Mechanism of Oxidation of Methylbenzenes by Palladium(II) in Trifluoroacetic Acid. One-electron Transfer and Electrophilic Substitution

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The oxidation of methylbenzenes by Pd^{II} in CF_3CO_2H to give diarylmethanes has been shown to occur *via* a one-electron transfer mechanism.

Traditionally, the oxidation of organic compounds by Pd^{II} in solution is considered to proceed by a two-electron mechanism involving formation of an organometallic intermediate and its decomposition without participation of free radicals.[1,2] We have obtained evidence that methylbenzenes are oxidized by Pd^{II} in CF_3CO_2H solution to give diarylmethanes *via* initial one-electron transfer from arene to Pd^{II} to form an aromatic radical cation. The following results indicate the Pd^{II} one-electron transfer process. (i) The products and the relative reactivities of the arenes were found to be the same for oxidation by Pd^{II} and the one-electron oxidant, $[Co^{III}W_{12}O_{40}]^{5-}$. (ii) A correlation between the reaction rate and the arene ionization potential was established. (iii) Radical intermediates were detected by e.s.r. spectroscopy during the oxidation of methylbenzenes by Pd^{II}.

The products of oxidation of methylbenzenes by Pd^{II} in CF_3CO_2H are biaryls (**1**), diarylmethanes (**2**) (Table 1), and small amounts of aldehydes ($\leqslant 3\%$).[3][†] Biaryls are known to form by a non-radical mechanism involving electrophilic substitution of Pd^{II} for hydrogen in the arene nucleus.[1,2,4] The mechanism of diarylmethane formation remains as yet unclear. It has been suggested[3] that diarylmethanes are formed through intermediates of the π-allyl type.

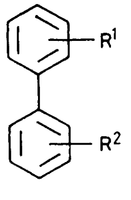
[†] Reactions were carried out in sealed glass ampoules. Products were analysed by g.l.c.–mass spectrometry (LKB-2091 instrument). E.s.r. spectra of radicals were obtained upon melting of thoroughly outgassed frozen solutions of ArMe (0.2—0.5 mol l^{-1}) and $Pd(OAc)_2$ (0.05 mol l^{-1}) in CF_3CO_2H in the cavity of an ER-200D Bruker spectrometer.

Table 1. Oxidation of (i) arenes and (ii) arenes in competition with benzene to give biaryls (**1**) and diarylmethanes (**2**) using $Pd(OAc)_2$ or $K_4H[CoW_{12}O_{40}]$ (CoW_{12}) (0.05 mol l^{-1}) in CF_3CO_2H (90 °C, 5—6 h).[a]

(i) $ArMe_n$[b]	Products, % yield[c]
C_6H_6	(**1a**) 44
MePh	(**1b**) 45; (**2b**) 25 [16]
p-$Me_2C_6H_4$	(**1f**) 7; (**2e**) 65 [36]
1,3,5-$Me_3C_6H_3$	(**2f**) 87 [26]; (**2g**)[d] 5 [12]
1,2,4,5,-$Me_4C_6H_2$	(**2h**)[e] 22 [11]; (**2i**) 10 [7]

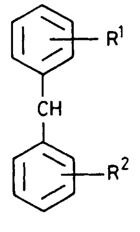
(ii) $ArMe_n$ + C_6H_6[f]	Products, % yield	$ArCH_2Ar'/ArCH_2Ph$
MePh	(**1a**) 7; (**1b**) 18; (**1c**) 15; (**2b**) 20 [9]; (**2a**) 7 [3]	3 [3]
p-$Me_2C_6H_4$	(**1a**) 2; (**1d**) 7; (**2e**) 80 [27]; *p*-(**2b**) 1.3 [0.5]	62 [54]
1,3,5-$Me_3C_6H_3$	(**1e**) 1; (**2g**)[d] 3 [7]; (**2f**) 74 [24]; (**2c**) 1.5 [0.5]	50 [48]
1,2,4,5-$Me_4C_6H_2$[g]	(**2h**)[e] 16 [5]; (**2i**) 7 [6]; (**2d**) 6 [5]	1 [1]

[a] The figures in square brackets are yields obtained on oxidation with CoW_{12}. [b] $[ArMe_n]$ = 1.5 mol l^{-1}. [c] Based on initial Pd^{II} or Co^{III}. [d] (**2g**) is formed owing to acid disproportionation of mesitylene to tetramethylbenzene and xylene. The yield of (**2g**) has not been used in the calculation of relative reactivity of mesitylene (Table 2) because it characterizes the reactivity of tetramethylbenzene rather than mesitylene. [e] (**2h**) is the product of substitution of the durene methyl group. [f] $[ArMe_n] = [C_6H_6]$ = 1 mol l^{-1}. [g] $[Me_4C_6H_2] = [C_6H_6]$ = 0.3 mol l^{-1}.



