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# PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH COMPLEXES OF TRANSITION METALS.

## VIII.* PHOTOCHEMICAL CHLORINATION OF SATURATED AND AROMATIC HYDROCARBONS WITH THE $AuCl_4^-$ COMPLEX

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We have previously found that light induces the reaction of the $PtCl_6^{2-}$ complex with a number of organic and organometallic compounds. Thus the reaction with aromatic compounds in acetic acid leads to the formation of σ-aryl complexes of Pt(IV) [2-4]. The photochemical reaction with olefins gives π-olefin complexes of Pt(II) in good yields, along with complex mixtures of products of oxidation of the olefins [2, 5, 6]. The irradiation of solutions of $PtCl_6^{2-}$ and methyl or ethyl derivatives of tin or germanium leads to the production of a σ-methyl complex of Pt(IV) or a π-ethylene derivative of Pt(III) [7]. In addition, a π-complex of 1-hexene and Pt(II) was isolated in 10% yield from the mixture of products of photochemical reaction of the $PtCl_6^{2-}$ ion with hexane in acetic acid [2].

In the present research we investigated the light-induced reaction of the $AuCl_4^-$ ion with saturated, alkylaromatic, and aromatic hydrocarbons. Since it is known that σ-aryl and π-olefin complexes of gold are unstable, we did not attempt to isolate such compounds. The course of the reaction was followed from the disappearance of the starting $AuCl_4^-$ ion, as well as from the accumulation of products of oxidation of the organic substrate.

Completely saturated (cyclohexane, pentane, hexane, heptane, 2-methylbutane, 2,2,4-trimethylpentane), aromatic (benzene), and alkylaromatic (toluene, ethylbenzene) hydrocarbons were used as substrates in photochemical oxidation with the $AuCl_4^-$ ion. Acetic acid served as the solvent. The kinetics of the reaction were investigated with respect to the consumption of the starting chloroauric acid, which is converted during the reaction to metallic gold, which is deposited on the walls of the flask. The concentrations of the alkyl or aryl chlorides formed in the oxidation of the hydrocarbons were also measured in individual cases. Other oxidation products (alcohols, alkyl acetates and, in the case of toluene, benzaldehyde) are formed in very small amounts (less than 5% of the amounts of the chlorides). Thus, the reaction proceeds primarily via the scheme

$$1.5RH + HAuCl_4 \rightarrow 1.5RCl + Au^0 + 2.5HCl.$$

The kinetic curves of the photoreduction of the $AuCl_4^-$ ion by hydrocarbons and of the accumulation of products of oxidation of the hydrocarbons are presented in Figs. 1 and 2. It is apparent that Au(III) is reduced most rapidly by cyclohexane and more slowly (at approximately equal rates) by normal alkanes (pentane, hexane, heptane). Gold(III) is reduced appreciably more slowly in the presence of alkylaromatic hydrocarbons, viz., ethylbenzene and toluene:

$$\text{cyclo-}C_6H_{12} > C_5H_{12} > C_6H_{14} > C_7H_{16} > C_6H_5C_2H_5 > C_6H_5CH_3 > C_6H_6.$$

The kinetics of the photoinduced reduction of Au(III) were investigated in somewhat greater detail in the case of the reaction of $AuCl_4^-$ with hexane. The reaction is first order in hexane, since for small degrees of transformation of Au(III) conversion α, which is determined by the expression

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*See [1] for communication VII.

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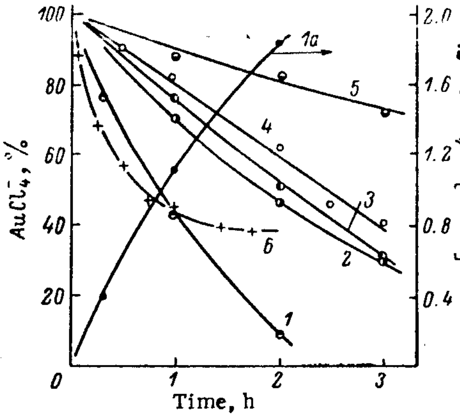

Fig. 1

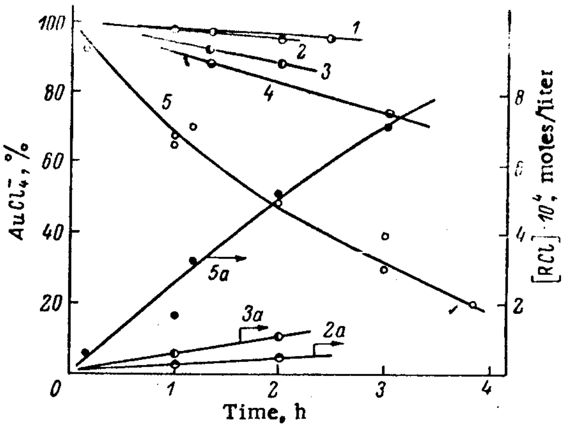

Fig. 2

Fig. 1. Consumption of $AuCl_4^-$ in the chlorination, under irradiation, of 1.3 M solutions of the hydrocarbons with a 0.04 M solution of $HAuCl_4$ in $CH_3COOH$: 1) cyclohexane; 2) pentane; 3) heptane; 4) hexane; 5) ethylbenzene; 6) 0.13 M solution of 1-hexene; 1a) accumulation of cyclohexyl chloride corresponding to the consumption of $AuCl_4^-$ in the reaction with cyclohexane (1).

