxydisulphate ion, the oxidation of arylmethanes involves electron transfer with formation of a radical-cation [mechanism (1)], which then loses a proton in the rate-determining stage of the reaction[10].

Silver(II) picolinate can also be used in neutral media[11,12]: the oxidation of alkylarenes by an aqueous suspension of $Ag(pic)_2$ gives rise to carbonyl compounds[11], while the reaction with PhMe in dimethyl sulphoxide (DMSO) at 65 °C[12] makes it possible to obtain $PhCH_2OH$, PhCHO, and $PhCO_2H$ in succession, depending on the amount of the oxidant (the yields are 60, 15 and 45% respectively in each case).

In principle, the reactions of silver(II) salts may involve the participation of silver(III) species formed via the reaction

$$2Ag(II) \rightleftarrows Ag(I) + Ag(III).$$

However, it has been shown that this equilibrium is greatly displaced to the left and silver(III) plays an insignificant role in the processes occurring, for example, in the $Ag^+-S_2O_8^{2-}$ system[8]. Such reactions follow second-order kinetics, which is inconsistent with the involvement of silver(III).

At the same time it is known that stable silver(III) compounds can be obtained in the form of complexes of AgX_3 ($X = HSO_4$, NO_2, ClO_4, or OH) with biguanidine, ethylenebiguanidine, etc. and also in the form of the oxide Ag(I).$\cdot$Ag(III)O_2.[13] A solution of Ag_2O_2 in mixtures of aqueous acids (H_3PO_4, AcOH) oxidises methylarenes to the corresponding aldehydes in fairly high yields (54% for PhMe and 90% for *p*-MeC_6H_4OMe).[14] It is of interest that diphenylmethane is inert under these conditions, while the yield of Ph_2CO in the oxidation in the $Ag(pic)_2-H_2O$ system is 43%.[11]

It is noteworthy that, according to Crivello's data[15], Ag_2O_2 in a trifluoroacetic acid–trifluoroacetic anhydride mixture oxides aliphatic hydrocarbons and in the case of adamantane, for example, gives rise to 1-adamantyl trifluoroacetate in 98% yields.

2. Cobalt(III)

Like silver(II), cobalt(III) is a powerful oxidant in acid media. A study of the Co(III)/Co(II) oxidation-reduction potential in aqueous solutions of HCl, H_2SO_4, AcOH, and $HClO_4$ showed that the potential of the above pair decreases with increasing acid concentration[16].

Like Ag_2O_2, cobalt(III) hydroxide in aqueous solutions of acetic and phosphoric acids oxidises methylarenes to the corresponding aldehydes in yields ranging from 25% (mesitylene) to 95% (*p*-methylanisole). Toluene is inert under these conditions[16]. An advantage of this process is its relatively high selectivity.

Cobalt trifluoride oxidises benzene at 200–250 °C to a mixture of cyclic polyfluoro-derivatives (25–30 products), mainly octafluorocyclohexanes[18]. It has been shown that the first stage of the reaction is electron transfer with formation of a radical-cation[18]. Under the same conditions, potassium tetrafluorocobaltate gives rise to a mixture of polyfluorocyclohexenes[19]. The proportions of the products in the case of the tetrafluorocobaltates of other alkali metals depend greatly on the nature of the cation[20]. The reaction requires increasing temperatures on passing from lithium (100–130 °C) to caesium (250 °C) and only in the last case does the reaction mixture contain, apart from the products of the successive saturation of the aromatic system (mainly 3,3,6,6-tetrafluorocyclohexadiene), polyfluorobenzenes, including hexafluorobenzene (6%).[20] It remains obscure how the variation of the cationic component influences the structure of the salt and its reactivity. However, it is of interest that, according to the data of Edwards et al.[20], potassium hexafluorocobaltate is inert under the same conditions.

The study of the heterogeneous oxidation of toluene and xylenes with potassium 12-tungstocobaltate(III) $K_5[CoO_4W_{12}\cdot O_{36}]\cdot H_2O$,[21] which gives rise to mixtures of diarylmethanes, monoaldehydes, and the corresponding alcohols, showed that the radical-cation of the aromatic compound is formed as a result of an outer-sphere electron transfer [mechanism (1*b*)]. The subsequent transformations of the radical-cation proceed via mechanisms (6) and (7).

Under homogeneous conditions ($AcOH-H_2O$), the reactions of potassium 12-tungstocobaltate(III) with aromatic compounds are in many respects analogous to the anodic oxidation processes and reactions involving silver(II) salts[22]. Thus anisole, biphenyl, and naphthalene gives rise to aromatic ring acetoxylation products in the presence of potassium acetate, the oxidation of 4-fluoroanisole in the same system being accompanied by the substitution of fluorine by the acetoxy-group. Mesitylene is also partly acetoxylated in the ring under these conditions (as in anodic oxidation), although in the reaction with cobalt(III) carboxylates, even in the presence of potassium acetate, only α-acetoxylation is observed (see below). Toluene, xylenes, and hexamethylbenzene give rise to only α-hydroxy- and acetoxy-derivatives in the absence of potassium acetate, while 4-methoxytoluene also forms the dehydrodimer 2-(4-methoxybenzyl)-4-methylanisole. In the presence of potassium acetate the rate of oxidation falls and oxidative coupling is fully suppressed by toluene and xylenes give rise also to acetoxymethylation products [see mechanism (3)] whose yield increases sharply in anhydrous acetic acid. The isotope effect in the oxidation of α,α,α-d_3-*p*-methoxytoluene, amounting to ~6, has been interpreted[22] as evidence for a reaction mechanism involving the concerted transfer of an electron and the proton of the α-C–H bond to the oxygen atom of the heteropolyion as the rate-limiting stage.

However, simpler cobalt(III) salts—the perchlorate and carboxylates—are frequently used. In aqueous $HClO_4$ cobalt(III) perchlorate steadily oxidises benzene with formation of a mixture of *p*-benzoquinone, muconic acid, and its lactone[23]. The reaction kinetics obey the equation

$$-\frac{d[Co(III)]}{dt} = \left(k_1 + \frac{k_2}{[H^+]}\right)[Co(III)][PhH].$$

This has been interpreted[23] as evidence for the involvement in the process of two types of oxidising species—the aquo-complex of cobalt(III) and the more active hydroxy-complex $Co(OH)^{2+}$.

In the $HClO_4$–H_2O–MeCN system cobalt(III) perchlorate oxidises alkylarenes to mixtures of the corresponding alcohols, aldehydes, and acids. According to the data of Cooper and Waters[24], the reaction of toluene involves outer-sphere electron transfer and is accelerated with increase of the concentration of acetonitrile in the solvent. In the mixture with 50% MeCN the products resulting from the oxidation of the methyl group are formed exclusively, but in the presence of higher contents of acetonitrile the formation of methylbenzophenones and benzylbenzaldehyde—the products of the reaction of toluene with the benzyl radical arising in the oxidation of benzaldehyde—was also noted. The reactivity of the substrates increases in the sequence p-$NO_2C_6H_4CH_3 < PhCH_2CH_2Ph \cong PhMe \cong PhEt < Ph_2CH_2 <$ t-$BuC_6H_4CH_3 < Ph_2$.

It is of interest that benzyl alcohol is oxidised faster under these conditions than diphenylmethanol. This phenomenon has been attributed[24] to the steric characteristics of the complexes formed on direct coordination of alcohols to a cobalt atom; it is suggested that the electron transfer takes place in this instance via an inner-sphere mechanism [see mechanism (1*a*)].

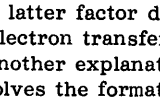
The oxidation of toluene by cobalt(III) perchlorate is appreciably accelerated when aliphatic acids are introduced into the reaction mixture[25].

The slow electron transfer from the toluene molecule is replaced under these conditions by the rapid abstraction of hydrogen from the methyl group by the alkyl radical formed via the reaction

$$RCOOH + Co(III) \rightarrow R^{\cdot} + CO_2 + Co(II) + H^+ . \qquad (12)$$

The benzyl radical is rapidly oxidised further via mechanism (6) and partly dimerises with formation of bibenzyl [mechanism (5)].

Aryl-substituted aliphatic acids are oxidised by cobalt triacetate (CTA) with formation of a radical-cation [mechanism (1)] and then a benzyl-type cation [mechanism (6)].[26] Under these conditions, γ-phenylbutyric acid gives rise to an intramolecular oxidation product—γ-phenylbutyrolactone:

$$PhCH_2(CH_2)_2CO_2H \xrightarrow[-H^+]{2Co(III)} PhCH(CH_2)_2CO_2H \xrightarrow[-H^+]{} \text{} .$$

In the presence of LiCl or trifluoroacetic acid the yield of the lactone increases from 25 to 60%.[26]

In the presence of arylacetic acids the radical-cation formed is decarboxylated and gives rise to substituted benzyl acetates, in conformity with mechanism (6):[26]

$$[ArCH_2CO_2^-]^{\cdot} \xrightarrow{-CO_2} ArCH_2^{\cdot} \xrightarrow{Co(III),\ AcO^-} ArCH_2OAc .$$

Cobalt(III) carboxylates oxidise alkylbenzenes to the corresponding benzyl carboxylates[26–37] and the ligand environment of Co^{3+} plays a significant role in this reaction, whose first stage is believed[27–30] to involve the insertion of the substrate in the inner coordination sphere of cobalt(III). Neutral ligands, which strongly coordinate cobalt(III)—bipyridyl, pyridine, and acetonitrile—lower the rate of reduction of cobalt(III) with increase of their concentration in the reaction mixture up to the complete suppression of the oxidation process[27]. When water is added, the rate of reduction of cobalt(III) initially increases and then falls to the initial value at $[H_2O] > 2.2$ M. With increase of the size of the carboxylate anion, the electron transfer of the cobalt(III) atom is suppressed and the main reaction pathway becomes the decomposition of the oxidant [via a mechanism analogous to mechanism (12)], whose contribution is 82% for pelargonic acid and 100% for isobutyric acid[27]. The ligand effect is in this case attributed to the steric hindrance in the formation of the Co(III)–RH complex and not to the decrease of the oxidation potential of cobalt(III).[27]

The addition of potassium acetate accelerates the oxidation of toluene by CTA in acetic acid[31,32] but has little influence on the proportions of the products (31% $PhCH_2OAc$, 7% PhCHO, and 2% of bibenzyl are formed at 37 °C [31]). An increase of temperature lowers the overall yield of products and is accompanied by the formation of small amounts of xylenes and methylbenzyl acetates [see mechanism (3)]. The thermolysis of CTA in acetic acid is accompanied by the liberation of CO_2 and small amounts of methane and is almost completely suppressed in the presence of aromatic substrates[31], which differs sharply from the behaviour of manganese(III), lead(IV), and cerium(IV) acetates under analogous conditions (see below). On oxidation with CTA, 2-methylnaphthalene gives rise also to 1-acetoxy-2-methylnaphthalene (18%) apart from the products formed as a result of the oxidation of the methyl group (~50%) [see mechanism (8)].[31]

The kinetics of the oxidation of aromatic compounds by cobalt triacetate are described by the following equation according to a series of data[28,29,30]:

$$-\frac{d[Co(III)]}{dt} = k_{obs}[ArH][Co(III)]^2[Co(II)]^{-1},$$

where k_{obs} is independent of the association energy of the C–H bond of the substrate but is correlated with its ionisation potential and its ability to coordinate to the cobalt(III) ion[28].

In the presence of O_2 the kinetic parameters of the reaction remain unchanged[33], but the products are the corresponding aldehydes and acids. Thus the presence of oxygen does not affect the rate-determining stage of the reaction—the loss of a proton by the radical-cation formed via mechanism (1). The reactivity of arylalkanes decreases in the sequence p-xylene > PhMe > PhEt > PhPr-iso > p-ClC_6H_4Me. [31,32]. The rate of reaction increases in the presence of AcO^- and decreases as cobalt(II) accumulates in the reaction mixture[28,32]. The latter factor demonstrates, in particular, the possibility of electron transfer in reaction (1).

