

OXIDATION OF TOLUENE BY THE PtBr_6^{2-} ION IN $\text{CF}_3\text{COOH-H}_2\text{O}$
SOLUTION

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When a solution of the PtBr_6^{2-} ion is heated with toluene in a $\text{CF}_3\text{COOH-H}_2\text{O}$ medium there are formed, after a period of induction, the following isomers of bitolyl (percent content in parentheses): 3,3' (2.5), 3,4' (27.5), and 4,4' (70.0). The bitolyl is formed from the σ -tolyl-Pt(IV) complex.

We showed earlier that the PtCl_6^{2-} ion reacts with arenes and with toluene in particular in a medium of $\text{CF}_3\text{COOH-H}_2\text{O}$ or CH_3COOH at 60-95°C. After reaction for a short time, from the reaction mixture we can isolate in high yields (up to 90%) σ -aryl complexes of Pt(IV), stabilized by the replacement of one of the ligands by NH_3 [1-3]. With prolonged heating we observe the decomposition of the σ complexes and the formation of biaryls [3-6]. We made a detailed study of the process of the formation of bitolyl isomers in the decomposition of the Pt(IV) σ -tolyl complex formed in the reaction of toluene with PtCl_6^{2-} in $\text{CF}_3\text{COOH-H}_2\text{O}$ solution [7]. The metal atom enters only the para and meta positions of the benzene ring, but not the ortho position for steric reasons. The process of the accumulation of the σ -tolyl complex is accompanied by reversible para-meta isomerization. After the induction period the reaction mixture is found to contain 3,3'-, 3,4'-, and 4,4'-bitolyl isomers and, which is particularly important, considerable amounts also of 2,3' and 2,4' isomers, probably arising from the reaction of the σ -aryl complex with free toluene.

In the present work we investigated the thermal reaction of the PtBr_6^{2-} ion with toluene in a mixture of CF_3COOH and H_2O at 85°C. Several products were obtained. The σ -aryl complex formed, unlike the complex with platinum(IV) chloride, proved to be unstable, and

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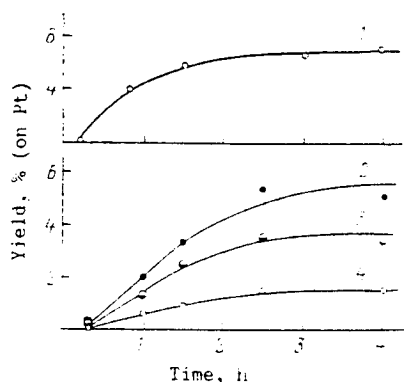


Fig. 1. Accumulation of isomeric bitolyls (1) in the reaction of PtBr_6^{2-} with toluene, and the accumulation of methylbiphenyls (2), bitolyls (3), and biphenyl (4) in the reaction of PtBr_6^{2-} with a 1:1 mixture of toluene and benzene.

it was not isolated. However, the induction period on the kinetic curve for the accumulation of isomeric bitolyls (Fig. 1, curve 1) may indicate that, as in the case of PtCl_6^{2-} , such a complex is present in the reaction solution and that its decomposition leads to the formation of bitolyls. The relative contents of the isomers in the mixture do not change with time: 2.5% (3,3'), 27.5% (3,4'), and 70% (4,4'). This indicates that the complex is unstable and decomposes before para-meta isomerization occurs to an appreciable extent. It is noteworthy that bitolyls are formed in small amount. This is probably because the toluene mainly reacts with the free bromine liberated when a solution of PtBr_6^{2-} in $\text{CF}_3\text{COOH-H}_2\text{O}$ is heated. The yield of bromotoluene isomers is ~50%. A certain amount of unidentified products is also formed; in the mass spectrum these give a molecular peak at m/z 227. These products and the bromotoluenes accumulate without any appreciable induction period.

Finally, the GLC-mass spectrometry of the heavier fraction of the reaction products revealed the formation of a number of other compounds (unfortunately, not all of the compounds could be identified; the mass spectra of all the products are given in the experimental part). Of particular interest is the formation of phenyltolylmethane (possibly as a mixture of isomers). This compound could be formed in an attack on toluene by a benzyl radical formed after the transfer of an electron from toluene to Pt(IV) and the subsequent elimination of a proton. There may also occur the reaction of the tolyl radical cation with toluene. Analogous processes are known for complexes of Pd(II) [8] and Pt(IV) chloride [9]. However, we cannot rule out the direct reaction of Pt(IV) with the CH_3 group of toluene, as a result of which a benzyl radical or carbocation is formed. The bitolyls formed in the reaction are brominated to mono- and di-bromobitolyls. It is characteristic that 2,3'- and 2,4'-bitolyls are not formed in the reaction of toluene with PtBr_6^{2-} , which is probably to be explained by the low stability of the σ -tolyl complex of platinum(IV) bromide.

We also carried out the reaction of PtBr_6^{2-} with an equimolecular mixture of toluene and benzene. In this case, after the induction period we observed the accumulation of isomers of bitolyl, methylbiphenyl, and also biphenyl (Fig. 1, curves 2-4). The isomeric composition does not change with time: 7.6% of 3,3'-, 33.1% of 3,4'-, and 59.3% of 4,4'-bitolyls, and 20.5% of m- and 79.5% of p-methylbiphenyls. The ratio $k(\text{toluene})/k(\text{benzene}) = 1.5$. On the assumption that biaryls are formed in the decomposition of σ -aryl complexes, we can calculate the partial-rate factors [10] of the platination of toluene: f_0 0, f_m 0.73, f_p 7.7.

EXPERIMENTAL

In the work we used a Chrom-5 chromatograph (Chromaton N-AW carrier with 5% of silicone S-550) and a Varian GLC-mass spectrometer.

A solution of 1.0 g of $\text{Na}_2\text{PtBr}_6 \cdot 6\text{H}_2\text{O}$, 4 ml of toluene, and 6 ml of water in 15 ml of CF_3COOH was heated with stirring in a thermostated (85°C) vessel with a reflux condenser.

At definite intervals 3-ml samples of the reaction solution were taken. Water (5 ml) was added to each sample, and the mixture was extracted with three 3-ml portions of CHCl_3 . The extract was washed with water and dried over Na_2SO_4 , solvent was evaporated, and the residue was analyzed by means of GLC. The reaction with a mixture of toluene and benzene was carried out in an analogous way.

Mass spectra of the reaction products. Below we give the chromatographic peak No. and then the principal signals in the mass spectrum, m/z (relative intensity, %, in parentheses).
1, 2: 168 (100), 153 (16), 83 (16); 3: 182 (78), 167 (100), 104 (58), 91 (35), 77 (20);
4-6: 182 (100), 167 (35), 90 (15); 7: 198 (100), 140 (28), 105 (15), 77 (50); 8: 248 (100), 246 (100), 167 (76), 165 (74), 153 (26), 83 (45); 9, 10: 213 (100), 196 (45), 185 (30), 168 (100), 165 (100), 153 (93), 129 (40); 11: 262 (100), 260 (100), 181 (65), 166 (80), 89 (65); 12-14: 227 (100), 210 (55), 165 (65); 15: 213 (100), 183 (10), 165 (25), 152 (35); 16, 17: 307 (85), 305 (85), 290 (15), 288 (15), 266 (45), 198 (100), 166 (100); 18: 340 (50), 226 (46), 198 (48), 165 (80), 89 (85), 76 (100).

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