Fig. 2. Consumption of $AuCl_4^-$ and accumulation of chlorinated hydrocarbons in the chlorination, under irradiation, of hydrocarbons with the $HAuCl_4$ complex in $CH_3COOH$: 1) consumption of $AuCl_4^-$ in the absence of a hydrocarbon, $[AuCl_4^-]_0$ = 0.15 mole/liter; 2) consumption of $AuCl_4^-$ in the reaction with benzene (3.7 moles/liter), $[AuCl_4^-]_0$ = 0.1 mole/liter; 2a) accumulation of $C_6H_5Cl$ in the same reaction; 3) consumption of $AuCl_4^-$ in the reaction with toluene (3.0 moles/liter), $[AuCl_4^-]_0$ = 0.1 mole/liter; 3a) accumulation of $C_6H_5CH_2Cl$ in the same reaction; 4) consumption of $AuCl_4^-$ in the reaction with ethylbenzene (3.0 moles/liter), $[AuCl_4^-]_0$ = 0.12 mole/liter; 5) consumption of $AuCl_4^-$ in the reaction with hexane (1.8 moles/liter), $[AuCl_4^-]_0$ = 0.12 mole/liter; 5a) accumulation of hexyl chlorides (sum of the isomers) in the same reaction.

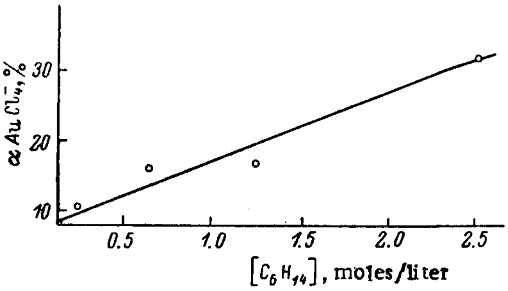

Fig. 3. Dependence of the relative decrease in the $AuCl_4^-$ concentration (conversion α, %) after 1 h in the photooxidation of hexane in $CH_3COOH$ on the hexane concentration ($[AuCl_4^-]_0$ = 0.04 mole/liter).

$$\alpha = \{([Au(III)]_0 - [Au(III)])/[Au(III)]_0\} \cdot 100\%,$$

increases linearly with an increase in $[RH_0]$ (Fig. 3). The reaction proceeds with self-inhibition, and this effect is manifested more distinctly, the higher the $[Au(III)]_0$ concentration (Fig. 4). The use of wire gauzes that absorb a known amount of light made it possible to establish that in the case of a sufficiently high light intensity the reaction rate no longer depends on the light intensity. Thus, for $[AuCl_4^-]_0$ = 0.12 mole/liter and $[hexane]_0$ = 1.8 moles/liter after irradiation for 1 h:

| | | | |
|---|---|---|---|
| Light intensity (relative units) | 0.05 | 0.4 | 1.0 |
| Conversion α, % | 4 | 30 | 31 |

Let us note that under these conditions substantial self-inhibition is observed for conversion α greater than 60-70%.

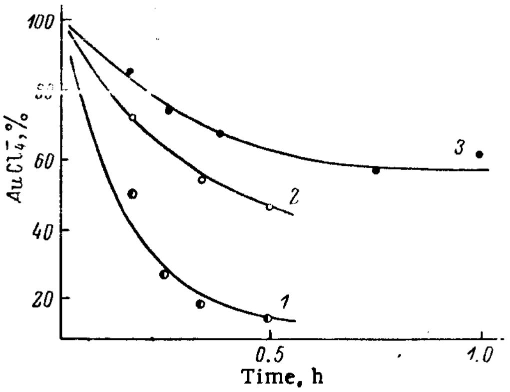

Fig. 4. Consumption of $HAuCl_4$ in the photochemical reaction with hexane (1.3 moles/liter) in $CH_3COOH$ for various initial $[AuCl_4^-]_0$ concentrations: 1) 0.05; 2) 0.15; 3) 0.5 mole/liter.