Another explanation of the inhibiting effect of cobalt(II) involves the formation of dinuclear Co(III)–Co(II) complexes with a greatly reduced oxidation-reduction potential[27–35]. According to Kawai and Kamiya[34], the addition of manganese, platinum, and cerium acetates in both the highest and lowest oxidation states also reduces the oxidising capacity of cobalt(III) up to the complete disappearance of activity for certain molar proportions. The inhibition sequence is as follows: Mn(II) > Mn(III) ≅ Ce(IV) > Cu(II). The formation of polynuclear cobalt(III) complexes has also been confirmed by spectroscopic methods[34]. However, it is of interest that the Co(III)–Co(II) combination, which is inactive in the oxidation of toluene, exhibits the same activity as cobalt(III) in the oxidation of 1-methylnaphthalene[34].

The activity of cobalt(III) increases appreciably in the presence of halide ions (Cl^- and Br^-) [31,38-40] and also organic bromo-derivatives—bromobenzene, dibromoethane, butyl bromide, etc.[38] It has been shown[39] that in the presence of an excess of chloride ions in the CTA–AcOH system the highly reactive hexachlorocobaltate(III) anion is formed and decomposes rapidly with formation of Cl_2 and $CoCl_2$. In the presence of smaller amounts of Cl^- the formation of mixed cobalt(III) acetate-chloride complexes, which also exhibit an enhanced reactivity, is more likely. The existence of such complexes has been confirmed by spectroscopic data[31].

The main product of the oxidation of toluene by CTA in the presence of LiCl is benzyl chloride, but, with increase of the Cl^- concentration, its yield falls as a consequence of the formation of ring-chlorination products[31]. The reaction of 2-methylnaphthalene proceeds analogously[31]. On the other hand, in the presence of Br^-, toluene gives rise exclusively to benzyl bromide[40].

It is of interest to note that the interaction of CTA with Br^- in acetic acid at 70 °C is complicated, which is believed[41] to be due to the presence in solution of two forms of CTA—$[Co(AcOH)_6]^{3+}(OAc)_3$ and $[Co(OAc)_3(AcOH)_3]$ in proportions of ~1:1. It has been suggested that the oxidation of Br^- takes place after the exchange of the ligands of the cobalt atom from bromide, the first form reacting rapidly with Br^- and the second form slowly, i.e. the rate of reaction is limited by the ligand exchange stage.

On the other hand, X-ray diffraction studies[42] have shown that CTA has the structure of an O-centred trimer $[Co_3O(OAc)_6(AcOH)_3]OAc$ containing two types of acetoxy-groups—bridging and chelate, which may also be the cause of the existence of two stages in the reaction of cobalt(III) with Br^-.

The formation of benzyl bromide in the oxidation of toluene in the presence of Br^- is attributed[33,41] to the simultaneous reactions involving the bromination of the substrate by the liberated bromine and the "cobalt bromide" complex via the mechanism

$$Co(III) + Br^- \rightleftarrows [Co(II)\ldots Br^{\cdot}]\ ;$$
$$RH + [Co(II)\ldots Br^{\cdot}] \rightarrow Co(II) + R^{\cdot} + Br^- + H^+\ ;$$
$$R^{\cdot} + [Co(II)\ldots Br^{\cdot}] \rightarrow RBr + Co(II)\ .$$

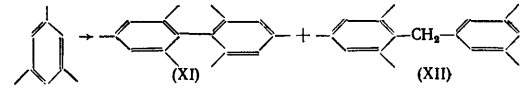
The Co(III)–Br^- system is widely used as a catalyst in industrial liquid-phase oxidation of alkyl derivatives of aromatic compounds, but the mechanism of the so-called cobalt bromide catalysis is still controversial (see, for example, Emanuel' [1] and Zakharov[43]).

The oxidising properties of cobalt(III) increase appreciably in the presence of strong acids. The addition of H_2SO_4, CCl_3CO_2H, $HClO_4$, H_3PO_4, and BF_3 increases the rate of oxidation of alkylarenes by cobalt(III) acetate so much that these reactions can be carried out at room temperature[36]. Thus, in the oxidation in acetic acid in an inert atmosphere, the reaction products are substituted benzyl acetates, while in the presence of O_2 they are aldehydes and acids[36]. The activating effect of strong acids has been explained[36,44] by the destruction of the cobalt(III) cluster complexes (see above), by the formation of monomeric species, and by the enhanced electrophilic properties of the metal atom. However, one should note that the increase of the concentration of strong acid increases the activity of cobalt(III) so much that the oxidation of the solvent (acetic acid) becomes a competing process at 25 °C.[36]

The benzyl acetate formed in the oxidation of toluene in the CTA–AcOH–$HClO_4$ system reacts with toluene when the temperature is raised (up to 114 °C), giving a mixture of phenyltolylmethanes[45]. Under these conditions, other alkylbenzenes (PhEt, p-$ClC_6H_4CH_3$, xylenes, and mesitylene) also give rise to mixtures of diarylmethanes and small amounts of monoaldehydes, whose relative content increases in the presence of oxygen[45].

Trifluoroacetic acid (TFAA) occupies a special place among acid activators. The formation of complexes involving charge transfer between cobalt(III) and the aromatic substrate has been discovered in TFAA solutions[46]. The dissociation products of such complexes are cobalt(II) and the substrate radical-cation [see mechanism (1)] stabilised by the TFAA.[46] The efficiency of such stabilisation is so great that it makes it possible to obtain well resolved EPR spectra of the radical-cations even in the case of the relatively unstable dialkylbenzenes[46].

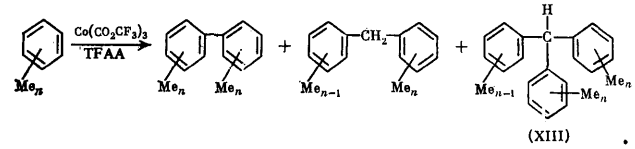
On the other hand, the breakdown of the cluster structure of the CTA and the ligand exchange in the interaction between CTA and TFAA are fairly slow, so that solutions of cobalt(III) acetate and trifluoroacetate in TFAA exhibit different reactivities[48,49]. The reaction of mesitylene with cobalt triacetate in TFAA proceeds via the mechanism



(13)

and yields 2% of compound (XI) and 20% of compound (XII), while in the analogous reaction with $(CF_3CO_2)_3Co$ the yields of compounds (XI) and (XII) are respectively 16 and 9%. It is of interest that the yield of compound (XI) increases in the latter case with decrease of temperature and reaches 41% at −12 °C with simultaneous formation of 21% of nonamethyl-*m*-terphenyl.[49] When reaction (13) is carried out in the $(CF_3CO_2)_3Co$–TFAA–$C_2Cl_2H_4$ system (80 °C), the product ratio (XI):(XII) varies from 0 to 1.8 as the TFAA concentration rises from 0 to 100% [in pure $C_2Cl_2H_4$ and in mesitylene compound (XII) is formed in 28% yield].[49]

The oxidation of toluene, xylenes, pseudocumene[49], and durene[48] proceeds via the general mechanism



The biaryls (X) are hardly formed in the case of toluene, *p*-xylene, and durene, while the yield of compounds (XIII) and (X) is a maximum for *m*-xylene and pseudocumene.

The use of this reaction for the oxidation of mixtures of aromatic hydrocarbons[48] can be regarded as a valuable method of synthesising asymmetric biaryls and diarylmethanes (see, for example, Kozhevnikov and Matveev[50]). Under analogous conditions, benzene is readily oxidised to phenyl trifluoroacetate (the yield reaches 90%,[51,52] falling in the presence of an excess of benzene owing to the formation of a mixture of polyphenyls). Chlorobenzene and trifluoromethylbenzene are formed similarly albeit in lower yields[52].

The oxidation of aromatic substrates by cobalt trifluoroacetate in the presence of inorganic anions makes it possible to obtain in high yields the products of nucleophilic substitution in the aromatic ring via mechanism (8).[54] Thus the oxidation of benzene in the TFAA–LiCl–$Co(OCCF_3)_3$ system yields a mixture of phenyl trifluoroacetate and chlorobenzene (~1:1) for the ratio $Co(III)/Cl^- = 1$. An increase of the Cl^- concentration fully suppresses trifluoroacetoxylation, while the yield of chlorobenzene reaches 90%. Bromo- and iodobenzenes can be obtained analogously but in lower yields[53].

The oxidation of toluene under these conditions leads to a complex mixture containing chlorotoluenes, benzyl chloride, and compounds of types (X), (VII), and (XIII).[53] It is of interest that in the presence of air the main products are chlorotoluenes, while in an inert atmosphere benzyl chloride is mainly formed. The reaction thus involves processes described by mechanisms (5)–(10). The reactions of $Co(OCOCF_3)_3$ in the presence of F^-, CN^-, NO_2^-, and NO_3^- have also been studied[53].

In aqueous solutions of trifluoroacetic acid in the presence of halide ions, even toluenes containing strongly electron-accepting substituents can be oxidised by cobalt(III) acetate. Thus *p*-toluic acid is oxidised in the $CF_3COOH–H_2O–Hal$ system at room temperature and gives rise to the products of the oxidative halogenation of the aromatic ring and (or) the side chain[54,55]. In the presence of KCl the main product is 3-chloro-4-methylbenzoic acid, while the reaction in the presence of NaBr gives rise mainly to 4-carboxybenzyl bromide[54]. In the latter case the side products are hydroxy-, acetoxy- and trifluoroacetoxy-methylbenzoic acids. 4-Hydroxymethylbenzoic acid—a valuable monomer for the synthesis of polymeric materials, which are superior as regards many parameters to the analogous materials based on terephthalic acid—can be obtained by hydrolysing the above reaction mixture[55].

The use of cobalt(III) chelates (acetylacetonate, benzoate, δ-quinolinate, etc.) makes it possible to carry out the reaction in non-polar solutions[56–58]. Thus the oxidation of 2,6-xylenol with cobalt(III) salicylideneaminates in toluene proceeds via an oxidative coupling mechanism and gives rise to a mixture of 4,4′-dihydroxy-3,5,3′,5′-tetramethylbiphenyl and the corresponding quinone[57]. It has been suggested[54] that the reaction involves the dimerisation of a radical formed via the mechanism

$$CoL_3 + RH \rightleftarrows CoL_2 + R^{\cdot} + HL \quad .$$

The kinetics of the oxidation of cumene by cobalt(III) chelates have been studied[58], but there are no data on the products of this reaction.

3. Manganese(III)

The reactions of manganese triacetate (MTA) in acetic acid with *p*-methoxytoluene[59] or toluene in the presence of NaBr[40] and with alkylbenzenes in the presence of strong acids[36] proceed analogously to the corresponding reactions of cobalt triacetate and are characterised by the same kinetic features i.e. they include the stage of the reversible electron transfer to the metal atom [mechanism (1)].

Like cobalt(III) acetate, manganese(III) acetate oxidises *p*-toluic acid in trifluoroacetic acid in the presence of chloride and bromide ions with formation of products of the oxidative halogenation of the aromatic ring and (or) side chain, but in this instance the reaction in the $Mn(III)–Cl^-$ system leads almost exclusively to a 3-chloro-4-methylbenzoic acid (yield ~100%).[54]

In the absence of activators, the reactions with manganese(III) salts require increased temperatures and are accompanied by radical substitution reactions because of the lower oxidising capacity of the metal ion (Table 1). The thermolysis of manganese(III) carboxylates proceeds, in conformity with mechanism (3), via two pathways, depending on the structure of the ligand[60]. The formation of carboxymethyl radicals is the preferred pathway (98 to 100%) for MTA. In the reaction involving manganese(III) propionate the alternative pathway involving decomposition with formation of $CH_3\dot{C}H_2$ makes a contribution of ~6%, while the thermolysis of phenylacetate proceeds almost exclusively via this pathway [see mechanism (3)].[60] Thus, on oxidation with MTA in acetic acid (110 °C), benzene and chlorobenzene give rise to mixtures of the corresponding phenylacetic acids, benzyl acetates, benzylidene acetates, and benzaldehydes, while toluene gives rise to methylbenzyl acetate (67%), benzyl acetate (10%), benzaldehyde (3%), and traces of bibenzyl[61]. Acetoxymethylation products also arise from the oxidation at 100 °C of anisole[60,62], dimethoxybenzenes[61], and 2-methylnaphthalene[60].

