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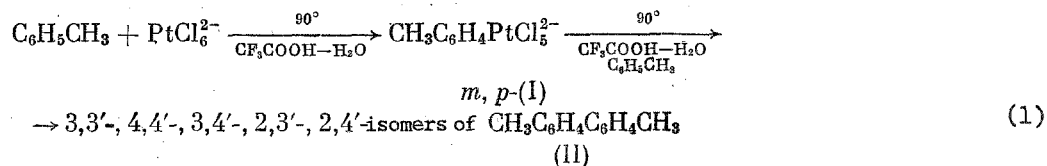
ISOMERIC COMPOSITION OF DITOLYLS FORMED UPON THE THERMAL DECOMPOSITION OF AN ANIONIC Pt(IV) σ -TOLYL CHLORIDE COMPLEX

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Heating a solution of PtCl_6^{2-} ion (chloroplatinic acid or its sodium salt) and an aromatic compound ArH in aqueous $\text{CF}_3\text{CO}_2\text{H}$ or in acetic acid leads to the formation of a Pt(IV) σ -aryl complex which may be separated by chromatography on silica gel containing NH_3 as a salt of $[\text{ArPtCl}_4\text{NH}_3]^-$ [1, 2]. Upon more prolonged heating of the solution, the σ -complex decomposes with the formation of diaryls [1]. The removal of the free arene from the reaction solution leads to a marked decrease in the rate of decomposition of the σ -complex, indicating that one of the decomposition pathways involves the reaction of the complex with the free arene [3, 4].

In the present work, we studied the isomeric composition of ditolylys formed upon the decomposition of the Pt(IV) σ -tolyl complex (I). The reaction was carried out in 4.5:1 $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$ at 90°C . Reaction (1) was followed relative to the loss of starting PtCl_6^{2-} ion over time by electronic spectroscopy and the accumulation of (I) by electronic spectroscopy and isomeric ditolylys by gas-liquid chromatography. In addition, PMR spectroscopy was used to determine the ratio of the *m*- and *p*-isomers of (I) formed in the platination of toluene (the *o*-isomer is not formed due to steric factors). A large excess of toluene was employed.



The kinetic data are illustrated in Fig. 1. All the PtCl_6^{2-} ion is virtually completely consumed after 3 h. At this time, the concentration of (I) reaches a maximum (the yield of (I) is 69%) and then (I) begins to decompose rapidly. While the fraction of the *p*-isomer of (I) formed at the onset Y^d is about 0.9, its relative content in the mixture drops to about 0.3. Isomers of (II) begin to form even in the initial stage of the reaction but an induction period in their accumulation is noted. The inflection on the kinetic curves for the accumulation of isomers (II) approximately corresponds to the maximum on the kinetic curve for the formation and decomposition of complex (I).

Gas-liquid chromatography revealed five isomers of (II) in the reaction mixture, namely, the 3,3'-, 4,4'-, 3,4'-, 2,4'-, and 2,3'-isomers. The 3,3'-isomer is formed in the least amounts at any moment in time. In the initial period (1h after the reaction onset), the concentration of 4,4'-(II) exceeds the concentration of any other isomer but after 2 h, the amount of 3,4'-(II) exceeds that of 4,4'-(II). Isomers of (II) containing the methyl group

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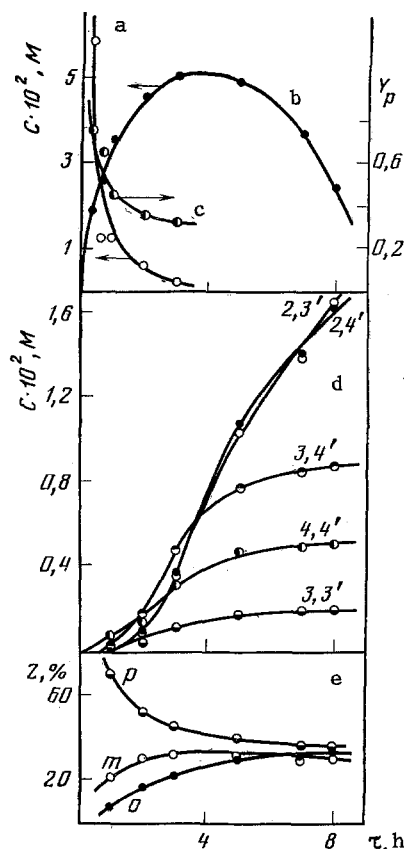


Fig. 1. Kinetics of the reaction of 0.074 M H_2PtCl_6 and 1.5 M toluene in 4.5:1 $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$ at 90°C : a) PtCl_6^{2-} consumption, b) accumulation and decomposition of the Pt(IV) σ -tolyl complex, c) p-m isomerization of the σ -tolyl complex, d) accumulation of ditolyl isomers, and e) percentage composition of isomers in the ditolyl mixture.

