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The oxidation of o- and p-xylenes by palladium(II) in  $CF_3COOH$  can proceed according to an ion-radical mechanism of one-electron transfer [1], together with the well-known nonradical mechanism, including electrophilic substitution in the arene ring with the formation of an organopalladium intermediate:

 $\left. \operatorname{Pd}\left( \operatorname{II}\right) + \operatorname{ArH} - \right|_{\rightarrow}^{\rightarrow} \operatorname{ArH}^{+} + \operatorname{Pd}\left( \operatorname{II}\right) \\ \rightarrow \operatorname{ArPd}\left( \operatorname{II}\right) + \operatorname{H}^{+}$ 

In this work we investigated the influence of the nature of the arenes on the mechanism of their oxidation by Pd(II) in  $CF_3COOH$  medium, which promotes the mechanism of one-electron transfer, and in the basic medium (HOAc + NaOAc), promoting the occurrence of two-electron transfer with the participation of an organopalladium intermediate [1].

#### EXPERIMENTAL

We used cp or AR grade arenes without additional purification, as well as toluene-de with more than 99% enrichment. The reaction was conducted in sealed glass ampuls. The experimental technique was cited in [1]. The oxidation products of the arenes were analyzed by gas-liquid chromatography (7, 6, and 5% Apiezon L on Chromaton H, 200-260°C; katharometer) and chromatography/mass spectrometry. The kinetic isotope effect (KIE) of one-electron oxidation was determined according to the yield of diarylmethanes in the competing reactions in CF<sub>3</sub>COOH at 95°C. A mixture of benzene and toluene (10:1) was subjected to oxidation; the toluene contained equal amounts of  $C_7H_8$  and  $C_7D_8$ . The isotopic composition of the diphenyl-methane formed was analyzed mass spectrometrically (MS). The KIE was assumed equal to the ratio of the intensities of the peaks m/z 168 and 175, corresponding to diarylmethane-do and diarylmethane- $d_7$ . In CF<sub>3</sub>COOH, H-D exchange of toluene occurs (probably in the ring [2]); the degree of exchange is 5% (95°C, 6 h), i.e., one D atom of toluene-d<sub>8</sub> is exchanged to an extent of 40%. The same degree of exchange is observed for diphenylmethane. Exchange does not depend on the presence of Pd(II) and  $CoW_{12}$ . In the reaction with Pd(II) the KIE was also found in the separate oxidation of mixtures of  $C_6H_8 + C_6D_5CD_3$  (10:1) and  $C_6H_6 + C_6H_5CH_3$ (10:1) according to the equation  $k_H/k_D = (S_H/S)/(S_D/S)$ , where  $S_H$ ,  $S_D$ , and S are the areas of the chromatographic peaks of diphenylmethane-do, diphenylmethane-do, and diphenyl, respectively. The values of  $k_{\rm H}/k_{\rm D}$ , found from MS and GLC analysis, are in good agreement. The KIE of the two-electron reaction forming ditolyls was determined analogously [3].

## DISCUSSION OF RESULTS

It is believed that in the reaction of many arenes with Pd(II), diaryls are formed primarily according to a mechanism of electrophilic substitution of H by Pd(II) in the arene ring [1, 4] [Scheme (1)], while diarylmethanes are formed according to a mechanism of oneelectron transfer with the participation of the aromatic radical cation [1] [Scheme (2)]:

$$\operatorname{ArH} + \operatorname{Pd} (II) \to \operatorname{ArPd} (II) + H^{+}$$

$$\operatorname{2ArPd} (II) \to \operatorname{Pd} (II) + \operatorname{Ar_{2}Pd} (II) \stackrel{1}{\longrightarrow} \operatorname{Ar_{2}} + \operatorname{Pd} (0)$$

$$\operatorname{ArCH_{3} \xrightarrow{-\tilde{e}}} \operatorname{ArCH_{3}^{+} \xrightarrow{-H^{+}}} \operatorname{ArCH_{2}^{-\tilde{e}}} \operatorname{ArCH_{2}^{+} -} \xrightarrow{\operatorname{ArCH_{2}Ar'}} \operatorname{ArCH_{2}Ar'} + H^{+}$$

$$(1)$$

$$(2)$$

In certain cases diaryls can also be formed according to a mechanism of one-electron transfer, for example, in the oxidation of o-xylene [1].