The thermolysis of MTA (including electrolytically generated MTA[63]) in acetic acid can also be used for the introduction into the aromatic substrate molecule of other radicals generated via the mechanism

$$RH + \dot{C}H_2CO_2H \rightarrow R^{\cdot} + AcOH \quad .$$

For example, the nitromethylation ($R = CH_2NO_2$) [63,64] and acetylmethylation ($R = CH_3COCH_2$) [65] of toluene and substituted benzenes have been achieved in this way.

It is of interest that the oxidation of methylferrocene with MTA in acetic acid does not yield acetoxymethylation products, but leads to a mixture of diarylmethanes[66]:

$$AcOH \xrightarrow{MTA} \dot{C}H_2CO_2H \xrightarrow{RCH_2} RCH_2^{\cdot} \xrightarrow{MTA} RCH_2^{+} \xrightarrow{RCH_2} RCH_2R' \quad ,$$

where R = ferrocenyl and R′ = 2-methylferrocenyl, 3-methylferrocenyl, or 3′-methylferrocenyl.

In the oxidation of substrates with fairly low ionisation potentials (<8 eV) an electron transfer process competes with radical substitution. Thus 1- and 2-methoxynaphthalenes are acetoxylated in the ring at 100 °C,[67] while *p*-methoxytoluene yields mainly *p*-methoxybenzyl acetate[59,60]. The selectivity of the reaction can therefore be regulated by suppressing or activating one of these processes.

The thermolysis of MTA in acetic acid (140 °C) is accelerated by a factor of 3–4 when potassium acetate is added[62] and also increases appreciably when acetic anhydride is added to the reaction mixture[68] or anhydrous MTA is used[60,68]. The relative yield of the acetoxymethylation product also increases following the addition of manganese(II), which retards the electron transfer reaction, as in the case of cobalt(III) (see above)[60].

On the other hand, radical processes are fully suppressed in the presence of strong acids, which makes it possible to reduce the reaction temperature to 20–40 °C.[36] The products of the oxidation of alkylarenes under these conditions are, as for cobalt(III), benzyl acetates in an inert atmosphere and carboxy-compounds in the presence of oxygen.

The oxidation of alkylbenzenes in boiling acetic acid in the presence of H_2SO_4, CF_3SO_3H, and particularly $HClO_4$ leads to the formation of diarylmethanes in high yields[45]. Under these conditions, the effect of MTA is analogous to those of CTA (see above) and the iron(III) perchlorate normally employed in this reaction (see below), differing, however, by a greater selectivity (the amount of disproportionation and polymerisation products is in this instance minimal), which makes the process synthetically valuable.

In contrast to alkylbenzenes, *p*-methoxytoluene yields under these conditions biaryls, but in the presence of weaker acids (CCl_3CO_2H, CF_3CO_2H) or at lower $HClO_4$ concentrations the main products become diarylmethanes[42]. It is of interest that in the analogous reaction with $Fe(OAc)_3$ only diarylmethanes are formed in both cases. The different behaviour of manganese(III) and iron(III) acetates has been explained[42] by the different stabilities of the trinuclear clusters of the type $[M_3O(OAc)_6L_3]OAc$ (L = AcOH for manganese and H_2O for iron), which act as bases in the reaction involving the elimination of a proton from the radical-cation (see above).

Manganese(III) trifluoroacetate reacts with mesitylene[48,49] and durene[49] in TFAA with formation of mixtures of dehydrodimers [see mechanisms (7)–(10)], but, in contrast to cobalt(III) (again see above), mainly diarylmethanes are formed in this instance and the reactivities of MTA and $Mn(OCOCF_3)_3$ solutions in TFAA are virtually identical[48].

Manganese(III) sulphate oxidises the methyl group in 1-methylnaphthalene, giving rise to the corresponding aldehyde and 1,4-naphthoquinone, but in the case of 2-methylnaphthalene the oxidation does not involve the methyl group and the reaction products are only 2- and 6-methyl-1,4-naphthoquinones[69].

The oxidation of 1-bromonaphthalene under these conditions is accompanied by a 1,2-shift to the substituent and the formation of 2-bromo-1,4-naphthoquinone, as in the oxidation with cerium ammonium sulphate (see below).

Like CoF_3, manganese(III) fluoride oxidises benzene to a mixture of cyclic polyfluoro-derivatives[18], but it acts more selectively and yields mainly polyfluorocyclohexenes.

4. Cerium(IV)

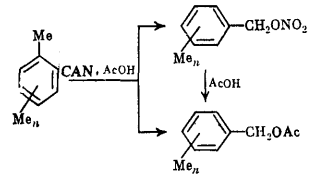
The first data on the oxidation of substituted toluenes to benzaldehydes by cerium dioxide in H_2SO_4 were obtained at the beginning of this century[70,71], but the yields of these reactions were not indicated and the yield of benzaldehyde in the oxidation of toluene by electrolytically generated cerium(IV) sulphate, described much later[72], amounted to only 8%.

Systematic studies of the oxidation of alkyl derivatives of aromatic compounds by cerium(IV) salts probably began towards 1965 when the quantitative oxidation of benzyl alcohols to benzaldehydes by cerium ammonium nitrate (CAN) in 50% acetic acid solution was described[73]. It was later shown[74] that under these conditions benzaldehydes are the main products of the oxidation of toluenes (benzyl alcohols and benzyl acetates are formed simultaneously). The yield of benzaldehydes increases on passing from toluene to *p*-xylene from 36 to 73%, but the introduction of stronger electron-donating substituents (OH, NH_2, or OMe) leads to the charring of the reaction mixture. Electron-accepting substituents lower the overall yield of oxidation products and in the case of *p*-chlorotoluene a simultaneous increase of the fraction of *p*-chlorophenylmethanol was observed[73]. In 100% acetic acid the main reaction products are benzyl acetates, whose yield also falls on passing to *p*-halogenotoluenes with a simultaneous increase of the fraction of carbinols and aldehydes in the reaction products; *p*-nitrotoluene is not oxidised at all under these conditions, but the replacement of acetic acid by 6 *N* $HClO_4$ or 3.5 *N* HNO_3 makes it possible to oxidise to aldehydes even chloro- and nitro-toluenes (with yields up to 75 and 50% respectively)[74,75]. Under the same conditions, toluene and mesitylene give rise to monoaldehydes in a quantitative yield, while ethylbenzene and diphenylmethane are oxidised to acetophenone and benzophenone with yields of 78 and 76% respectively[75]. The quantitative synthesis of anisaldehyde in 90% acetic acid from *p*-methylanisole, which completely charred in 50 and 100% acetic acid according to Trachanovsky and Young[74], has also been described[75].

The reactivity in the oxidation by CAN in aqueous acetic acid solutions decreases in the sequence *p*-xylene > *m*-xylene > *o*-xylene > toluene[76]. The reaction is accelerated in the presence of HNO_3 and is retarded by the addition of AcO^-, the rate of oxidation being a maximum in ~85% of acetic acid in all cases. The activating effect of HNO_3 is attributed[76] to the formation of the cation $Ce(NO_3)_2^{2+}$, but the inhibiting effect of added AcO^- is believed to be due to a decrease of oxidising activity when the ligands in the hexanitratocerate(IV) anion are exchanged for acetate ions[76].

The kinetics of the oxidation of toluene[77,78], xylenes[78], and nitro- and chloro-toluenes[76] by cerium(IV) in an AcOH–$HClO_4$ mixture are described by a second-order equation and the reaction mechanism is said to include[77,78] electron transfer and the formation of a benzyl-type radical as the rate-limiting stage. However, it is of interest that *p*-chlorotoluene is oxidised faster than toluene under these conditions; this has been explained[77] by the "specific features of the resonance interaction". The primary and main products of the oxidation of substituted toluenes by CAN are benzyl nitrates, which can be isolated in a fairly satisfactory yield when the reaction is carried out in hydrocarbon solvents, but in reactions in aqueous acids they are rapidly hydrolysed to carbinols, which are subsequently oxidised to aldehydes[79]. In the case of *o*-xylene the nitrate/aldehyde ratio varies from 1.5 to 4, the yield and ratio of the products depending on the rate of addition of the CAN solution, the nature of the acid (HNO_3, H_2SO_4, or AcOH), and the presence of an aliphatic hydrocarbon solvent. It is believed[79] that the reaction involves the formation of a cyclic transition state with a dimeric cerium(IV) complex, leading to nitrates and carbinols as a result of the transfer of two electrons and a proton. In the case of toluene and *p*-xylene, containing a sterically unshielded methyl group, the nitrates formed are more labile and both reactions terminate with formation of an aldehyde.

The oxidation of polymethylbenzenes (mesitylene, isodurene, hemimellitol and hexamethylbenzene) by CAN in acetic acid is described by a similar mechanism[80]:



The required stoichiometric ratio CAN/substrate = 2 decreases in the presence of oxygen. The nitrate/acetate ratio depends on the reaction time and the rate of solvolysis of the nitrate and varies from 1.5 for mesitylene to 5 for hemimellitol, increasing with increase of the fraction of undissolved CAN under heterogeneous conditions and being virtually independent of the structure of the substrate in the presence of NH_4NO_3 in the reaction mixture.

The proportions of the products in the case of isodurene and hemimellitol show that the oxidation involves mainly the 2-methyl group, which confirms the formation of a substrate radical-cation (the radical substitution takes place mainly in the 5-position[81]). The benzyl radical formed in the second stage of the reaction is oxidised further, according to the data of Baciocchi et al.[80], but not via carbonium ion [mechanism (6)]; it results from ligand transfer and proceeds via an intermediate with a Ce(IV)–CH_2Ar linkage, undergoing subsequently competitive oxidative solvolysis with formation of the acetate or with oxidative substitution yielding the nitrate#.

According to Eberson and Oberrauch[82], the anodic oxidation of isodurene in the AcOH–Bu_4NNO_3 mixture and the reaction of isodurene with CAN give virtually identical results, but the authors[82] suggest that the first stage in the

#For further details about the mechanism of oxidative substitution and solvolysis, see C.L.Jenkins and J.K.Kochi, J.Amer.Chem.Soc., 92, 856 (1972).

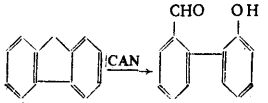
reaction with CAN involves the transfer of an α-hydrogen from the substrate molecule via mechanism (2*a*) (X = NO_3).

Among all the polymethylbenzenes, only mesitylene undergoes ring acetoxylation apart from benzyl oxidation, the yield of 2,4,6-trimethylphenyl acetate amounting to 50% of the beginning of the reaction and falling to 25% towards its end[78] (however, one should note that the oxidation of mesitylene by CAN in acetonitrile gives rise only to 3,5-dimethylbenzyl nitrate[83]). The formation of a "ring" acetate in the case of mesitylene is consistent with data for the oxidation of methylbenzenes by cerium(IV) trifluoroacetate in the presence of $LiOCOCF_3$, which leads to the preferential formation of biaryls (X) (40%) [together with diarylmethanes (VII) (10%) and benzyl trifluoroacetate (~1%)—see mechanisms (6)–(10)][84], the ratio (X):(VII) falling with increase of reaction temperature and with increase of the $LiOCOCF_3$ concentration. Under these conditions, benzene is oxidised with difficulty (8% of phenyl trifluoroacetate and 1% of biphenyl are formed), toluene gives rise only to a mixture of phenyltolylmethanes (15%) and benzyl trifluoroacetate (15%), *p*-xylene yields methylbenzyl trifluoroacetate (8%) and diarylmethanes (10%), while durene is converted into biduryl (2%) and diarylmethanes (97%).[84]

Another example of ring acetoxylation is the oxidation of anisole by CAN in acetic acid (40 °C, N_2),[85] which leads to a mixture of *o*- and *p*-acetoxyanisoles (*o*/*p* = 0.82). The reaction is of first order with respect to PhOMe and CAN and of the reciprocal order with respect to cerium(III); it is greatly accelerated by the addition of ammonium nitrate. The reaction products do not contain nitrates and the proportions of the isomeric acetates are consistent with the distribution of electron density in the anisole radical-cation [the EPR spectra of the aromatic radical-cations obtained by oxidation with cerium(IV) salts have been described[86]]. The reactions have mechanism (8) (see above).

