PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION METAL COMPLEXES

II *. REACTION OF $PtCl_6^{2-}$ WITH ACETONE TO GIVE A σ-ACETONYL COMPLEX OF PLATINUM(IV). DETECTION OF PLATINUM(III) COMPOUNDS BY ESR

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Summary

Light irradiation of a $PtCl_6^{2-}$ solution in acetone affords a σ-acetonyl complex of platinum(IV), $[CH_3COCH_2PtCl_5]^{2-}$. Prolonged irradiation yields CH_3COCH_2Cl and $PtCl_4^{2-}$. The signals of a platinum(III) complex and $CH_3COCH_2^{\cdot}$ are detected in the ESR spectrum of the frozen solution of $PtCl_6^{2-}$ in acetone irradiated at 77 K. The proposed mechanism of the reaction involves electron transfer from the enol tautomer of acetone to $PtCl_6^{2-}$.
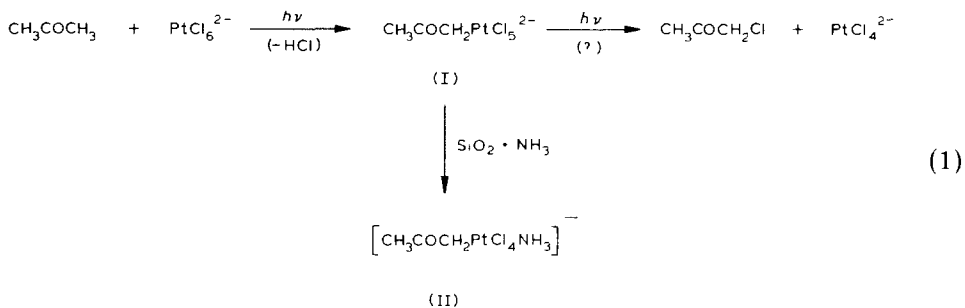
Introduction

When irradiated with light, the $PtCl_6^{2-}$ anion reacts with arenes [1,2], alkyl derivatives of tin and germanium [3], olefins [2,4,5], and saturated hydrocarbons [2] in organic acid solutions to give σ- and π-complexes of platinum(IV) and platinum(II). This ion is also known to be active in the photochemical oxidation of methanol [6]. The photoinduced reactions of $PtCl_6^{2-}$ with the organic compounds mentioned above appear to proceed via intermediate complexes of platinum(III) [1,3–6]. In the present paper, we report the reaction of $PtCl_6^{2-}$ with acetone induced by light irradiation.

Results

Irradiation of an acetone solution of $Na_2PtCl_6 \cdot 6H_2O$ with full light of a 1000 W high-pressure mercury lamp affords a σ-acetonyl complex of platinum(IV) (I), which

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* For part I see ref. 1, and for a Preliminary communication ref. 2.

was isolated in the form $[CH_3COCH_2PtCl_4NH_3]NH_4$ (II) after chromatography on silica gel containing ca. 1% ammonia. Chloroacetone is also formed in this reaction. Figure 1 presents the yields of complex II and chloroacetone (with respect to the initial platinum complex) versus time. Up to approximately 25 min, the yield of the σ-acetonyl complex increases with time and after that rapid decomposition of complex I is observed. The formation of chloroacetone proceeds with an induction period of about 10 min and the region of maximum slope of the kinetic curve corresponds approximately to the maximum concentration of complex I (at ca. 20–30 min).

$$CH_3COCH_3 \;+\; PtCl_6^{2-} \xrightarrow[(-HCl)]{h\nu} \underset{(I)}{CH_3COCH_2PtCl_5^{2-}} \xrightarrow[(?)]{h\nu} CH_3COCH_2Cl \;+\; PtCl_4^{2-}$$

$$\Big\downarrow \; SiO_2 \cdot NH_3 \tag{1}$$

$$\underset{(II)}{\Big[CH_3COCH_2PtCl_4NH_3\Big]^{-}}$$

When small amounts of NaOH or CF_3COOH are added to the reaction mixture, the initial rate of the reaction of the σ-complex formation increases.