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Arene	Conditions*	Product, † mole %
Benzene	Pd - A, B Co - A, B	Diphenyl 44-56
Toluene	Pd – A	Ditoly1 41 (2.2' - 0; 2,3' - 9; 2,4' - 11; 3,3' - 22; 3,4' - 40; 4,4' - 18), Benzaldehyde 2, benzyl acetate 1
	Pd — B	Ditolyl 45 (2,2' - 7; 2,3' - 17; 2,4' - 30; 3,3' - 7; 3,4' - 23; 4,4' - 16), benzaldehyde 2, phenyltolylmethane two isomers 25 (I)
	Co - A Co - B	Benzylacetate 28, benzaidenyde 3, (1) 2
P-Xylene	Pd – A	2,5,2',5'-Tetramethyldiphenyl 18 (II), 2,5,4'-trimethyl- diphenylmethane 1 (III), 4-methylbenzaldehyde 5 (IV), 4-methylbenzyl acetate 2 (V)
	Pd - B Co - A	(III) 65, (II) 7, (IV) 3 (IV) 40, (V) 20, (III) 1
Mesitylene	Pd - A	(111) 36 3,5-Dimethylbenzaldehyde 18 (VI), 2,4,6,3',5'-pentamethyl- diphenylmethane 3 (VII), 3,5-Dimethylbenzyl (VIII)‡
	Pd - B Co - A	(VII) 87, (VI) 1,hexamethyldiphenylmethane 5 (IX) ** (VI) 44, (VIII) 16, (VII), 15
Durene ††	Co - B Pd - A	(VII) 26, (IX) 12, (VI), 1 2,4,5-Trimethylbenzaldehyde 3 (X), 2,4,5-trimethylbenzyl acetate 2 (XI)
	Pd — B	2,4,5,2',4',5'-Hexamethyldiphenylmethane† 22 (XII), 2,4,5,2',3',5',6'-heptamethyldiphenylmethane 10 (XIII) †
	Co - A Co - B	(X) 26, (XI) 21 (XII) 11, (XIII) 7

TABLE 1. Oxidation of Arenes (1.5 M) by Pd(II) and  $CoW_{12}$  (0.05 M), 95°C,5-6 h

\* Pd-A, Co-A-0.05 M PdCl<sub>2</sub> or CoW<sub>12</sub> in HOAc + 0.5 M NaOAc, Pd-B, Co-B -0.05 M Pd(OAc)<sub>2</sub> or CoW<sub>12</sub> in CF<sub>3</sub>COOH. +Yield calculated on the basis of the initial amount of Pd(II) or Co(III). # Presumed structure; migration of CH<sub>3</sub> groups is not excluded. \*\* Structure not established. ++ [ArH] = 0.3 M.

In the oxidation of arenes by Pd(II) in the series benzene-durene, in which the ionization potential of the arene decreases, the yield of diarylmethanes increases, while that of diaryls falls (Table 1). At the same time, the similarity of the composition of the reaction products of Pd(II) and  $CoW_{12}$ , which is characterized by a one-electron mechanism [1], increases. Such a tendency is more pronounced in  $CF_3COOH$  medium, which promotes one-electron transfer as a result of an increase in the redox potential of the oxidizing agent [1]. These data indicate replacement of the nonradical mechanism (1) by the radical mechanism (2). The general nature of the mechanism of diarylmethane formation in the oxidation of arenes by Pd(II) and  $CoW_{12}$  is confirmed by the fact that in competitive oxidation of  $ArCH_3$  and PhH (Table 2) the ratio of the yields of the diarylmethanes[ $ArCH_2Ar'$ ]/[ $ArCH_2Ph$ ] is the same for the reactions of  $CoW_{12}$  and Pd(II) (Pd, Co-B)

	Toluene	p-Xylene	Mesitylene	Durene
Pd(II)	3	$\begin{array}{c} 62 \\ 54 \end{array}$	50	1
CoW12	3		50	. 1

This is evidence that in both cases the intermediate is the  ${
m ArCH_2}^+$  cation.

A difference in the mechanisms of the formation of diaryls and diarylmethanes in the oxidation of arenes by Pd(II) is clearly indicated by the KIE (Table 3). For the formation of ditolyls from toluene in acid and basic media  $k_H/k_D = 4.0-4.8$ , which is close to  $k_H/k_D = 5.0$ , obtained for oxidative coupling of benzene to diphenyl [3, 5]. For diarylmethanes  $k_H/k_D = 2.4$ , and, moreover, the KIEs for the reactions of Pd(II) and CoW<sub>12</sub> are close. These data show that in the formation of diaryls and diarylmethanes, the C-H bond is broken in the slow step, but the nature of the limiting step in the indicated reactions differs [see Schemes (1) and (2)].