In 90% trifluoroacetic acid in the presence of alkali metal chlorides and bromides CAN reacts fairly readily with *p*-toluic acid to form products of the oxidative halogenation of the aromatic ring—3-halogeno-4-methylbenzoic acids[54]. It has been suggested that the occurrence of a reaction via mechanism (8) is facilitated in this instance by the formation of cerium(IV) complexes containing ligands in steric proximity—halides and 4-methylbenzoate ions[54]. It is of interest that, with increase of the water content in the reaction system, the yield of ring halogenation products falls owing to the formation of the corresponding benzyl halides, which is associated, according to the authors[54], with the displacement of arenecarboxylate ligands from the inner coordination sphere of the oxidant by water.

In the oxidation of 1,2-diarylethanes by CAN in 70% aqueous acetonitrile[87] the first stage also involves the formation of a radical-cation, which decomposes into a benzyl radical and a benzyl cation, leading to benzaldehydes, benzyl nitrates, and benzyl alcohols. The rate of reaction increases after the introduction of electron-donating substituents into the aromatic ring and falls when electron-accepting substituents are introduced. The oxidation of fluorene[88] and aryl triarylmethyl ketones by CAN in acetic acid also involves the oxidative cleavage mechanism[89]:



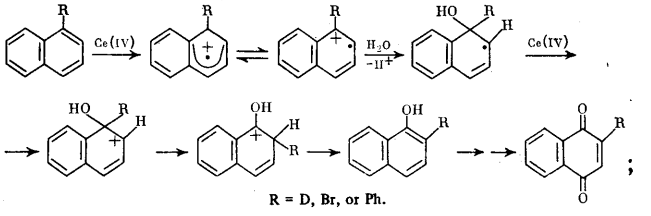
$$Ar_3CCOAr' \xrightarrow[-2Ce(III)]{2Ce(IV)} Ar_3C^+ + Ar'CO^+ \rightarrow Ar_3COH + Ar'CO_2H \ .$$

In the first stage of its oxidation with CAN in methanol or acetic acid[90], anthracene gives rise to 9-anthryl nitrate, whose reaction with the anthracene radical-cation produces 9-anthryl nitrite and the anthrol radical, which is then converted into bisanthrone or is oxidised by CAN to 10-acetoxy- and 10-methoxy-anthrols and also to anthraquinone (via 9,10-dihydro-10-oxo-9-anthryl nitrate). On the other hand, it has been shown[91] that the analogous reaction in acetonitrile gives rise to a 3:1 mixture of anthraquinone and 9-nitroanthracene. Ring nitration products are formed under these conditions also from benzene, nitrobenzene, toluene, and naphthalene.

The oxidising properties of CAN can be used successfully also in reactions of alkylarenes with acyl peroxides, for example, via the mechanism[92]

$$(iso\text{-}PrCO_2)_2 + 2[Ce(NO_3)_6](NH_4)_2 + PhMe \rightarrow o\text{-}MeC_6H_4Pr\text{-}iso + 2Ce(NO_3)_3 + 4NH_4NO_3 + 2HNO_3 \ .$$

An interesting reaction (a 1,2-shift of the substituent) has been discovered in the study of the oxidation of 1-substituted naphthalene by cerium ammonium sulphate[93]. The anodic oxidation of the same substrates proceeds analogously[94]:



R = D, Br, or Ph.

Cerium pyridinium chloride $(C_5H_5N)_2CeCl_6$ (CPC) has been used to oxidise polymethylbenzenes in methanol and ethanol[95]. In the case the oxidant consists of the products Ce(IV) $(Cl)_x(RO)_y$ of the ligand exchange between CPC and the solvent, which exhibit different reactivities depending on R. The rate of the oxidation and "spontaneous" reduction of CPC in methanol is higher by two orders of magnitude than in ethanol. In the absence of oxygen, the reaction products are the corresponding benzyl chlorides and alkoxymethylbenzenes, the latter becoming the sole reaction product after more prolonged refluxing of the reaction mixture, which makes this process valuable from the synthetic point of view. It is of interest that, in contrast to hexamethylbenzene and durene, which give satisfactory yields of products, mesitylene is almost inert with respect to oxidation under these conditions.

The ratio of the chloro- and methoxy-derivatives in the oxidation of durene by CPC in methanol remains constant during the reaction, increasing after the addition of LiCl, but under these conditions methoxylation is not fully suppressed, which confirms the ligand transfer mechanism in the benzyl radical oxidation stage proposed by the author[95] (see above). In the reaction in the presence of oxygen, the dimethylacetate of 2,4,5-trimethylbenzaldehyde is formed from durene, but hydrolyses during isolation (the yield of aldehyde is 65%). It is of interest that the oxidation of Cl^- to Cl_2, which takes place with difficulty in alcohols, occurs readily when CPC is refluxed in acetonitrile.

Like cobalt(III) and manganese(III) fluorides (see above), cerium tetrafluoride is used to synthesise cyclic polyfluoro-derivatives from benzene (250–480 °C). However, this results in a mixture containing polyfluorobenzenes, polyfluorocyclohexenes, and polyfluorocyclohexadienes[18,96].

Cerium tetra-acetate reacts with toluene in acetic acid (110 °C) via the general mechanism (3) and give rise to three products: (I)–(III).[97] The thermolysis of $Ce(OAc)_4$ in acetic acid takes place in the same way as for $Mn(OAc)_3$

with formation of carboxymethyl radicals, but, in contrast to manganese(III), the acetoxymethylation is in this case suppressed by the addition of acetic anhydride and potassium acetate. The reaction with benzene and chlorobenzene yields only arylacetic acids (41 and 36%). The authors suggest[97] that the role of acetic anhydride consists in binding the acids produced into mixed anhydrides, which are resistant to oxidation.

It is of interest that the photolysis of $Ce(OAc)_4$ is accompanied by decarboxylation and the formation of methyl radicals [see mechanism (3)].[97]

5. Iron(III)

Potassium hexacyanoferrate(III) $K_3Fe(CN)_6$ and iron(III) chloride $FeCl_3$ are most frequently used as oxidants. The hexacyanoferrate(III) is normally employed in aqueous solutions and, being a weak oxidant, is capable of oxidising only aromatic compounds with a fairly low ionisation potential (such as methylphenols[98,99] and alkoxybenzenes[99]), giving rise thereby to substituted biphenyls.

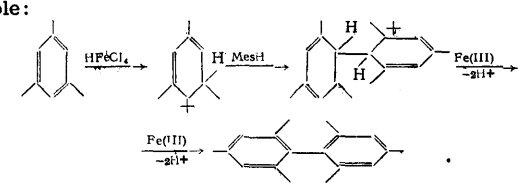
Under alkaline conditions (DMSO–H_2O–OH^-), substituted toluenes containing powerful electron-accepting groups (NO_2 or Me_3N^+) can also be oxidised as a result of the formation of benzyl anions:

$$ArCH_3 \xrightarrow[DMSO]{OH^-} ArCH_2^- \xrightarrow{Fe(III)} ArCH_2^{\cdot} \xrightarrow{Fe(III),\ H_2O} ArCH_2OH \ .$$

The rate of reaction increases with increase of the DMSO content in the solvent and after the introduction of halide ions (Cl > Br > I).[100]

In contrast to the hexacyanoferrate(III), anhydrous iron(III) chloride is a fairly powerful oxidant and interacts with aromatic compounds to form chlorination and dehydrodimerisation products. These reactions have been known since the end of the last century and have been discussed in fair detail in reviews[101,102]. It is noteworthy that interest in reactions of this type has not flagged. Thus conditions have been found for the polychlorination of benzene with iron(III) chloride in a melt with NaCl in the presence and absence of O_2.[103] The oxidative coupling of alkylarenes by iron(III) salts is being particularly vigorously investigated[49,104–107].

The mechanism of the formation of biaryls proposed by Kovacic and coworkers[102] presupposes the protonation of the substrate by the HCl–$FeCl_3$ complex and further transformations of the type of cationic polymerisation, for example:



The reactivity of polymethylbenzenes should thus be determined by their basicity, but it has been shown[104–106] that the ionisation potential of the substrate is of decisive importance in these reactions and the formation of biaryls and diarylmethanes under the influence of $FeCl_3$ has much in common with anodic oxidation and includes therefore electron transfer [mechanism (1)] and electrophilic attack on the substrate via mechanisms (7), (9), and (10).

The oxidation of polymethylbenzenes by iron(III) chloride leads to the formation of diarylmethanes in all cases, except for *m*-xylene and mesitylene[49,103–106]. A detailed study of the oxidation of mixtures of methylbenzenes under these conditions showed that radicals of the benzyl type and hence diarylmethanes [see mechanism (6)] are formed from radical-cations with a high charge density in the substituted position of the aromatic ring (for example, in the case of durene). Accordingly, durene in mixtures with benzene, *p*-xylene, toluene, and mesitylene yields only diarylmethanes[103], while the analogous reaction of naphthalene can serve as a preparative method for the synthesis of 1-arylnaphthalenes[105]. The yield of products in the latter case depends on the nucleophilic properties of the alkylarene relative to the naphthalene radical-cation.

It is of interest that even durene and xylene give rise to ring-chlorinated compounds only as side products on treatment with $FeCl_3$.[49,102] Only mesitylene is appreciably chlorinated in the ring under these conditions[49]. The yield of chloromesitylene decreases with increase of the reaction temperature and in the presence of water and also increases with increase of the $FeCl_3$ mesitylene ratio. Chlorination thus probably proceeds via ligand transfer in the complex of $FeCl_3$ with the substrate radical-cation and not via mechanism (5).[49] The reactions under the influence of copper(II) halides takes place similarly (see below).

The oxidation of methylbenzenes by various iron(III) salts (chloride, nitrate, sulphate, acetate, and perchlorate) in boiling acetic acid in the presence of $HClO_4$ also leads to the selective synthesis of diarylmethanes[45,106]. It is of interest that the yield of diarylmethanes increases in the sequence PhPr-iso << PhEt < *p*-ClC_6H_4Me, while in the reactions of $FeCl_3$ with the same substrates in the absence of a solvent the opposite sequence obtains: PhMe < *p*-ClC_6H_4Me < PhEt < PhPr-iso.[101] The catalytic nature of the reaction in relation to the iron(III) salt in the presence of $HClO_4$, noted in many instances[105], has been shown[107] to be caused by the oxidation by perchloric acid of the $FeCl_2$ produced, so that the synthesis of diarylmethanes can be carried out in the $FeCl_2$–$HClO_4$ system[107].

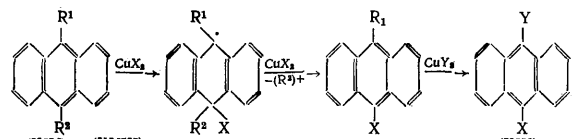
6. Copper(II) §

Copper(II) halides are usually employed as halogenating agents under both heterogeneous[107–117] and homogeneous[117–126] conditions. The photolysis of $CuCl_2$ in toluene affords benzyl chloride (86%) via the mechanism

$$PhCH_3 + Cl^{\cdot} \rightarrow PhCH_2^{\cdot} \xrightarrow{CuCl_2} PhCH_2Cl + CuCl \ .$$

Small amounts (0.5%) of chlorotoluenes and bibenzyl are formed at the same time[108].

The heterogeneous reactions of copper(II) salts usually involve the oxidation of a radical intermediate formed as a result of ligand transfer in the first stage [mechanism (2)]. The halogenation of anthracene and 9-substituted and 9,10-disubstituted anthracenes (XIV)–(XVIII) in non-polar solvents (PhCl, CCl_4, etc.) takes place in this way[109,110]:



(14)

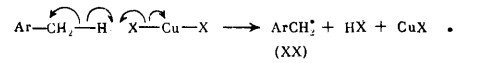
(XIV) – (XVIII) (XIX)

X,Y = Cl or Br

(XIV) a) R^1 = X, Y, Alk or Ar; R^2 = H; b) R^1 = X or Y; R^2 = Alk or Ar;
(XV) a) R^1 = OAlk or COAlk; R^2 = H; b) R^1 = H, R^2 = COAlk;
(XVI) R^1 = Alk or Ar; R^2 = Ar, Et or CH_2Ph;
(XVII) R^1 = Ar, Et, CH_2Ph, X or Y; R^2 = Me;
(XVIII) a) R^1 = OAlk or COAlk; R^2 = Me; b) R^1 = OAlk or OCOAlk; R^2 = H, Ph, Et or CH_2Ph.