in the ortho position (2,3'- and 2,4'-(II)) are formed in the reaction with a significant induction period but 2,2'-(II) is not formed. The maximum rate for the formation of these isomers corresponds to the reaction time at which the concentration of (I) is greatest. At the end of the reaction (8 h), when a relatively small amount of (I) is present, the concentrations of 2,3'- and 2,4'-(II) significantly exceeds the concentration of the other isomers of (II). Figure 1 also shows the relative percentage content of the isomers of ditolyl with the CH_3 group in the o-, m- and p-positions. Thus, for example, Z_p was calculated using the formula

$$Z_p(\%) = Z_{4,4'} + \frac{1}{2}(Z_{3,4'} + Z_{2,4'})$$

where Z is given in relative percentage content of the corresponding isomers of (II). During the reaction, Z_p drops steadily, Z_o increases and Z_m initially increases but after about 2 h, remains unchanged.

We also carried out a preliminary study of the products of the decomposition of the σ -aryl complex obtained in the reaction of H_2PtCl_6 with anisole isolated as the $[\text{CH}_3\text{OC}_6\text{H}_4\text{PtCl}_4-\text{NH}_3]^-$ salt upon chromatography on silica gel. Isomers of chloroanisole and a small amount of dianisyl isomers were detected in the reaction mixture after heating this complex in $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$ for 2 h at 99°C . On the other hand, on the Pt(IV) σ -anisyl complex was found in the reaction mixture formed upon the irradiation of the PtCl_6^{2-} ion and anisole in $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}$ at 20°C for 15 h [5-7], while chloroanisole and dianisyls were not detected.

Thus, our experimental data indicate that ditolyl isomers appear in reaction (1) only as a result of the decomposition of intermediate complex (I). The formation of (II) apparently may occur by two different pathways. Pathway 1 involves the decomposition of (I) with-

out the participation of free toluene. The first step of this pathway may be the reaction of two molecules of (I) with the formation, for example, of bis(σ -tolyl)platinum. This complex reductively eliminates Pt(II) and gives (II). In this case, clearly only the 3,3'-, 4,4'- and 3,4'-isomers may be formed. Pathway 1 is apparently the major conduit for the formation of these three isomers. Figure 1 indicates that 4,4'(II) is mainly formed at the onset, which is in accord with the circumstance that a significant fraction of (I) is present as the p-isomer in this period.

Pathway 2 requires the participation of free toluene in the reaction and is realized when the concentration of (I) is high (about 3 h after the reaction onset). The major products of this pathway are 2,3'- and 2,4'-(II). This pathway may be seen as the reaction of m- and p-platinated toluenes with free toluene. The latter substitutes predominantly the ortho-hydrogen by an aryl group. The nature of this substitution is not yet clear. We may propose that the thermal homolysis of the Pt-Ar bond leads to aryl radicals Ar \cdot , which attack free toluene, predominantly in the ortho position. The radicals may have a free electron in either the meta or para position, which accounts for the absence of 2,2'-ditolyl among the reaction products. The radical intermediate arising upon the attack of Ar \cdot on toluene is oxidized by the Pt(III) complex formed upon homolysis. All these processes may occur in the solvent cage. Since the arene (or olefin [3, 4]) is an acceptor for Ar \cdot , the presence of free arene in solution should accelerate the homolytic decomposition of (I). The complexation of the free arene may lead to labilization of the Pt-C bond in the σ -complex [8-10]. However, there may be alternative mechanisms for the formation of ortho-substituted ditolyls such as the heterolytic decomposition of the Pt-C bond and attack of the Ar $^+$ ion formed on free arene or the formation of a Pt σ -aryl- π -allyl complex from free toluene and (I) upon the loss of a hydrogen atom from the CH $_3$ group of free toluene.

EXPERIMENTAL

A solution of 0.5 g H $_2$ PtCl $_6$ ·6H $_2$ O, 2 ml toluene and 1 ml water in 9 ml CF $_3$ CO $_2$ H was heated in a glass vessel at constant 90°C. At regular intervals, 1-ml samples were taken, 2 ml water was added and the probe was extracted with three 3-ml chloroform portions. The aqueous layer was evaporated at reduced pressure and the residue was dissolved in acetone. Chromatography on a column packed with silica gel containing NH $_3$ was carried out with 2:1 acetone-hexane as eluant. The amount of complex formed was determined spectrophotometrically on a Specord UV-VIS spectrometer. The PMR spectra were taken on a Bruker SXP-4-100 spectrometer at 90 MHz. The chloroform solution was washed with water and dried over Na $_2$ SO $_4$. Chloroform was evaporated. The ditolyl isomers in the residue were determined by gas-liquid chromatography. The gas-liquid chromatographic analysis procedure was described in our previous work [11].

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CONCLUSION

Heating a solution of PtCl $_6$ $^{2-}$ ions and toluene in CF $_3$ CO $_2$ H-H $_2$ O leads to the formation of a platinum(IV) σ -tolyl complex which decomposes in the presence of free toluene to give 3,3'-, 4,4'-, 3,4'-, 2,3'- and 2,4'-ditolyls.

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