

FORMATION OF THE σ -ACETONYL Pt(IV)
COMPLEX IN THE REACTION OF IODOACETONE
WITH PtCl_4^{2-} IN AQUEOUS SOLUTION

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The oxidative addition of alkyl iodides to acido Pt(II) complexes in aqueous solution is a convenient synthetic method for organoplatinum compounds [1-3]



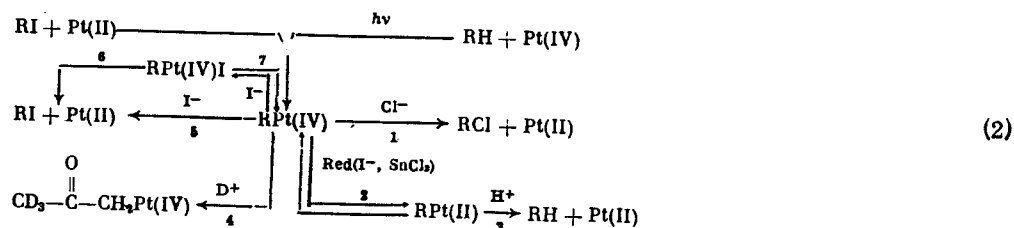
In particular, unstable methyl [1] and ethyl [2] Pt(IV) complexes, proposed previously by Shilov and Shteiman [4] as intermediates in the oxidation of methane and ethane by platinum(IV), were obtained for the first time by this method. Estimates using the kinetic data for the decomposition of MePt(IV) in aqueous chloride solutions [5] and direct measurements showed that, under methane oxidation conditions, the methyl Pt(IV) complex may accumulate only in concentrations of the order of 10^{-6} - 10^{-4} M.

It was of interest to clarify the possibility of obtaining the σ -acetyl Pt(IV) complex ($\text{MeCOCH}_2\text{Pt(IV)}$) from platinum(II) and iodoacetone. This complex was recently isolated [6] as the product of the photoinduced reaction of PtCl_6^{2-} with acetone. It might be expected that the stability of this complex would be markedly higher than that for MePt(IV).

We have found that the reaction of K_2PtCl_4 with iodoacetone in aqueous solution at about 20°C for several hours gives the σ -acetyl Pt(IV) complex which was isolated as the potassium salt of the $\text{MeCOCH}_2\text{PtCl}_5^{2-}$ ion (I) and characterized by spectral methods. This complex was compared with the σ -acetyl platinum(IV) derivative obtained photochemically [6].

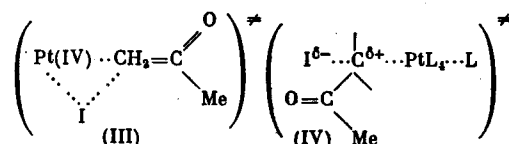
The complexes obtained in both reactions give identical PMR spectra in dilute D_2O solutions: two singlets for the Me and CH_2 groups; the CH_2 signal has characteristic satellites with $J_{\text{H-}^{195}\text{Pt}} = 98.4$ Hz. Upon chromatography on silica gel containing ammonia, complex (I), obtained both by the oxidation-reduction addition of iodoacetone to Pd(II) and by the photochemical reaction of acetone with Pt(IV), is converted to the complex $[\text{MeCOCH}_2\text{PtCl}_4\text{NH}_3]^-$ ion (II). The introduction of NH_3 into the complex, apparently in the position trans to the acetyl group, leads to a reduction in $J_{\text{H-}^{195}\text{Pt}}$ to 87 Hz.

In contrast to MePt(IV) [5], σ -acetyl complex (I) does not decompose to any significant extent upon heating in aqueous solution for 30 min at 80°C. In 2M NaCl at 60°C, this complex is slowly converted to chloroacetone (scheme 2, pathway 1). The pseudo-first-order rate constant $k = -[\text{RPt(IV)}]^{-1}d[\text{RPt(IV)}]/d\tau = 3.86 \cdot 10^{-4} \text{ sec}^{-1}$ found under these conditions relative to the decrease in the PMR signal of the complex is about 30 times less than the corresponding value for the methyl complex [5].