§ The use of copper(III) complexes of oxidants has been described only for ascorbic acid and catechol [see Y.Yano, S.Takano, V.Kato, and W.Tagaki, J.Chem.Soc., Perkin Trans.II, 1227 (1979)].

According to mechanism (14), these reactions are accompanied by "transhalogenation" or substitution of hydrocarbon [compounds (XVI) [111,112]] or acyl [compounds (XVb) [113]] groups by the halogen. 9-Methylanthracene also reacts via mechanism (14),[109] but 10-substituted 9-methylanthracenes (XVII) and (XVIIIa) form under these conditions radicals of the benzyl type in the first stage[111,112] via the mechanism



(XX)

In the case of substrates (XVII) the radical (XX) is oxidised further via mechanism (5) to a halogenomethyl derivative $ArCH_2X$. More stable radicals containing an acyl or alkoxy-group [compounds (XVIIIa)] dimerise to the corresponding diarylethanes under these conditions via mechanism (6).[114]

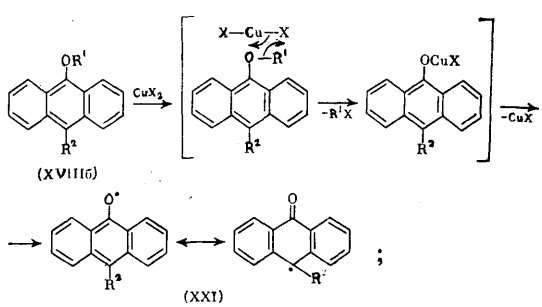
In the case of 9-alkoxy- (particularly methoxy) and 9-acyloxy-anthracenes (XVIIIb) there is also a possibility of the mechanism invcolving the "radicalisation" of the substrate[115].

Depending on the substituents in the 10-position, the radical (XXI) dimerises further to bianthronyl (XXII), is halogenated to halogenoanthrone (XXIII), or gives rise to quinomethides (XXIV).[115]

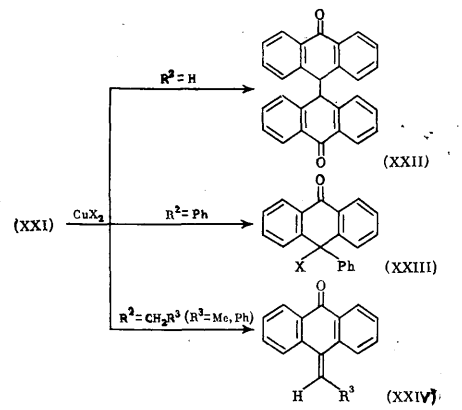
The reaction between $CuBr_2$ and 2-benzyloxynaphthalene proceeds analogously to reaction (15).[116] The product is a mixture of 2-benzyloxy-1-bromonaphthalene (17%), 1-bromo-2-naphthol (61%), di-β-naphthol (1.4%), and benzyl bromide (10%). It is of interest that $CuCl_2$ yields only products of the chlorination in the 1-position under these conditions. The reaction of $CuBr_2$ with 2-ethoxy- or 2-methoxy-naphthalene takes place in the same way[116]. The halogenation of pyrene, perylene, and tetracene by anhydrous copper(II) halides in non-polar solvents has also been described[117,118]. It has been suggested[116] that the reaction proceeds as homolytic decomposition of a π-complex of $CuCl_2$ with a substrate molecule. It is of interest that the oxidation proceeds in this instance in PhCl but not in CCl_4.[118]

Under homogeneous conditions, the CuX_2 molecule is as a rule solvated and cannot participate in the ligand transfer. In this case the mechanism involving electron transfer becomes more probable [mechanism (1)].

Thus, on treatment with CuX_2 (X = Cl or Br) in MeOH, 9-alkyl- and 9-aryl- anthracenes are converted by successive three-stage oxidation via mechanisms (1) and (8) into 10-alkyl and 10-aryl-10-methoxyanthrones (XXV).[119] As in other cases, when a methyl group is present, a benzyl-type radical is also formed from the substrate radical-cation and is converted via mechanisms (5) and (6) into methoxymethyl derivatives and diarylethanes (XXVII) (see above).



(XVIIIб) (XXI) (15)

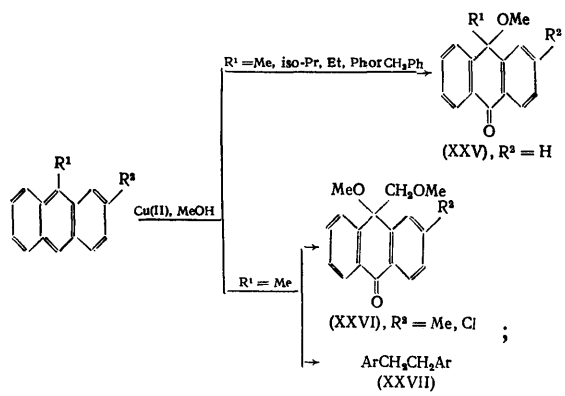


(XXI) (XXII) (XXIII) (XXIV)

It is of interest that the products of type (XXVI) and (XXVII) are not formed in the presence of a substituted methyl group R^1, which is believed[119] to be due to steric factors, preventing the stabilisation of the radical ArĊHR.

Under homogeneous conditions, copper(II) bromide brominates 3,4,5-trimethylanisole in the ring[120]. Alkylbenzenes react similarly with anhydrous $CuBr_2$, but in the presence of even small amounts of water the main products are diarylmethanes (benzyl bromides are also formed in smaller amounts). Mesitylene gives rise to only bromomesitylene in both cases[121].

The heterogeneous oxidation of toluene, *p*-xylene, and mesitylene with copper(II) chlorides also proceeds via a radical-cation formation stage according to Cummings and Milner[122] and leads to the formation of diarylmethanes and ring-chlorination products in conformity with mechanisms (7) and (8), the yield of the latter increasing with increase of the stability of the radical-cation and amounting to 20% for $C_6H_4Me_2$ and 90% for $C_6H_3Me_3$.



(XXV), $R^3 = H$; (XXVI), $R^3 = Me, Cl$; $ArCH_2CH_2Ar$ (XXVII)

$Ar = C_{14}H_9$, 2-$MeC_{14}H_8$ or 2-$ClC_{14}H_8$.

The yield of diarylmethanes decreases correspondingly from 90% for C_6H_5Me to 80% for $C_6H_4Me_2$. Diarylmethanes are formed exclusively when *p*-xylene is refluxed with $Cu(OAc)_2$ in acetic acid containing $HClO_4$.[45]

The ability of $CuCl_2$ to react via the ligand transfer mechanism [mechanism (2*b*)] has been used to oxidise the radical-cations generated by other oxidants[123]. The reaction of methylbenzenes with the peroxydisulphate anion in aqueous acetonitrile in the presence of $CuCl_2$ yields exclusively ring-chlorination products[123], while the pathway followed in the reaction of Cl^- with the corresponding radical-cations depends on the stability of the latter and the contributions of α-chlorination in the sequence mesitylene < *m*-xylene < *p*-xylene ≅ toluene are 25, 90, 100, and 100% respectively[123].

On the other hand, in the reaction of methylbenzenes with peroxydisulphate in acetic acid containing 9% of TFAA, the introduction of copper(II) acetate suppresses ring acetoxylation and promotes the formation of substituted benzyl acetates and trifluoroacetates. In the case of mesitylene the relative yield of the corresponding product is 92% [33% in the absence of copper(II)].[124]

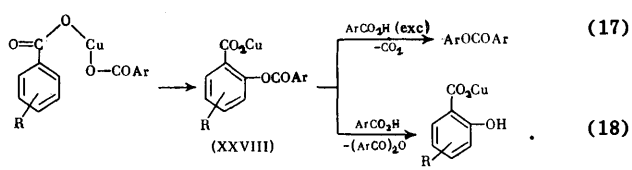
In conformity with the electron transfer mechanism, the oxidation of *p*-cymene in the AcOH–$S_2O_8^{2-}$–$Cu(OAc)_2$ system leads to isopropylbenzyl acetate[125]. The oxidation of the radical intermediate by copper(II) via mechanism (8) plays an important role in the acetoxylation of naphthalene under the same conditions. In the absence of copper(II) the reaction does not occur and the replacement of copper(II) by iron(III) leads to the formation of methyl- and acetoxymethyl-naphthalenes[125].

Copper(II) carboxylates introduce the acyloxy-group into the rings of alkyl derivatives of aromatic substrates via the following mechanism[126,127]:

$$2(R^1CO_2)_2Cu + PhR^2 \rightarrow R^2C_6H_4OCOR^1 + 2R^1CO_2Cu + R^1CO_2H \quad (16)$$

The yield of acyloxy-derivatives increases in the presence of copper(II) oxide, reacting with the liberated acid and (or) oxygen, which regenerates the copper(II) salt[127,128].

Substituted copper(II) benzoates can also be oxidised by an intramolecular mechanism with formation of *o*-benzyloxybenzoates (XXVIII):[128]



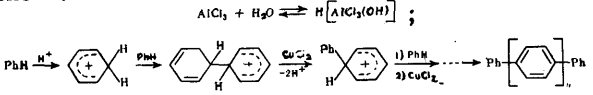
(17)

(18)

In the presence of water and an excess of acid, compound (XXVIII) is decarboxylated [mechanism (17)] with formation of the corresponding phenol after hydrolysis. Thus *o*- and *p*-toluic acids yield *m*-cresol under these conditions and *m*-toluic acid gives rise to a mixture of *o*- and *p*-cresols[126]. The thermolysis of copper(II) benzoate in benzoic acid produces phenyl benzoate, whose yield can be increased in the presence of oxygen, which regenerates copper(II). This reaction constitutes the basis of an industrial method for the synthesis of phenol from toluene via benzoic acid[126–128]. In aprotic media (Ph_2O, Ph_2CH_3, cyclohexane, etc.) the decarboxylation is suppressed and the reaction of compound (XXVIII) with the liberated acid molecule leads to the formation of salicylates [mechanism (18)].[126]

The interactions of alkylbenzenes (and also benzene, anisole, and diphenyl ether) with copper(II) benzoates usually yield the products of all three reactions. Thus in the case of toluene 51, 16, and 33% of the products correspond to the contributions of reactions (16), (17), and (18) respectively[126].

An interesting variant of the utilisation of the oxidising capacity of copper(II) is the application of $CuCl_2$ in combination with $AlCl_3$ for the cationic polymerisation of benzene[129]:

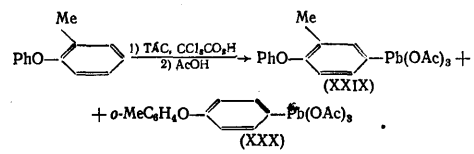


7. Lead(IV)

The reactions of aromatic compounds with lead(IV) salts include three main types of transformations depending on the type of substrate, nature of the ligands, and the conditions of synthesis: (a) the substitution of lead (plumbation) in the aromatic ring via S_E-type reactions, leading to the formation of aryl lead(IV) tricarboxylate[130–142], which then decomposes via heterolytic[138–142] or homolytic[130–137] mechanisms; (b) radical substitution via mechanism (3) under the conditions of thermal[128,143–154], photochemical[143–145], or radical-initiated[147] decomposition of lead(IV) carboxylates; (c) electron transfer from the substrate molecule via mechanism (1) with subsequent transformations of the radical-cation via mechanisms (5)–(10).[45,49,140,141,147]

Plumbation is usually less important in the reactions of lead(IV) carboxylates than, for example the substitution of thallium (thallation) in the case of thallium(III) (see below), but the contribution of this reaction becomes appreciable with increasing nucleophilicity of the aromatic ring in the presence of strong electron-donating substituents. Anisole and dimethoxybenzenes[130–133] are plumbated even on treatment with lead tetra-acetate (LTA) in acetic acid at 80 °C. Acetoxylation via a one-electron transfer mechanism with formation of a radical-cation [mechanisms (1) and (8)] and giving rise to acetoxyanisoles in the case of anisole (*o*/*p* = 35/65) is a competing reaction under these conditions. *m*-Dimethoxybenzene, which is the most reactive in plumbation reactions, exhibits the smallest tendency towards acetoxylation under these conditions[133]. The role of plumbation increases also with the increase of the electrophilicity of the lead(IV) atom as a result of the addition of strong acids. The replacement of acetic acid by halogenoacetic acids leads to the formation of lead(IV) halogenoacetates, giving rise to plumbation products even at room temperature[134–137]. The plumbation of 2,4-dimethoxybenzene by lead(IV) monohalogenoacetates leads to the trishalogenoacetates $ArPb(OCOCH_2X)_3$ (X = Cl, Br, or I) in yields of 94–99%.[134] The reaction with aromatic ethers PhOR (R = Me, Et, n-Bu, or Ph) proceeds similarly, but, when they are isolated from reaction mixture, hydrolysis products are formed—the oligomers of plumboxanes $\{[ArPb(OCOR)_2]_2O_2\}_m$, which readily form aryl-lead triacetates on treatment with acetic acid[134–137].