Upon irradiation of a frozen acetone solution of $Na_2PtCl_6 \cdot 6H_2O$ for several hours, an ESR spectrum which contains characteristic signals of the perpendicular orientations of platinum(III) complexes in the region corresponding to $g \simeq 2.4$ is observed (Fig. 2a). The perpendicular components of the platinum(III) spectrum include an intensive central singlet line due to the non-magnetic [196]Pt isotope and two satellites due to the splitting on [195]Pt ($I = \frac{1}{2}$, natural abundance 33.8%) [6,7].
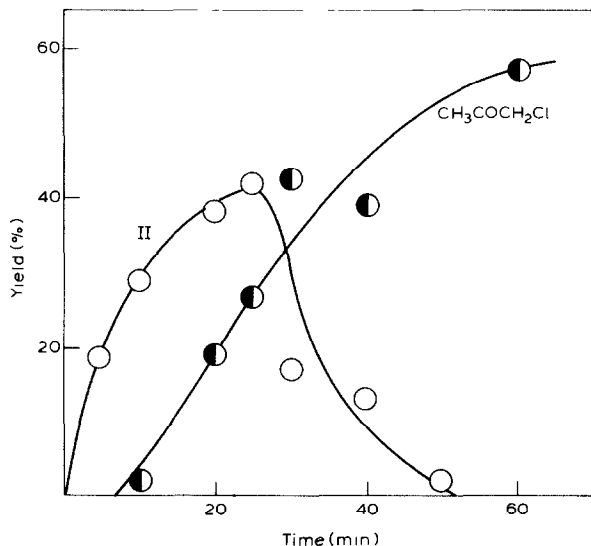

Fig. 1. Yields (%) of complex II and chloroacetone (with respect to the initial platinum(IV) complex) versus time. Initial concentration of $[Na_2PtCl_6 \cdot 6H_2O]_0$ 9×10^{-3} M; 15 °C.
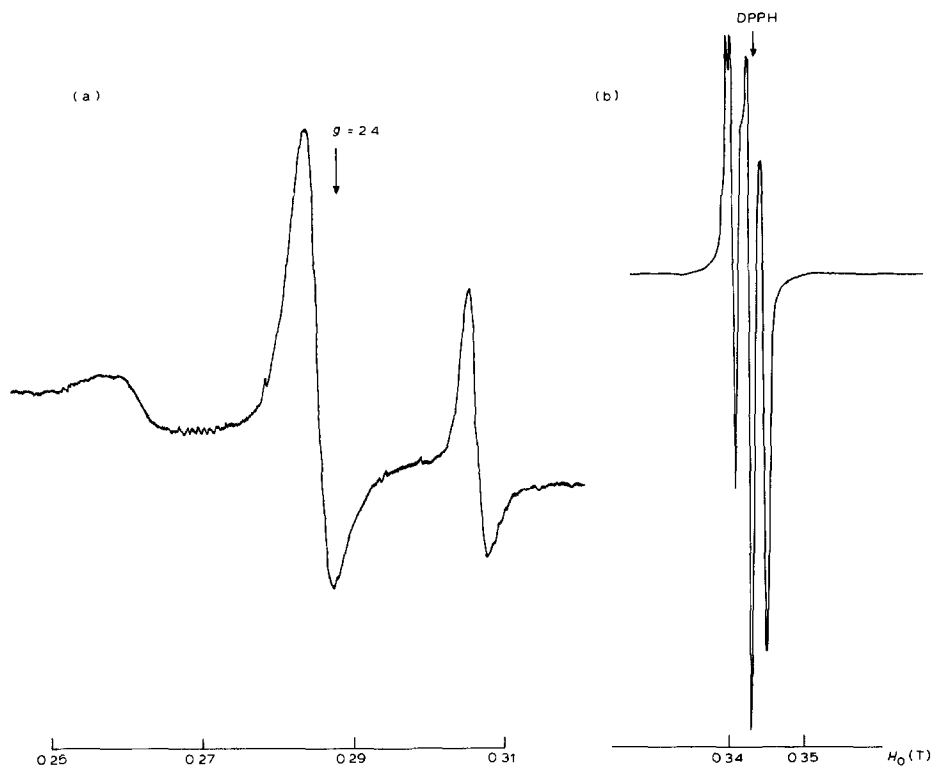
Fig. 2. ESR spectrum of the frozen solution of $Na_2PtCl_6 \cdot 6H_2O$ in acetone at 77 K after light irradiation for 0.5 h. The regions of the platinum(III) complex (a) and the acetonyl radical (b) are shown.