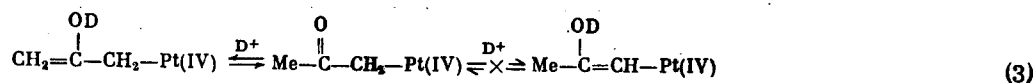


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The reaction of reducing agents such as SnCl_2 or I^- in acid medium leads, as in the case of the methyl [1] and ethyl complexes [2], to the separation of RH : The acetyl complex rapidly gives acetone (pathway 2). In neutral medium, the addition of I^- to a solution of (I) in D_2O immediately gives a change in the PMR spectrum: the $J_{\text{H}-195\text{Pt}}$ coupling constant drops to 87 Hz and the methyl group signal is shifted upfield ($\delta = 2.17$ ppm). The apparent reason for these changes in the PMR spectrum is the replacement of water (or chloride ions) in the coordination sphere of the complex by the iodide ion (equilibrium 7). Then, the intensity of the signal of the iodide complex formed decreases ($\tau_{1/2} \sim 2$ min in about 1 M KI) with the appearance of a signal corresponding to iodoacetone. We note that reductive elimination with the formation of iodoacetone may proceed (see our previous work [5]) either within the coordination sphere (pathway 6, model for transition state (III)) or by $\text{S}_{\text{N}}2$ attack of the iodide ion on the α -carbon atom of the acetyl complex (pathways 5 and 6, model for transition state (IV), where $\text{L} = \text{I}^-$, Cl^- , or H_2O). The difference in the products of the reaction of the σ -acetyl complex with iodide ions in neutral and acid media may be explained by competition of steps 3 and 5 with reversibility of step 2 in scheme 2. These conditions were found to hold in the reduction of methyl iodide to methane by iodide ions catalyzed by platinum(II) [7]:



In conclusion, we note an interesting effect: Rapid deuteration of the methyl groups occurs with $\tau_{1/2} \sim 15$ min at 60°C (pathway 4), while the CH_2 group hydrogen atoms do not undergo exchange, upon heating a solution of complex (I) in 2.5 M DClO_4 in D_2O :



This finding indicates that enolization of the ketone in the complex due to the removal of protons from the α - CH_2 group is impossible or very hindered.

EXPERIMENTAL

All the reactions were carried out in the air. The PMR spectra were taken on a Bruker SXP-4-100 spectrometer at 90 MHz.

Reaction of PtCl_4^{2-} with Iodoacetone. A solution of 0.87 g K_2PtCl_4 and 1 ml iodoacetone in 5 ml water was stirred for 3 h at $\sim 20^\circ\text{C}$. The black platinum iodide precipitate was filtered off and the unreacted iodoacetone was extracted with ether and the aqueous solution was evaporated to dryness in vacuum at about 20°C to yield 0.63 g (59%) yellow-orange complex $[\text{MeCOCH}_2\text{PtCl}_5]\text{K}_2$. PMR spectrum (δ , ppm from TMS, in D_2O , the sodium salt of 2,2-dimethyl-2-silapentane-5-sulfonic acid was the internal standard): 2.26 s (Me), 4.72 s (CH_2), $J_{\text{H}-195\text{Pt}} = 98.4$ Hz. IR spectrum (in vaseline oil): 1670 cm^{-1} ($\text{C}=\text{O}$). UV spectrum (in saturated aqueous NaCl): $\lambda_{\text{max}} 267$ nm. Chromatography of the complex on silica gel containing ammonia with 2:1 acetone-hexane as eluant gives $[\text{MeCOCH}_2\text{PtCl}_4\text{NH}_3]\text{NH}_4$ which was identified by comparison with a sample obtained in the photochemical reaction (see below).

Photoinduced Reaction of PtCl_5^{2-} with Acetone. A solution of 0.2 g $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 7 ml acetone was irradiated for 0.5 h by the total light of a DRSr-1000 high-pressure mercury lamp. The solvent was evaporated in vacuum. Chromatography of the residue on silica gel containing ammonia gave 40 mg (66%) of the complex, $[\text{MeCOCH}_2\text{PtCl}_4\text{NH}_3]\text{NH}_4$ as a yellow-orange oil which slowly crystallizes. Found: C 9.57; H 3.22; N 6.43%. Calculated for $\text{C}_3\text{H}_{12}\text{Cl}_4\text{N}_2\text{O}_5\text{Pt}$: C 8.34; H 2.79; N 6.52%. PMR spectrum (δ , ppm from TMS, in acetone- d_6): 2.16 (Me), 4.38 (CH_2), $J_{\text{H}-195\text{Pt}} = 87$ Hz. IR spectrum: 1680 cm^{-1} ($\text{C}=\text{O}$).

CONCLUSIONS

The reaction of K_2PtCl_4 with iodoacetone in aqueous solution at about 20°C gives the σ -acetyl Pt(IV) complex which is more stable to the action of nucleophilic reagents than the analogous methyl and ethyl complexes.

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