An increase of the number of halogen atoms in halogenoacetic acids makes possible direct plumbation of *o*-halogeno-substituted (F, Cl, Br, or I) anisoles and phenetoles, derivatives of diphenyl ether, alkylbenzenes, biphenyl, benzene, and halogenobenzenes[137]. It is of interest that the oxidation of iodobenzene with LTA in trichloroacetic acid yields iodosobenzene diacetate $PhI(OAc)_2$ (after treating the reaction mixture with acetic acid) and not the plumbation product[137]. The plumbation reactions involving substituted benzenes are highly selective and lead almost exclusively to *p*-derivatives. Monosubstituted diphenyl ethers are usually plumbated in the *p*-position of the unsubstituted ring. Only in the case of 2-methyl-1-phenoxybenzene were two products obtained [(XXIX)/(XXX) = 7/3]:[137]



The high selectivity of the plumbation reaction has been explained[137] by the increased reactivity of the *m*- and *o*-isomers in the protodeplumbation reaction under the influence of the acid in the reaction mixture, although this explanation is inconsistent with the reactivity sequence of other organometallic compounds in the protodemetallation reaction[146]. When the substrate is highly nucleophilic, the $ArPbX_3$ formed can react as an electrophile and can give rise to the products Ar_2PbX_2 or $ArAr'PbX_2$.[137]

On treatment with TFAA, aryl-lead tricarboxylates decompose rapidly with formation of aryl trifluoroacetates or (in the presence of aromatic substrates) biaryls via the mechanism[138,139]:

$$ArPb(OCOCF_3)_3 \underset{HOCOCF_3}{\overset{H^+}{\rightleftharpoons}} \overset{+}{Ar}Pb(OCOCF_3)_2 \xrightarrow{-Pb(OCOCF_3)_2} Ar^+ \begin{cases} \xrightarrow[-H^+]{Ar'H} ArAr' \\ \xrightarrow[-H^+]{TFAA} ArOCOCF_3 \end{cases}$$

The rate of decomposition of aryl-lead tristrifluoroacetates is proportional to the relative stability of the aryl cations formed, so that the derivative of *m*-nitrophenyl-lead is most resistant to the action of TFAA.[138] It is of interest that the rate of formation of biaryls under these conditions is higher than the rate of trifluoroacetoxylation; this has been explained[139] by the preliminary formation of a π-complex between the hydrocarbon molecule and the species in which the Ar–Pb band is still preserved. The yield of biaryl increases with increase of the number of electron-donating substituents in the substrate ring.

It is noteworthy that the oxidation of xylenes, durene, mesitylene, and hexamethylbenzene by lead(IV) trifluoroacetate in the TFAA–CH_2Cl_2 system yields, apart from biaryls, also diarylmethanes (together with products of acetoxylation in the ring and in the side chain), i.e. the process also includes an electron transfer stage and the formation of radical-cations [see mechanisms (1), (7), and (9) [49,140,141]]. The oxidation of toluene with lead tetraacetate in TFAA produced after hydrolysis a mixture of cresols (28%),[140–142] bitolyls (4.5%), and *p*-tolylphenylmethane (0.6%), the yield of bitolyls increasing with increase of the ratio TFAA/LTA.[140,141]

In the absence of strong acids, the reactions of alkylarenes with LTA in acetic acid at 80 °C lead exclusively to α-acetoxylation products[132,149–152]:

$$R^1\text{—}C_6H_4\text{—}CH_2R^2 \rightarrow R^1\text{—}C_6H_4\text{—}CHR^2OAc\ ;$$

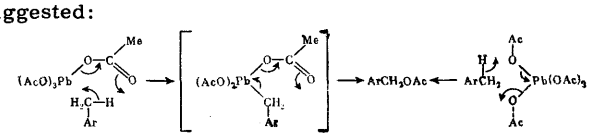
R^1 = H, OMe, Me, t-Bu, Br, or NO_2; R^2 = H or Me.

Di- and tri-phenylmethanes, fluorene, and hexamethylbenzene react similarly. According to Radhakrishnamurti and Mohapato[152], the reaction kinetics are described by the equation

$$-\frac{d[Pb(IV)]}{dt} = k[ArH]^n[Pb(IV)],$$

where $n = 2$ for substituted toluenes (R^1 = H, OMe, or Me and R^2 = H) and $n = 1$ for Ph_2CH_2, Ph_3CH, and fluorene. The rate of reaction remains unchanged in the presence of small amounts of H_2O (5% in acetic acid) and increases when acetic acid is replaced by propionic acid and also in the presence of Cl^-, Mn^{2+}, and dimethylformamide (DMF). The addition of other solvents inhibits the reaction: Me_2SO > MeCN ≅ cyclohexane > CH_2Cl_2 > $PhNO_2$ > PhH.[152]

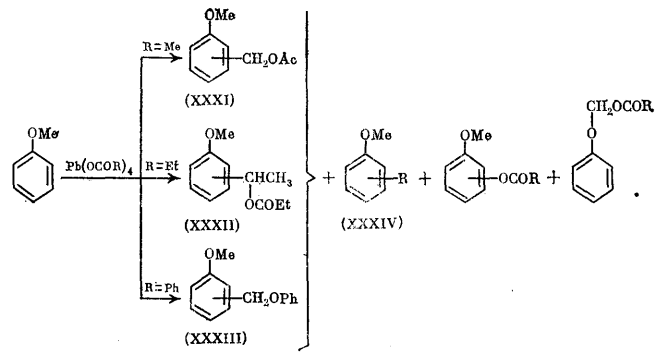
The detailed mechanism of this reaction has still not been elucidated. It is believed that the principal stage is the decomposition of the complex of the substrate with LTA[149–152] involving a cyclic transfer of an electron pair, which results in the immediate formation of the two-electron oxidation product. The intermediate formation of a benzyl derivative of lead, i.e. plumbation of the side chain, has actually been suggested:



On irradiation (at 20–30 °C) and at temperatures above 80 °C, the reaction has a distinct radical character. Thermal[149,151,153] and photochemical[143,144,154] decomposition of lead(IV) carboxylate is accompanied by decarboxylation and the formation of aryl or alkyl radicals. The rate of decarboxylation increases in the presence of pyridine[144] and alkali metal acetates[101] and halides[144]. In conformity with mechanism (3), LTA oxidises toluene in acetic acid at 100 °C with formation of benzyl acetate, a mixture of xylenes, methylbenzyl acetates, and toluooylacetic acid[153]. The yield of benzyl acetate increases with increase of the ratio PhMe/AcOH and diminishes with increase of reaction temperature. Benzyl acetate is also formed in the photochemical reaction at room temperature[143,144]. Under these conditions, benzene gives rise to a mixture of toluene, benzyl acetate, and bibenzyl[145].

It is of interest that, when *p*-toluic acid is refluxed with LTA in trifluoroacetic acid in the presence of alkali metal chlorides or bromides, products of the oxidative halogenation of the aromatic ring are formed in high yields—3-halogeno-4-methylbenzoic acids[54]. Since the selectivity of this reaction is extremely high (>90%) for a purely radical process, the authors[54] do not rule out an appreciable contribution of the reaction via mechanism (8) with participation of mixed halide–arenecarboxylate complexes of lead [cf. the analogous reaction for cerium(IV)—see above].

In the presence of radical reaction initiators (monomethyl oxalate, di-isopropyl peroxydicarbonate), even substrates such as anisole can be oxidised via a radical mechanism[146]. The reactions with lead(IV) tetracarboxylates proceed under these conditions via the mechanism



It has been shown that, when the products (XXXI), (XXXII), and (XXXIV) are formed via mechanism (3), acyloxylation involves the intermediate formation of an anisole radical-cation [see mechanisms (1) and (8)]. The radical $PhOCH_2^{\bullet}$, formed from this radical-cation, reacts with the substrate to give compound (XXXIII).

Lead(III) derivatives formed via the mechanisms

$$RCO_2Pb(IV) \rightarrow R^{\bullet} + CO_2 + Pb(III)\ ;$$
$$R^{\bullet} + RCO_2Pb(IV) \rightarrow [R^+] + RCO_2Pb(III)$$

play an important role in the radical reactions. These derivatives act further either as one-electron oxidants or as sources of radicals[144,146].

As already mentioned above, one-electron oxidation processes, particularly acyloxylation in the ring and in the side chain and the formation of diarylmethanes in oxidative coupling reactions, compete with electrophilic and radical substitution processes. The role of such reactions increases with diminution of the ionisation potential of the substrate and with increasing electrophilicity of the oxidant. As for cobalt(III) (see above), LTA in an AcOH–$HClO_4$ mixture[45]

and lead(IV) trifluoroacetate in dichloroethane[49] oxidise mesitylene, pseudocumene, durene, and other methylarenes only to diarylmethanes. In contrast to toluene, 2-methylnaphthalene undergoes ring acetoxylation on treatment with LTA in acetic acid to a greater extent (~33%) than α-acetoxylation (~16%) or α-oxidation (~11%).[128] Finally at 105 °C LTA in acetic acid oxidises selectively the methyl group in 4-isopropyl-1-methylanisole to give the corresponding benzyl acetate in 55% yield[147].

8. Thallium(III)

The reactivity of thallium(III) salts depends greatly on the nature of the ligands. Thus the covalent thallium(III) sulphate and chloride are almost inert in reactions with aromatic hydrocarbons[155,156]. The slow reaction of alkylarenes with thallium(III) acetate in acetic acid is appreciably accelerated in the presence of H_2SO_4, HNO_3, BF, and particularly $HClO_4$.[156] The main product in the last case is the organothallium compound $ArTl(OAc)ClO_4.H_2O$. Biaryls, benzyl acetates (from methylarenes), bibenzyl (from PhMe), and diarylmethanes (in the case of *p*-xylene) are formed in smaller amounts[155,156].

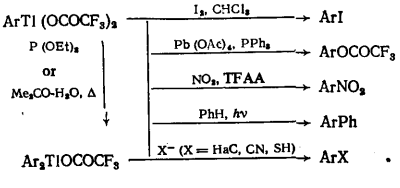
Under the same conditions, thallium(III) nitrate nitrates benzene (1.6%) and toluene (13%), but the reaction with *p*-xylene leads to a mixture of *p*-toluic acid (16.2%), toluic aldehyde (7.5%), and nitroxylene (6.1%).[156]

Thallium(III) carboxylates decarboxylated photochemically with formation of alkyl radicals. In the presence of benzene the photolysis of $Tl(OAc)_3$ gives a very low yield of a mixture of xylenes and phenylacetic acid[157].

The ionic thallium(III) trifluoroacetate (TTFA) shows the highest reactivity. The mode of its reaction with aromatic compounds is determined primarily by the oxidation potential of the substrate. Benzene, alkylbenzenes, and other compounds with fairly high ionisation potentials (>8 eV) react with TTFA to form products of S_EAr reactions—arylthallium bistrifluoroacetates[158-160].