The parallel components of the platinum(III) spectra located at $g \simeq 2.0$ [6,7] are obscured by radicals present in the irradiated samples. The parameters of the observed spectra ($g_{\parallel} = 2.0$, $g_{\perp} = 2.4$; $A_{\parallel} \sim 300 \times 10^{-4}$ cm^{-1} *, $A_{\perp} = 500 \times 10^{-4}$ cm^{-1}) are close to the corresponding values for $PtCl_5{}^{2-}$ complexes produced by γ-radiolyses of K_2PtCl_4 monocrystals [7].

It should be noted that in addition to the main triplet platinum(III) signal a weak additional remains at $H = 250.7$ mT was detected in some runs. The position of this signal is close to that of the additional resonance of the perpendicular orientation observed by Krigas and Roges (see Fig. 3b in ref. 7). To account for the signal in question, Krigas and Roges assumed the existence of magnetically non-equivalent sites of platinum(III) in the monocrystal. Since such an assumption seems unlikely for polycrystalline frozen acetone solution, the additional signal in this case is possibly due to a platinum(III) chloride complex with a different mode of coordination.
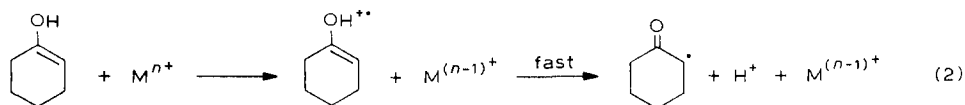
A composite ESR spectrum is observed at $g \simeq 2.0$ (Fig. 2b). The most intensive component of this spectrum is a triplet signal with an intensity distribution of ca.

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* The value of $A_{\parallel}$ (accuracy $\pm 50\%$) was estimated from the non-equidistant positions of the signals of perpendicular orientation using formulae of the second-order perturbation theory [8].
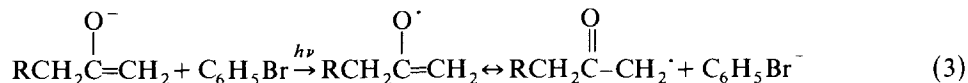
$1/1.4/1$ and a splitting constant of 19.6×10^{-4} cm^{-1}. This signal can be attributed to the acetonyl radical $CH_3COCH_2{}^{\cdot}$, which was observed earlier in γ-irradiated pure acetone at 77 K [9]. It should be noted that no acetonyl radicals are found in frozen pure acetone under photolysis so that the formation of these radicals in the solutions studied is exclusively due to the effect of platinum complexes.
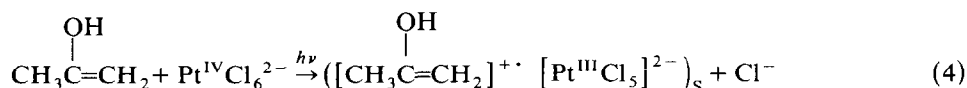
Discussion