(1)

	R^1	R^2
a;	H	H
b;	Me	Me (6 isomers)
c;	H	Me (3 isomers)
d;	H	2,5-Me_2
e;	H	2,4,6-Me_3
f;	2,5-Me_2	2',5'-Me_2



(2)

	R^1	R^2
a;	H	H
b;	H	Me (2 isomers)
c;	H	3,5-Me_2
d;	H	2,4,5-Me_3
e;	2,5-Me_2	4'-Me
f;	2,4,6-Me_3	3',5'-Me_2
g;	Hexamethyl derivative	(R^1,R^2 unknown)
h;	2,4,5-Me_3	2',4',5'-Me_3
i;	2,4,5-Me_3	2',3',4',5'-Me_4

We have found a similarity between the oxidation of methylbenzenes to diarylmethanes by Pd^{II} and by the standard one-electron oxidant $K_4H[Co^{III}W_{12}O_{40}]$ (CoW_{12}), which is known to oxidize arenes *via* a one-electron transfer mechanism,[5,6] equation (1). From a competitive oxidation of ArMe and benzene (Table 1) the ratio of yields of diarylmethanes, $ArCH_2Ar' : ArCH_2Ph$, was found to be the same for the reactions with CoW_{12} and Pd^{II}. This indicates that in both cases the $ArCH_2^+$ cation is an intermediate.

Table 2. Relative rates of arene oxidation by Pd^{II} to give diarylmethanes (**2**) and biaryls (**1**).

$ArMe_n$	Relative rates[a] (**2**)[b]	(**1**)[c]	Ionization potential/eV
C_6H_6	—	1.0	9.25
MePh	0.9	1.8	8.82
p-$Me_2C_6H_4$	7.3	0.6	8.45
1,3,5-$Me_3C_6H_3$	75	—	8.39
1,2,4,5-$Me_4C_6H_2$	>100[d]	—	8.03

[a] The rates are related to benzene reactivity toward biaryl formation. The values are obtained from the data on competitive oxidation of arenes given in Table 1. [b] The ratios of yields of diarylmethanes to biaryls, calculated as (**2**)/[2 × (**1a**) + (**1c**—**e**)]. [c] The ratios of yields of biaryls, calculated as [2 × (**1b,f**) + (**1c**—**e**)]/[2 × (**1a**) + (**1c**—**e**)], ref. 7. [d] Based on biaryl yield of < 0.1%.

$$ArMe \xrightarrow{-e} ArMe^{\cdot +} \xrightarrow{-H^+} ArCH_2^{\cdot} \xrightarrow{-e} ArCH_2^+ \xrightarrow{Ar'H} ArCH_2Ar' + H^+ \quad (1)$$

The relative rate of diarylmethane formation in the presence of Pd^{II} increases as the arene ionization potential decreases (Table 2). Different dependence is observed for biaryl formation: benzene < toluene > *p*-xylene. This order is characteristic of electrophilic substitution in the arene nucleus, and is due to electron-donating and steric effects of methyl groups. These data indicate that diarylmethanes and biaryls are formed *via* different pathways.

We have observed e.s.r. spectra of radical intermediates produced during oxidation of methylbenzenes by Pd^{II} in CF_3CO_2H. To our knowledge, this provides the first example for the Pd^{II} oxidation of organic compounds. For toluene, mesitylene, and pentamethylbenzene only partly resolved spectra were obtained. The signals quickly vanished upon melting the samples. In the absence of Pd^{II}, no signals were

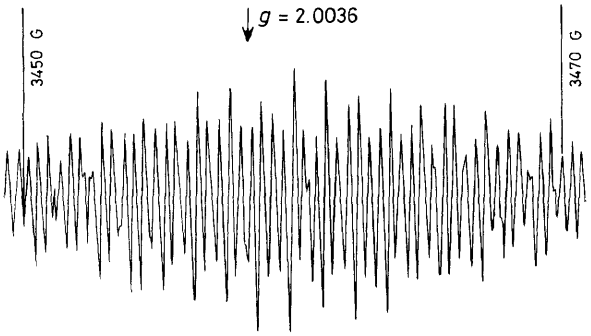


Figure 1. E.s.r. spectrum (central part) obtained during the oxidation of durene in the presence of $Pd(OAc)_2$ in CF_3CO_2H. 1 G = 10^{-4} T.

observed. Durene led to a well resolved e.s.r. spectrum in the liquid phase at room temperature (see Figure 1). It has more than 120 lines and is characterized by $g = 2.0028$ and three splitting constants ($a_1 = 3.36$, $a_2 = 1.12$, and $a_3 = 0.76$ G). This spectrum may be attributed to heptamethyldiphenylmethane (**2i**) radical cation. The observed e.s.r. spectra are probably due to oligomeric species derived by further addition of the parent short-lived radical cation to another arene molecule.

The results obtained indicate that arene oxidation by Pd^{II} in CF_3CO_2H to give diarylmethanes takes place *via* a one-electron transfer mechanism, equation (1). Central to this mechanism is the formation of the arene radical-cation. Simultaneously, the arenes are oxidized to biaryls by a non-radical mechanism involving electrophilic substitution in the arene nucleus, equation (2). The contribution of the one-electron mechanism depends upon the ionization potential of arene and the acidity of the medium, which determines the oxidation potential of Pd^{II}.

$$\mathrm{ArH} + \mathrm{Pd^{II}} \begin{array}{l} \nearrow \mathrm{ArH^{\cdot +}} + \mathrm{Pd^{I}} \\ \searrow \mathrm{ArPd^{II}} + \mathrm{H^{+}} \end{array} \qquad (2)$$

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