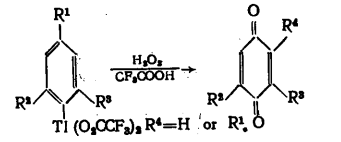
Dithallation on treatment with an excess of TTFA in TFAA has been observed only for anisole[161]. It is of interest that the monothallium derivative, formed in the presence of an equimolar ratio of the reactants (−25 °C, 15 min), is partly converted into 2,4-di(bistrifluoroacetoxythallium)anisole on standing for a week; the authors[161] explained this result by the stabilisation of the *o*-derivative as a result of the formation of a four-membered chelate ring. The thallation of 2,3,5,6-tetrafluoroanisole with TTFA does not occur in TFAA, but can be carried out in the presence of CF_3SO_3H.[162]

The kinetic and mechanistic aspects of thallation have been discussed in detail by Robey[159] and in reviews[158,160]. On the basis of arylthallium bistrifluoroacetates, McKillop and Taylor developed a whole series of valuable synthetic methods, particularly those represented schematically below:



These reactions have been described in fair detail in reviews[159,160]. Methods have also been found for the synthesis of aryl fluorides [by treating compound (XXXV) with KF in the presence of BF_3][163] and areneboronic acids (by reaction with diboranes in tetrahydrofuran)[164].

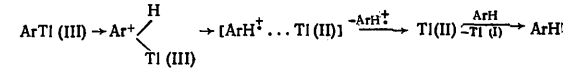
Treatment of compound (XXXV) with a solution of 90% H_2O_2 in TFAA gives rise to *p*-quinones, the reaction being accompanied by the migration or elimination of substituents in the aromatic ring:



;

Elimination is observed for R^1 = Cl or OMe and also for R^1 = Me in the case of mesitylene. In other cases the group R^1 migrates to the 2-position (R^1 = H, Me, Et, or t-Bu)[165].

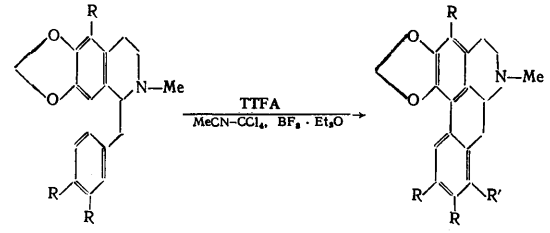
The final product of the reduction of thallium(III) is always a thallium(I) salt. In this case the transfer of two electrons [as for lead(IV)] can probably take place both synchronously and consecutively. According to Elson and Kochi[166], in the reaction of TTFA with alkylbenzenes thallium(III) acts as a one-electron oxidant and in the first stage gives rise via mechanism (1) to radical-cations of aromatic substrates, which were detected by EPR [the authors[166] also noted that thallium(III) makes it possible to generate a wide variety of radical-cations under static conditions, in contrast to the reaction of cobalt(III), which requires the use of a flow technique[47]]. Further reactions of the complex $ArH^{\ddagger}$ ... Tl(II) can be described by the following mechanism[167], depending on the substrate:



.

The reactions of TTFA via mechanisms (1) and (9) with substrates having low ionisation potentials (<8 eV) (polyalkoxybenzenes, naphthalenes, etc.) in TFAA, CCl_4, and acetonitrile give symmetrical biaryls in yields up to 99%.[167] The oxidation of durene in TFAA[167] and of *p*-xylene in the $Tl(OAc)_3$–AcOH–$HClO_4$ system leads to the formation of diarylmethanes[44,45].

Oxidative coupling can also take place intramolecularly[168], which has been used, in particular, in the synthesis of alkaloids of the type of homoaporphine and aporphine (XXXVIa):

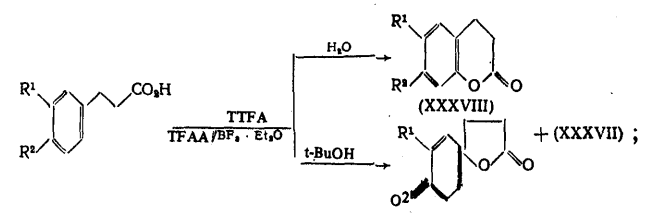


;

(XXXV) (a) R′ = H, (b) R′ = OAc .

It is of interest that the replacement of TTFA by $Tl(OAc)_3$ leads to the ring acetoxylation product (XXXVIb) under the same conditions[168].

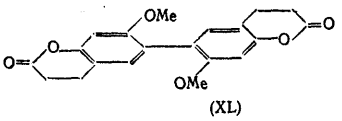
One should also note that the aromatic radical-cation can react intramolecularly with a carboxy-group to form dihydrocoumarins (XXXVIII) and spirolactones (XXXIX) [(XXXVII) : (XXXIX) = 3 : 1][169]:



(XXXVI) (XXXVIII) (XXXIX)

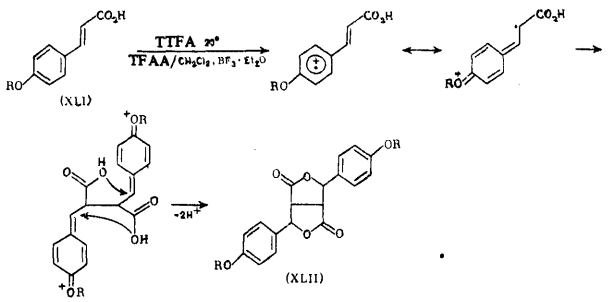
(a) $R^1 = R^2 = OMe$; (b) $R^1 = OMe$, $R^2 = H$; (c) $R^1 = H$, $R^2 = OMe$.

Not only the presence of the CO_2H group [the methyl ester of the acid (XXXVIIa) yields only the corresponding 2,2-biaryl] but also the position of the methoxy-group is important for the course of the reaction. Thus, under the reaction conditions, compound (XXXVIIb) only dimerises, while compound (XXXVIIc) gives rise to the product (XL) of simultaneous cyclisation and dimerisation[169]:



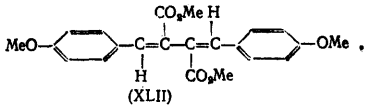
(XL)

The synthesis of the bislactone (XLII) is also extremely elegant[170]:



(XLI) (XLII)

The unsubstituted acid PhCH = CHCOOH does not react via this mechanism, while the methyl ester of the acid (XLI) yields the diene (XLII) as a result of the deprotonation of the radical dimerisation product:

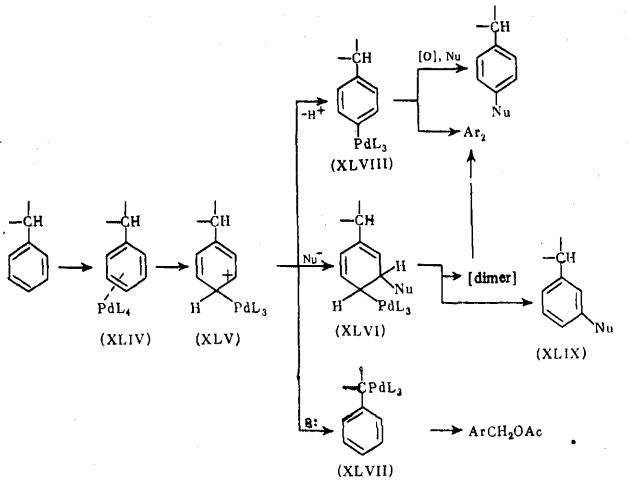


(XLII)

9. Palladium(II)

Palladium occupies a special place in the series of oxidants examined. Having the lowest oxidation potential, it exhibits the maximum selectivity in reactions with aromatic compounds and readily undergoes secondary oxidation on treatment with fairly mild oxidants, which makes it possible to use it in catalytic processes. On the other hand, the chemistry of palladium complexes is the most complicated and the mechanisms of its reactions are still controversial. The extensive applications of palladium(II) complexes in fine organic synthesis and technological processes have been described in a number of monographs[101,171,172] and reviews devoted to acetoxylation[128,173] and oxidative coupling[50,173,174] and for this reason the present review includes mainly general postulates concerning the mechanisms of the reactions of palladium(II) and new data not included in the reviews mentioned above.

The rate and mode of the reactions of alkylarenes with palladium(II) complexes depend very markedly on the composition of the palladium(II) coordination sphere. According to the existing ideas[171-175], the first stage in these reactions is the formation of the π-complex (XLIV) which, depending on the reaction conditions, is then converted into a σ-arylpalladium intermediate (XLV) and is attacked by a nucleophile with formation of the adduct (XLVI) or (in the presence of α-hydrogen and under the influence of a base) is converted into an α-substitution product—the benzylpalladium intermediate (XLVII):

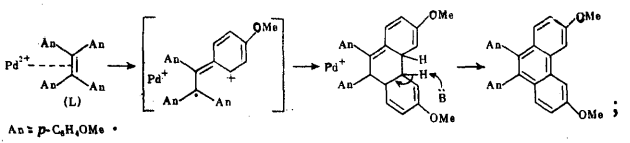


(XLIV) (XLV) (XLVI) (XLVII) (XLVIII) (XLIX)

On the basis of a comparison of the kinetics of the oxidative coupling and arylation reactions of olefins in the presence of palladium(II), it has also been suggested that palladium(II) can be inserted in the aromatic C–H bonds with formation of the species $ArPdH^{2+}$, whose stability has been explained[176] by the presence of a three-centre two-electron bond. According to the authors[176], a reaction of this type may constitute an intermediate stage in the slower reaction involving the formation of compound (XLVII), but there are as yet no data confirming this hypothesis.

The formation of π-complexes of benzene with $PdSO_4$ in 90% H_2SO_4 (23 °C) has been confirmed spectroscopically[177]. According to Rudakov et al.[177], the decomposition of these complexes leads to oxidative coupling products, benzene, and benzyl complexes of palladium(I), whose hydrolysis gives rise to zerovalent palladium, palladium(II), and benzene in proportions of 1 : 1 : 2.

The electron transfer in complexes of type (XLIV) proceeds, according to Eberson and Gonzalez[175], only in the presence of bases. Thus, on treatment with water, the complex (L) decomposes with liberation of the π-donor (tetra-anisylethylene), but on treatment with a stronger base (lutidine) it gives rise to an oxidation product:



(L)

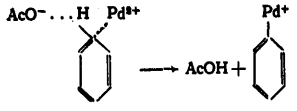
An = p-C_6H_4OMe .

The deprotonation of the complex (XLV) leads to the S_EAr reaction product—the arylpalladium compound (XLVII), which then decomposes with formation of a biaryl. The detailed mechanism of the last reaction is still not clear. It is

known that palladium(II) halides are inert in reactions with alkylarenes and that only $PdCl_2$ gives rise to oxidative coupling products in the presence of a fivefold excess of an alkali metal acetate in acetic acid[171-181]. It is believed[174,175,179-181] that the reaction proceeds in this case via the intermediate (XLVI) and involves its dimerisation with formation of bridge bonds involving chloride ions. The subsequent decomposition of the dimer gives rise to biaryl, zerovalent palladium, palladium(II), and acetic acid (Nu = OAc). At the same time the rate of oxidative coupling increases greatly in the presence of $HClO_4$, whereupon AcO^- is displaced from solution and the reaction proceeds via the usual S_EAr mechanism ($k_H/k_D = 5$ has been obtained for C_6H_6 and C_6D_6 [179,181] as in mercuration). It is believed[179] that in this instance the coupling reaction proceeds via a stage involving the formation of a mixed arylpalladium(II)–arene complex:

$$[Ar{-}Pd^+ \ldots ArH] \rightarrow Ar{-}Ar + H^+ + Pd\,(0)\ .$$

On the basis of the study of the kinetics of the oxidation of PhH to Ph_2 with palladium(II) perchlorate in the H_2O–AcOH–$HClO_4$ mixture[176], it is concluded that the rate-limiting stage of the reaction under these conditions is electrophilic attack on the aromatic ring by the $Pd(OAc)^+$ ions with simultaneous proton transfer to the coordinated or free acetate ion:



The σ-phenylpalladium cation disproportionates further to zerovalent palladium, palladium(II), and Ph_2. The rate of reaction decreases when acetic acid is replaced by TFAA and when Cl^- or Br^- is introduced. The activity of palladium(II) adsorbed on a carboxylic acid cation-exchange resin increases with increasing fraction of neutralised carboxy-groups[178].