The mechanism of electrophilic substitution (1) and one-electron transfer (2) in the series of methylbenzenes may differ in the nature of the influence of the type of arene on the reaction rate. The rate of one-electron oxidation is correlated with the ionization potential of the arene [6]. The rate of aromatic electrophilic substitution is determined by

TABLE 2. Competitive Oxidation of Methylbenzenes (1.0 M) and Benzene (1.0 M) by Pd(II) and  $CoW_{12}$  (0.05 M),\* 95°C, 5-6 h

Arene	Conditions	Product, mole %		
Toluene	Pd – A	Diphenyl 9, ditolyl 14, methyldiphenyl (o-5; m-50; p-45) 21		
	Pd — B	Diphenyl 7, ditolyl 18, methyldiphenyl (o-34; m-26; p-40) 15, diphenylmethane 7, (I) 20		
	Co - A	Benzyl acetate 16. benzaldehvde 2		
	Co - B	(I) 9, diphenylmethane 3		
p-Xylene	Pd - A	Diphenyl 20 (II) 1, (IV) 2, 2,5-dimethyldiphenyl 19 (XIV)		
	Pd — B	Diphenyl 2, (XIV) 7, (III) 89, (IV) 2, 4-methyldiphenylmethane 1.3 (XV)		
	Co — A	(IV) 28, (V) 15, (III) 1		
	Co - B	(III) 27, (XV) 0.5		
Mesitylene	Pd — A	Diphenyl 34, (VII) 3, (VI), 14, (VIII) 2, 2,4,6-trimethyl- diphenyl 1 (XVI)		
	Pd — B	(XVI) 1, (VII) 74, (IX) 3, 3,5-Dimethyldiphenylmethane 1.5 (XVII)		
	Co - A	(VI) 35, (VIII) 19, (VII) 14		
	Co - B	(VII) 24, (IX) 7, (XVII) 0.5		
Durene †	Pd – A	Diphenyl 13, (X) (1), (XI) 1		
	Pd - B	(XII) 16, (XIII) 7,2,4,5-Trimethyldiphenylmethane 6 (XVIII)		
	Co — A	(X) 23. $(XI)$ 22		
	Co — B	(XII) 5, (XIII) 6, (XVIII) 5		

\*For the conditions and notations, see Table 1.  $^{\dagger}$ [Me<sub>4</sub>C<sub>6</sub>H<sub>2</sub>] = [PhH] = 0.3 M.

TABLE 3. Isotope Effect in the Oxidation of Toluene-d<sub>0</sub> and Toluene-d<sub>8</sub> (95°C, 4-7 h)

	. k <sub>H</sub> /k <sub>D</sub>		
Conditions	diaryl	diarylmethane	
Pd – A Pd – B Co – B	4,8±0,2 4,0±0,5 -		

TABLE 4. Relative Reactivity of Arenes in Oxidation to Diaryls and Diarylmethanes by Pd(II), 95°C

	Relative read	Tantast	
Arene	diaryl † (Pd-A)	Diarylmethane † (pd-B)	potential, eV [7]
Benzene Toluene p-Xylene Mesitylene Durene	$ \begin{array}{cccc} 1,0 & (0) \\ 1,3 & (0) \\ 0,4 & (5) \\ 0,01 & (\sim 100) \\ <0,01 & (100) \end{array} $	$\begin{array}{ccc} - & (0) \\ 0.9 & (40) \\ 7.3 & (90) \\ 75 & (100) \\ >100 & (100) \end{array}$	9,25 8,82 8,44 8,39 8,02

\* An estimate of the contribution of the one-electron pathway (%) under conditions of Pd-A and Pd-B from the data of Table 1 is given in parentheses as the ratio of the yield of diarylmethanes to the sum of the yields of diaryls and diarylmethanes. + The value of  $(2[Ar_2]+[ArPh])/(2[Ph_2]+[ArPh])$  [3]. ‡ Ratio of the yield of diarylmethanes to the value of  $(2[Ph_2]+[ArPh])$ , which characterizes the reactivity of benzene.

the electronic and steric influence of the methyl groups: the former facilitates the reaction, while the latter hinders it [2]. From the relative rates of formation of diaryls and diarylmethanes (Table 4), calculated from the data of Table 2, it can be seen that for diarylmethanes there is a correlation with the ionization potential of the arene, which is

TABLE 5. Influence of Preliminary Reduction of Pd(II) by Benzene on the Composition of Products of Oxidative Coupling of Toluene by Pd-B, [PhMe] = 1.3 M

T., °C	Reaction time, h	[Diarylmethane]*/ diaryl	T., ℃	Reaction time, h	[Diarylmethane]*/ diaryl
50 50	5 5	$^{0,12}_{0,20}$ +	95 95	1	0,41 2,0 †

\* Ratio of the yield of phenyltolylmethane and diphenylmethane to the yield of ditolyl.