The oxidation reactions of ketones by metal compounds are well known [10–12]. The mechanism of oxidation of cyclohexanone by iridium(IV) [13] or iron(III) [14] complexes was suggested to involve electron transfer from the enol tautomer to the metal complex as the first stage of the reaction. The subsequent loss of a proton
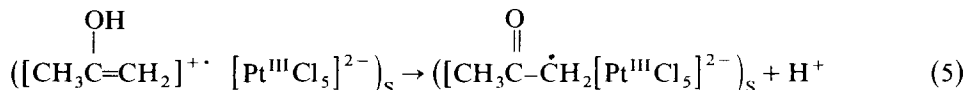
$$\text{(structure with OH)} + M^{n+} \longrightarrow \text{(structure with OH}^{+\cdot}) + M^{(n-1)+} \xrightarrow{\text{fast}} \text{(structure with O}^{\cdot}) + H^+ + M^{(n-1)+} \quad (2)$$

affords the β-oxocyclohexyl radical (eq. 2). β-Oxoalkyl radicals are also formed in the course of oxidation of ketone enolates by copper dichloride [15] and in photochemical reactions of ketones with aryl halides [11,12,16–19]. The formation of oxoalkyl radicals in the latter process is the first step of the radical chain substitution reaction ($S_{RN}1$):

$$\underset{|}{\overset{O^-}{RCH_2C}}=CH_2 + C_6H_5Br \xrightarrow{h\nu} \underset{|}{\overset{O^{\cdot}}{RCH_2C}}=CH_2 \leftrightarrow \underset{\|}{\overset{O}{RCH_2C}}-CH_2{}^{\cdot} + C_6H_5Br^- \quad (3)$$

By analogy with reactions 2 and 3, we assume that the first step of photoinduced reaction 1 is electron transfer from the enol tautomer of acetone to the ion $PtCl_6{}^{2-}$ which is accompanied with loss of a Cl$^-$ anion:

$$\underset{|}{\overset{OH}{CH_3C}}=CH_2 + Pt^{IV}Cl_6{}^{2-} \xrightarrow{h\nu} ([\underset{|}{\overset{OH}{CH_3C}}=CH_2]^{+\cdot} \left[Pt^{III}Cl_5\right]^{2-})_S + Cl^- \quad (4)$$
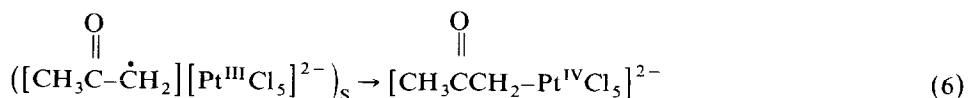
Here ( )$_S$ denotes a solvent cage. The subsequent or synchronous elimination of a proton results in the formation of the acetonyl radical within the solvent cage:

$$([\underset{|}{\overset{OH}{CH_3C}}=CH_2]^{+\cdot} \left[Pt^{III}Cl_5\right]^{2-})_S \rightarrow ([\underset{\|}{\overset{O}{CH_3C}}-\dot{C}H_2[Pt^{III}Cl_5]^{2-})_S + H^+ \quad (5)$$

The formation of the acetonyl radical and the platinum(III) complex is consistent with the observed ESR spectra of photolysed frozen solutions (see above).

The next step of reaction 1 is the coupling of the acetonyl radical and the platinum(III) containing species to form the σ-acetonyl complex of platinum(IV):
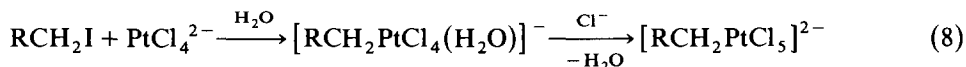
$$([\underset{\|}{\overset{O}{CH_3C}}-\dot{C}H_2][Pt^{III}Cl_5]^{2-})_S \rightarrow [\underset{\|}{\overset{O}{CH_3C}}CH_2-Pt^{IV}Cl_5]^{2-} \quad (6)$$

The proposed mechanism of the σ-acetonyl complex formation involving electron transfer and subsequent coupling of the intermediate paramagnetic particles (eq. 4–6) is similar to the radical non-chain mechanism suggested by Kurosawa et al. [20] for the reaction of $RTl(OAc)_2$ with the nitronate ion $Me_2CNO_2^-$:

$$RTl(OAc)_2 + Me_2CNO_2^- \rightarrow RMe_2CNO_2 + TlOAc + OAc^- \qquad (7)$$
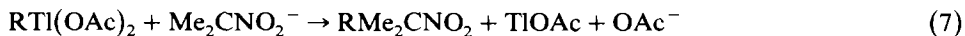
In contrast to the reaction of the nitronate ion with organothallium(III) compounds, the radical chain substitution mechanism labelled $S_{RN}1$ is operative in the reaction of the nitronate ion with alkylmercury compounds [20,21].

