

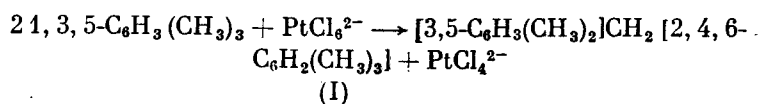
OXIDATION OF MESITYLENE BY PtCl_6^{2-} IONS IN TRIFLUOROACETIC ACID

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Heating of a solution of an aromatic compound and PtCl_6^{2-} ions in acetic acid or aqueous $\text{CF}_3\text{CO}_2\text{H}$ leads to the formation of σ -aryl Pt(IV) complexes. The platinum atom enters only the meta and para positions relative to the substituent [1, 2]. σ -Complexes are not formed in reactions with such hydrocarbons as p-xylene, mesitylene and pentamethylbenzene. However, an oxidation-reduction reaction of Pt(IV) ions with hydrocarbon proceeds giving a Pt(II) complex not containing organic ligands. In the present work, we studied this reaction for mesitylene (MS).

Heating of a solution of H_2PtCl_6 and MS in aqueous $\text{CF}_3\text{CO}_2\text{H}$ at reflux gives a single organic product, namely, (2,4,6,3',5'-pentamethyl)diphenylmethane (I) in 60% yield



The kinetic curves for the loss of PtCl_6^{2-} ions and accumulation of (I) are given in Fig. 1. The drop in the PtCl_6^{2-} concentration was followed for 40 min when the solution became non-homogeneous due to the formation of Pt(II) derivatives with poor solubility. The accumulation of (I) was linear. Bubbling of oxygen through the solution leads to a more rapid formation of (I) at the onset; the concentration of this product remains virtually invariant subsequently. The oxidation coupling of monosubstituted arenes to diaryls by the action of PtCl_6^{2-} ions proceeds with the intermediate participation of a σ -aryl Pt(IV) complex [3]. In the case of MS, the intermediate generation of such a complex is excluded because of steric factors. Thus, the most likely mechanism for the formation of diarylmethane from MS is the one-electron oxidation of the arene to a radical-cation, which may be readily converted to a substituted benzyl radical capable of attacking a free MS molecule. Oxidation of the intermediate by the Pt complex or O_2 gives diarylmethane (I).

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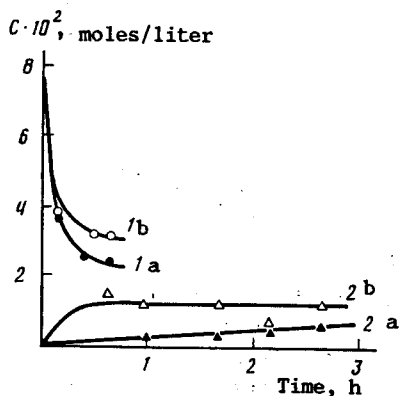


Fig. 1. Consumption of PtCl_6^{2-} ions (1) and accumulation of (I) (2) in the oxidation of mesitylene (1.23 mole/liter) in 4.5:1 $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$ at 84°C in the absence of oxygen (a) and with oxygen bubbling (b).

It is not excluded that the first step in the reaction of PtCl_6^{2-} ions with sterically hindered arenes is also a one-electron transfer. In this case, the second step is a recombination of radical species, namely, the arene radical-cation and Pt(III) complex, with the formation of a Wheland complex. Such a recombination of the MS radical-cation and the Pt(III) species is apparently impossible and reaction subsequently proceeds by a different mechanism. Analogous behavior was observed upon the oxidation of polymethylbenzenes by a Pd(II) complex in $\text{CF}_3\text{CO}_2\text{H}$ [4] and the formation of an arene radical-cation was detected by ESR spectroscopy for this system. The participation of a radical pair is proposed in the first step of the reaction of PtCl_6^{2-} ions with arenes stimulated by light irradiation [2, 5].

An alternative mechanism for the generation of a substituted benzyl radical (or carbocation) from MS may be cleavage of a C-H bond in the CH_3 group with the formation of a σ -alkyl Pt(IV) complex (an analogous σ -methyl complex was detected in the reaction of PtCl_6^{2-} ions with methane [6]). The benzyl radical in this case may be obtained in the homolysis of the Pt-C bond as proposed for σ -aryl complexes [3]. However, σ -alkyl Pt(IV) complexes readily react with water [7] and, thus, we might expect the corresponding benzyl alcohol in significant amounts among the reaction products.

EXPERIMENTAL

2,4,6,3',5'-Pentamethyldiphenylmethane (I). A solution of 1 g $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 2 ml mesitylene and 3 ml water in 12 ml $\text{CF}_3\text{CO}_2\text{H}$ was heated at reflux for 3.5 h. The solvent was evaporated at reduced pressure to 2 ml and 10 ml water was added to the residue, which was extracted thrice with chloroform. The extracts were combined, washed with water and dried over Na_2SO_4 . Chloroform was evaporated at reduced pressure. The residue was subjected to thin-layer chromatography on silica gel with hexane as eluant gave 0.19 g (60%) (I), mp $66-67^\circ\text{C}$ [8]. PMR spectrum (δ , ppm, CDCl_3): 6.81 s (2H, phenyl), 6.76 s (1H, phenyl), 6.57 s (2H, phenyl), 3.89 s (CH_2), 2.22 (CH_3), 2.18 s (CH_3).

Under similar conditions, the reaction was carried out by bubbling O_2 over the solution. Using this method, the yield of (I) was 76%.

CONCLUSION

The reaction of PtCl_6^{2-} ions with mesitylene in aqueous $\text{CF}_3\text{CO}_2\text{H}$ leads to the formation of 2,4,6,3',5'-pentamethyldiphenylmethane.

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