+ Before the addition of toluene, Pd(II) was reduced by benzene (1.3 M) for 1 h at 50°C.



Fig. 1. Kinetics of the accumulation of ditolyls (1) and phenyltolylmethanes (2) in the oxidation of toluene (1.5 M) by palladium(II) acetate (0.05 M) in  $CF_3COOH$ , 50°C.

evidence that the reaction proceeds according to a one-electron mechanism. In the case of diaryls there is no such correlation; the observed changes in the rate correspond to those expected for electrophilic substitution.

Thus the data obtained confirm the conclusion of [1], that the oxidation of methylbenzenes by Pd(II) can proceed according to a mechanism of one-electron transfer with predominant formation of diarylmethanes. In addition, there is a nonradical oxidation to diaryls. The yield of C-C coupling products permits an estimation of the contribution of the one-electron pathway in the oxidation of arenes by Pd(II) (see Table 4). Oxygen-containing compounds were not taken into account in this case, since their yield is low. It can be seen that benzene reacts with Pd(II) according to a two-electron mechanism. In the case of toluene and p-xylene, the one- and two-electron mechanism compete. Mesitylene and durene react virtually solely according to a one-electron mechanism. Just as we should have expected, the contribution of the one-electron mechanism in acid medium is higher than in basic medium.

The kinetics of the accumulation of ditolyls (the sum of the six isomers) and phenyltolylmethanes (two isomers) in the oxidation of toluene by Pd(II) in  $CF_3COOH$  (Fig. 1) is analogous to that observed for p-xylene [1]. It is characteristic that diarylmethane is formed substantially more slowly than diaryl, continuing to accumulate after completion of the reaction forming diaryl. This is explained in [1] by the participation of relatively nonreactive intermediates in the process - dimer complexes of Pd(I) [5, 8, 9], which are presumed to be active in the one-electron oxidation of arenes to diarylmethanes but inactive in two-electron oxidation to diaryls.

To test the hypothesis of the participation of  $[Pd(I)]_2$ , we investigated the oxidation of toluene, preliminarily producing  $[Pd(I)]_2$  in situ by the reduction of Pd(II) by benzene,

as in [5] (Table 5). The substantial increase in the ratio of the yields of diarylmethanes and ditolyls (twofold at 50°C and fivefold at 95°C) in experiments where  $[Pd(I)]_2$  was preliminarily formed agreed with the expected result.

The slow portion of the accumulation of diarylmethanes (see Fig. 1) can be explained [1] by assuming that the initial oxidation product of the arene is a benzyl ether, which then is slowly converted to diarylmethane:

$$PhCH_{2}O_{2}CCF_{3} + H^{+} \rightarrow CF_{3}COOH + PhCH_{2}^{+} \xrightarrow{PhCH_{2}} PhCH_{2}C_{6}H_{4}CH_{3} + H^{+}$$
(3)

Benzyl ethers are formed rapidly, parallel with diarylmethanes [1]. We conducted the reaction of benzyl alcohol (0.03 M) with toluene (1.5 M) in  $CF_3COOH$  and found that the conversion of benzyl alcohol to phenyltolylmethane in 0.5 h is equal to 40% at 50°C and 100% at 95°C. Thus, process (3) occurs rather rapidly and cannot be responsible for the formation of diarylmethane.

At the initial stage, the interaction of toluene with Pd(II) in  $CF_3COOH$  can be represented in the form

 $\begin{aligned} \operatorname{ArH} + \operatorname{Pd}(\operatorname{II}) &\to \operatorname{Ar}_2 + \operatorname{Pd}(0) (\operatorname{Two-electron transfer, Scheme}(1)] \\ &\operatorname{ArCH}_3 + \operatorname{Pd}(\operatorname{II}) \to \operatorname{ArCH}_3^{+} + \operatorname{Pd}(\operatorname{I}) \\ &\operatorname{ArCH}_3 + \operatorname{Pd}(\operatorname{I}) \to \operatorname{ArCH}_3^{+} + \operatorname{Pd}(0) \\ &\operatorname{Pd}(0) + \operatorname{Pd}(\operatorname{II}) \to [\operatorname{Pd}(\operatorname{I})]_2 \end{aligned}$ 

The subsequent reactions of  $ArCH_3$ <sup>+</sup> are cited in Scheme (2). Then there is a slower process with the participation of  $[Pd(I)]_2$ , the mechanism of the action of which still remains to be determined. We can tentatively consider both dimers and monomers of Pd(I) as active, assuming the existence of the equilibrium

# $[Pd(I)]_2 \rightleftharpoons 2Pd(I)$

Thus, our investigation showed that the oxidation of methylbenzenes by Pd(II) can occur under definite conditions according to a mechanism of one-electron transfer, in contrast to . the traditional two-electron mechanism for complexes of palladium(II) [6, 10, 11]. The contribution of the one-electron mechanism is determined by the nature of the arene (its ionization potential and steric factors), as well as the acidity of the medium and the nature of the ligands controlling the oxidation potential of Pd(II).