The detailed mechanisms of the σ-acetonyl complex decomposition and of chloro-acetone formation are unclear. The experimental data concerning these processes can be summarized as follows.

In the dark complex I is fairly stable in solution for several days. It is worth comparing the stabilities of the σ-methyl and σ-ethyl complexes. The three platinum(IV) σ-complexes can be prepared by oxidative addition of related iodides to the ion $PtCl_4^{2-}$ in aqueous solution [22–24]:

$$RCH_2I + PtCl_4^{2-} \xrightarrow{H_2O} \left[RCH_2PtCl_4(H_2O) \right]^- \xrightarrow[-H_2O]{Cl^-} \left[RCH_2PtCl_5 \right]^{2-} \qquad (8)$$

The methyl and ethyl complexes, however, react readily with nucleophiles (e.g. Cl^-, H_2O) [22,23] to give the corresponding alkyl chlorides or alcohols. The stability of the σ-complex under consideration decreases with increasing electron-releasing ability of $R = CH_3 < H \ll COCH_3$.

As already mentioned, an induction period is observed for chloroacetone forma-tion in the photochemical reaction (eq. 1), the maximum rate of this process corresponding to the region of maximum concentration of the σ-acetonyl complex (see Fig. 1). Thus, it can be suggested that complex I is an intermediate in the photooxidation of acetone to chloroacetone by the $PtCl_6^{2-}$ ion.

A rather abrupt decrease of the σ-acetonyl complex concentration at time > 30 min is perhaps evidence of the decomposition reaction being accelerated by products of the decay (e.g. by platinum(II) complexes, the concentration of which increases rapidly when the σ-acetonyl complex concentration falls). It is interesting to note that similar behaviour has been observed for the σ-aryl complexes of platinum(IV) in thermal reactions [25–27].

Unfortunately, these experimental data are too scarce to suggest a reliable scheme for the reactions of σ-acetonyl complex decay and chloroacetone formation. How-ever, it can be concluded that the radical chain mechanism similar to that proposed for the photoinduced oxidation of methanol by $PtCl_6^{2-}$ ions [6] is apparently not operative in this case, because it would predict the synchronous formation of complex I and chloroacetone.

Experimental

All the reactions were carried out in air. The ESR spectra were recorded on EPR-20 and Bruker SD-220D spectrometers. The NMR spectra were taken on a Bruker SXP-4-100 Fourier pulse spectrometer.

σ-Acetonyl complex of platinum(IV)

A solution of 0.2 g of $Na_2PtCl_6 \cdot 6H_2O$ in 8 ml of acetone was irradiated with full light of a 1000 W high-pressure mercury lamp for 30 min at 20 °C. The reaction was accompanied with the deposition of NaCl precipitate. Acetone was removed under reduced pressure and the residue was chromatographed on silica gel containing ammonia (prepared by exposing silica gel to aqueous ammonia in a desiccator). A mixture of acetone/hexane (2/1) eluted an orange-yellow band of complex II. Analysis: Found: C, 9.6; H, 3.2; N, 6.5. $C_3H_{12}Cl_4N_2OPt$ calcd.: C, 8.4; H, 2.8; N, 6.5%. IR spectrum (Nujol): 1670 cm^{-1} (C=O). ^1H NMR spectrum (in acetone-d_6): δ 2.26 (singlet, CH$_3$); 4.72 (singlet, CH$_2$), $J(^1H-^{195}Pt)$ 98.4 Hz.

Kinetic measurments were carried out under the same conditions. The yields of complex II were determined spectrophotometrically; the concentrations of chloro-acetone were determined by ^1H NMR spectroscopy.

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