The presence of an excess of acetate ions is not, however, essential for oxidative coupling. The complexes of $PdCl_2$ with ethylene, styrene, and cyclohexene give rise to Ph_2 in yields of 99, 63, and 3% respectively on oxidation of benzene, i.e. the yield varies in parallel with the decrease of the stability of the complexes (the yield in the absence of the olefin is 40%). The activity thus depends on the rate at which benzene exchanges with the olefin and $AgNO_3$ plays the role of a chloride ion acceptor and the co-oxidant (NO_2 is evolved in the reaction)[182,183].

Oxidative coupling under the influence of palladium(II) salts takes place readily with organic derivatives of boron, thallium, mercury etc., the arylpalladium intermediates being formed as a result of the substitution of the metal by palladium[171-174].

The scope of the method is extended by the fact that substituents in the aromatic ring have only a weak influence on the rate of the coupling reaction ($\rho = -0.4$).[184] A whole series of methods of synthesis of biaryls under the influence of palladium(II) complexes (including the sulphate and carboxylates[50,171-174,178] and the β-diketo-complexes[185,186]) in combination with thallium(III) and mercury(II) salts[187,189], metallic copper[188], and zirconium compounds[192] in stoichiometric[50,173,181] and catalytic[174,190] amounts in solvents (usually acetic acid) or in their absence[174,190] have been developed. The side reactions in the oxidative coupling (usually acetoxylation—see below) are effectively suppressed when the process is carried out under oxygen pressure (50–100 atm), which renders catalytic oxidation methods especially promising. In particular, the presence of heteropolyacids (HPA)—compounds soluble in water and organic solvents (HPA can contain phosphorus, silicon, arsenic, boron, etc.; the vanadium, molybdenum, and tungsten compounds are the most reactive) makes it possible to regenerate palladium at lower O_2 pressures (~25 atm) and in the absence of Cl^- ions and thus to avoid the chlorination of the substrate[191].

The second pathway in the decomposition of the intermediate (XLVI) involves its conversion into the product (XLIX) of nucleophilic substitution in the ring. The formation of acetoxy- and nitro-arenes under the influence of palladium(II) nitrate in acetic acid probably proceeds via this mechanism[192]. The addition of H_2O, $HClO_4$, and iron(III) salts shifts the reaction towards oxidative coupling.

Benzene, toluene, and chlorobenzene can be nitrated with preparative yields in the $Pd(NO_3)_2$–$NaNO_2$ and $Pd(OAc)_2$–$NaNO_2$ systems (100 °C, RCOOH; R = t-Bu, Me, or $ClCH_2$).[193] The reaction leads to a mixture of nitro- and acyloxy-arenes, the yield of nitration products being a maximum when palladium(II) and $ClCH_2COOH$ are used. On replacing $NaNO_2$ by N_2O_4, the nitration reaction in the presence of $Pd(OAc)_2$ takes place under catalytic conditions[193]. The analogous reaction in acetic acid (100 °C) yields in the case of benzene a mixture of nitrobenzene and phenyl acetate, whose proportions vary from 1:2 to 2:1 depending on the conditions[194].

The acetoxylation of alkylarenes under the influence of palladium(II) acetate requires, according to Eberson and Gonzalez[175], the involvement of the monomeric $Pd(OAc)_2$. The trinuclear cluster $Pd_3(OAc)_6$ is stable in the solid state and in acetic acid at temperatures below 35 °C (in benzene—below 80 °C) and decomposes on treatment with acetates [the monomeric $Pd(OAc)_2$ is formed on treatment with Et_4NOAc, while alkali metal salts give rise to the dinuclear complexes of $Pd(OAc)_2$ or MOAc promoting α-acetoxylation—see below][175].

In the absence of an excess of AcO^- the "nuclear" acetate can be obtained as the main product ($MeArOAc/HArCH_2OAc = 7/3$) when MeArH in boiling acetic acid is treated with $Pd(OAc)_2$ in the presence of O_2.[175] Although the reaction is catalytic, it is too slow for practical purposes[175]. In conformity with the structure of compound (XLVI), acetoxylation takes place preferentially in the *m*-position in the presence of *o*- and *p*-directing substituents in the substrate molecule (naphthalene gives rise to a mixture of different amounts of α- and β-acetates). The yield of aryl acetate greatly increases in the presence of co-oxidants. The best results were obtained for $Pd(OAc)_2$ using $K_2Cr_2O_7$, but LTA, $KMnO_4$, CrO_3, ClO_3^-, and O_2 are also fairly effective[195-198]. The isomeric composition of the ring acetoxylation products is determined under these conditions by the ratio of the rates of oxidation of the arylpalladium intermediates (XLVI) and (XLVII) and depends both on the reaction conditions (the yield of the *m*-isomer usually increases with increase of reaction temperature[195-198]) and on the nature of the co-oxidant).

In the presence of $Hg(OAc)_2$ the first stage involves the mercuration of the substrate. The subsequent transmetallation leads to compound (XLVII), whose oxidation in the presence of AcO^- gives rise to the acetoxylation product which retains the structure (XLVII). Thus mainly *p*-cresyl acetate is formed from toluene in the $Pd(OAc)_2$–$Hg(OAc)_2$–$K_2Cr_2O_7$ system[195]. The modification of this reaction using mercury derivatives of arenes and a number of nucleophiles makes it possible to obtain a wide variety of oxidative nucleophilic ring-substitution products (Nu = OAc, N_3, Cl, Br, NO_2, CN, or SCN).[193]

Potassium peroxydisulphate is particularly effective as a co-oxidant in the presence of palladium(II) complexes with

N-containing ligands (2,2-bipyridyl, pyridine, and isoquinoline), the ratio *o*/*p* amounting to 39/6 for pyridine and 5/44 for 2,2-bipyridyl [198] for the same yield of the *m*-isomer in both cases (54–51%).

An increase in the number of alkyl substituents in the substrate molecule shifts the reaction in the $K_2S_2O_8$–AcOH–$Pd(OAc)_2$–2,2′-py_2 system towards α-acetoxylation, whose contributions for toluene and *o*- and *p*-xylenes amount to 10, 39, and 86% respectively. Under these conditions, mesitylene and durene produce only the corresponding benzyl acetates under these conditions. The yield of the α-acetoxylated products also increases in the presence of an excess of acetate ions[196–198].

The practical value of the ring-acetoxylation process is very great, in particular as regards the development of methods for the direct oxidation of arenes to phenols. We may note that the oxidation of benzene to phenyl acetate via the reaction $PhH + AcOH + \frac{1}{2}O_2 \rightarrow PhOAc + H_2O$ requires the use of metallic palladium in combination with bismuth, selenium, cadmium, iridium, rhodium, ruthenium, and gold (in the latter case the conversion of PhH reaches 70–75%),[172] while according to the data of Venkateswar and Rao[199] the analogous process involving $PdCl_2$ on SiO_2 [in the presence of NaOAc and $Cd(OAc)_2$ at 170 °C] gives PhOAc in 8.43% yield and a selectivity of 100%.

The acetoxylation of a side chain constitutes yet another pathway in the reactions of alkylarenes with palladium(II) salts. In the absence of co-oxidants an increase of the AcO^- concentration and the $PdCl_2$–MOAc–AcOH–ArMe leads to the suppression of the oxidative coupling by α-acetoxylation. In the oxidation of toluene the ratio $MeC_6H_4C_6H_4Me$: $PhCH_2OAc + PhCH(OAc)_2$ changes from 38 to 0.0074 as the ratio NaOAc/$PdCl_2$ varies from 5 to 20.

According to Eberson and Gonzalez's data[175], α-acetoxylation is promoted by the formation of dinuclear complexes, which give rise to steric hindrance to attack by an external nucleophile in the stage of the intermediate (XLIV) or favour the reaction involving the formation of $ArCH_2OAc$ when the nucleophile is bound in the π-complex (XLIV) as the ligand. The yield of the substituted benzyl acetate depends both on the amount of MOAc and on the nature of the M^+. In most cases the maximum activity is shown by Pd/Rb system[175].

α-Acetoxylation is favoured by the addition of Ph_3P, in the presence of which two stable benzylpalladium complexes of the type of (XLVII) have been isolated[175]: $PdCl(Ph_3P)_2 \cdot CH_2Ph$ and $Pd_2Cl_2(Ph_3P)_2(CH_2Ph)_2$. On treatment with potassium acetate in acetic acid, both compounds give rise to benzyl acetate, while treatment with silver acetate under the same conditions results in the formation of benzyl acetate and benzylidene acetate.

In contrast to the weak influence of substituents on the rate of oxidative dimerisation[182,184], the "benzyl" oxidation depends markedly on this factor. Thus the reaction of PhMe with $Pd(OAc)_2$ in acetic acid (at 90 °C) leads to $PhCH_2OAc$ (80%), PhCHO (4%), and $PhCH(OAc)_2$ (6%), while *p*-$CH_3C_6H_4CH_3$ gives rise to 96% of the corresponding benzyl acetate and *p*-$NO_2C_6H_4CH_3$ gives 2% of this derivative[200].

Under these conditions, xylenes form a mixture of α-acetate and α,α- and α,α′-diacetates[180]. *o*- and *m*-Xylenes react more slowly than *p*-xylene but yield analogous products. The reactivity of methylarenes decreases in the sequence toluene > xylene > mesitylene > durene > hexamethylbenzene, i.e. contrary to the ability of the substrate to generate the radical-cation.

In the presence of $Sn(OAc)_2$ and solid carriers with a high surface area (wood charcoal, Al_2O_3) the acetoxylation of toluene under oxygen pressure becomes a catalytic reaction[171,172]. According to the data of Starchevskii et al.[201], the active centres under these conditions are cluster species containing palladium in the lowest oxidation states and not palladium(II) complexes.

The influence of oxygen on reactions in the $ArCH_3$–$PdCl_2$–MOAc–AcOH system has not so far found a satisfactory explanation. In the presence of O_2 and for low values of the ratio $AcO^-/PdCl_2 \cong 5$, the rate of oxidative coupling increases and acetoxylation slows down[172,175]. On the other hand, inhibition is not complete even at 50 atm O_2 [175] (the radical reactions of LTA, for example, are inhibited by even traces of molecular oxygen[175]), while the replacement of $PdCl_2$ by $Pd(OAc)_2$ results in the formation of aryl acetates in the presence of O_2 as the main reaction products[175]. Furthermore, the inhibiting effect of O_2 is absent for higher values of $AcO^-/PdCl_2$, amounting to 10–20, and under these conditions α-acetoxylation can be carried out catalytically (see above). Finally, on oxidation in the presence of O_2, aldehydes are formed only in the case of polymethylbenzenes[175]. The role of oxygen complexes of palladium(II) and zerovalent palladium[175] has so far been scarcely investigated in these reactions.

As for other oxidants, palladium(II) trifluoroacetate occupies a special place[202,203]. Trifluoroacetoxylation proceeds smoothly only in the case of naphthalene (120 °C) and yields exclusively 1-naphthyl trifluoroacetate[150] (the acetoxylation of naphthalene requires increased temperatures and gives rise to a mixture of two isomers—see above). In the case of benzene the analogous reaction proceeds in the presence of alkali metal trifluoroacetates and is suppressed by water[203]. In the absence of additives, fluoro-, chloro-, and nitrobenzenes give rise to biaryls, while benzene produces biphenyl and terphenyl (the relative yields depend on the reaction time)[203]. In the reaction with $Pd(OAc)_2$ in TFAA alkylarenes form mixtures of biaryls and diarylmethanes in the case of toluene, xylenes, hemimellitol, and pseudocumene, while in the case of durene and mesitylene biaryls are formed exclusively[204].

* * *

Thus analysis of the literature data shows that the oxidation of aromatic compounds by variable-valence metal complexes has been the subject of increasing attention by investigators during the last fifteen years. The range of reactions in which aromatic substrates can be involved is extremely wide and their products, which are in many instances obtained in preparative yields and are distinguished by a high selectivity, are just as varied. In addition to clearly synthetic problems, these processes make it possible to solve problems associated with the reactivity of highly active intermediates—aromatic radicals, radical cations, cations, as well as organometallic compounds and charge-transfer complexes.

There is no doubt that further development of this field of transition metal chemistry will prove to be extremely fruitful for the development of new synthetic methods and syntheses of compounds with valuable properties, for example, bifunctional monomers, derivatives of biphenyl and diphenylmethane, and phenols.

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