### CONCLUSIONS

1. The oxidation of methylbenzenes (toluene, p-xylene, mesitylene, durene) by palladium-(II) to diarylmethanes in  $CF_3COOH$  proceeds according to a mechanism of one-electron transfer. In addition, there is an oxidation of arenes to diaryls according to the well-known twoelectron mechanism, including electrophilic substitution in the ring of the arene.

2. The contribution of the one-electron mechanism increases with decreasing ionization potential of the arene and with increasing acidity of the medium.

3. Complexes of palladium(I) (probably dimers) are intermediates of the one-electron oxidation of methylbenzenes to diarylmethanes.

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## PECULIARITIES OF THE NITRATION OF SECONDARY POLYNITROALKANES

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The nitration of salts of unsubstituted secondary nitroalkanes RR'C =  $NO_2^{\Theta}$  by nitronium tetrafluoborate [1], as well as the oxidative nitration by Ag [2] or Na [3, 4] nitrites in alkaline or neutral medium, is well known. However, gem-dinitro compounds are not formed in the case when R or R' is an electron-acceptor group [5]. The nitration of compounds of this kind by nitric acid or nitrating mixtures has received little study; only two examples of the production of gem-dinitro derivatives for R = R' =  $CH_2C(NO_2)_3$  [6] and R = R' =  $CH_2C(NO_2)_2ME$  [7, 8] are shown.

Our preliminary experiments have shown that the nitration of 1,5-disubstituted 1,1,3,5,5pentanitropentanes proceeds complexly and is accompanied by side reactions, which are dominant under definite conditions.

In this work we studied the reactions of salts of the indicated compounds with various nitrating systems. It was shown that the main and side processes are determined by the composition of the nitrating systems and lead to the formation of the following products:

$$[XC(NO_2)_2CH_2]_2C=NO_2^{\odot}C_5H_5NH^{\oplus}$$
(I), (II)
$$[XC(NO_2)_2CH_2]_2C=NO_2^{\odot}C_5H_5NH^{\oplus}$$
(I), (II)
$$[XC(NO_2)_2CH_2]_2C=O$$
(IV a, b),
$$[XC(NO_2)_2CH_2]_2C=N$$

$$[XC(NO_2)_2CH_2]_2C=N$$

$$[XC(NO_2)_2CH_2]_2C=O$$
(V a, b),
$$NO_2$$

 $X = NO_2(a), F(b).$ 

In anhydrous  $HNO_3 - H_2SO_4$  systems at a 5-10%  $HNO_3$  content, when the equilibrium

 $HNO_3 + 2H_2SO_4 \approx NO_2 \oplus + H_3O \oplus + 2HSO_4 \oplus$ 

is almost entirely shifted to the right [9], the main products of the reaction with (I) or (II) are (Va, b) and (IVb), respectively (Table 1). In the system containing 10% HNO<sub>3</sub>, (IIIa) and (IIIb) are formed in negligible yields.

When water is introduced into the system  $(HNO_3:H_2SO_4:H_2O = 10:85:5)$ , the dissociation of  $HNO_3$  according to the indicated equation is sharply reduced, and the reaction with (I) proceeds by C-nitration in the 3 position with a 43% yield (IIIa) and oxidation with the formation of (IVa) and (Va).

Nitration of (I) and (II) by  $HNO_3 - H_2O$  systems at  $HNO_3$  concentrations of 98-70%, which are characterized by the presence of a large amount of nonionized  $HNO_3$  [10] and a negligible amount of  $NO_2^{\oplus}$  (in systems up to 5%  $H_2O$ ) [9], leads primarily to products of C-nitration (IIIa, b) up to 65%, as well as (IVa, b) as a result of oxidation processes of the Neff reaction. In this case the nitrating ability of the  $HNO_3 - H_2O$  system is preserved down to a 70%  $HNO_3$  content, which agrees with the data of [7]. At lower  $HNO_3$  concentrations, nitration does not occur, evidently on account of the insolubility of the nitro

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