TABLE 1. Selectivities (1°:2°:3°) in the Chlorination of Alkanes in Various Systems in Acetic Acid Solution ($[HAuCl_4]_0$ = 0.1 mole/liter, [RH] = 1-2 moles/liter)

| System | Alkane | |
|---|---|---|
| | 2-methylbutane | 2,2,4-trimethylpentane |
| $RH+AuCl_4^-$ | 1 : 3.5 : 4.5 | 1 : 3 : 1.5 |
| $RH+Cl_2$ (without a solvent) | 1 : 3 : 4 | 1 : 3 : 1.5 |
| $RH+Cl_2$ (in $CH_3COOH$) | 1 : 3.5 : 4.5 | 1 : 3.5 : 1.5 |
| $RH+Cl_2+AuCl_4^-$ | 1 : 4 : 4.5 | 1 : 3 : 1.5 |

Irradiation was usually carried out with the total light of a high-pressure mercury lamp in a quartz flask; however, virtually no decrease in the rate of reduction of Au(III) is observed when the reaction is carried out in a glass flask ($\lambda$ > 320 nm). We were able to establish by means of gas-liquid chromatography (GLC) that about 20% 1-chlorohexane and about 80% of a mixture of 2- and 3-chlorohexanes (the peaks of the 2- and 3-chloro isomers are not separated under the selected conditions) are formed in the chlorination of hexane.

To ascertain the nature of the active particle that develops during the irradiation of $HAuCl_4$ solutions we measured the selectivities of attack on the C–H bonds in branched alkanes such as 2-methylbutane and 2,2,4-trimethylpentane; these selectivities were compared with the selectivities in the case of chlorination by the chlorine atom. The selectivities were measured as the ratios of the yields in the reactions of the corresponding alkyl chlorides with allowance for the relative numbers of given bonds, i.e.,

$$1°:2°:3° = \{[\text{prim-R–Cl}]/(\text{No. of prim-C–H bonds})\}:\{[\text{sec-R–Cl}]/(\text{No. of sec-C–H bonds})\}:\{[\text{tert-R–Cl}]/(\text{No. of tert-C–H bonds})\}.$$

It was found that in 2-methylbutane the bonds at the secondary carbon atoms are more active than those at the primary carbon atoms by a factor of three to four, as compared with a factor of four to five in the case of the bonds at the tertiary carbon atoms: 1°:2°:3° = 1:3.5:4.5. It is easily estimated that a similar selectivity is also obtained in the case of hexane: 1°:2° = 1:3. This value is somewhat different for the more sterically hindered 2,2,4-trimethylpentane: 1°:2°:3° = 1:3:1.5.

To measure the selectivities of attack on the C–H bonds of alkanes by the chlorine atom we carried out the photoinitiated chlorination with molecular chlorine. It is known that chlorination is realized via a radical-chain mechanism in this case.

The chlorination was carried out up to no more than 5-10% conversion with respect to the alkane. It was found that in this case the selectivities are vitually independent of the presence of a solvent and are close to the selectivities of the photoinduced chlorination by the $AuCl_4^-$ ion (see Table 1). One might have assumed that reactions of alkyl radical $R^\cdot$ with Au(III) play a substantial role in the formation of chlorine-containing products and thereby change the yields of the corresponding chlorides. However, it was found that the chlorination of alkanes by molecular chlorine in the presence of $HAuCl_4$ proceeds with the same selectivities as without $HAuCl_4$ (see Table 1) (the time of irradiation of the $Cl_2$ + RH + $HAuCl_4$ system was much shorter than that of the RH + $HAuCl_4$ system).

Thus the data obtained convincingly demonstrate that the particle that attacks the C–H bonds of alkanes during irradiation of solutions of $HAuCl_4$ is the chlorine atom.

Let us examine a possible mechanism for the photoinduced chlorination of alkanes by the Au(III) complex. Excitation of the trivalent gold complex by light evidently occurs in the first step (1) [8]. A redox reaction with electron transfer from $Cl^-$ to Au(III), which leads to the formation of a chlorine atom, which subsequently, with a certain degree of probability, emerges from the solvent cage into the volume (2), may proceed in the coordination sphere of the excited Au(III) complex. Two-electron reduction of Au(III) with the formation at once of $Cl_2$ is also not excluded in this case: (3) and (4).

$$AuCl_3 \xrightarrow{h\nu} AuCl_3^* \quad (1)$$

$$AuCl_3^* \longrightarrow AuCl_2 + Cl^\cdot \quad (2)$$

$$AuCl_3^* \longrightarrow AuCl + Cl_2 \quad (3)$$

$$Cl_2 \xrightarrow{h\nu} 2Cl^\cdot \quad (4)$$

$$Cl^\cdot + Au(II) \longrightarrow Cl^- + Au(III) \quad (5)$$

$$Cl^\cdot + RH \longrightarrow R^\cdot + HCl \quad (6)$$

$$R^\cdot + Cl{-}Au(III) \longrightarrow R{-}Cl + Au(II) \quad (7)$$

$$R^\cdot + Au(III) \longrightarrow \sigma - R{-}Au\,(IV) \longrightarrow R^+ + Au(II) \quad (8)$$

$$2Au(II) \longrightarrow Au(III) + Au(I) \quad (9)$$

$$2Au(I) \longrightarrow Au(II) + Au(0) \quad (10)$$

$$n\,Au(0) \longrightarrow Au_n^0\ (\text{metal}) \quad (11)$$

$$Au(II) + Au(I) \longrightarrow Au(III) + Au(0) \quad (12)$$

$$Au(III) + ArH \longrightarrow Au(III) + ArH^* \quad (13)$$

$$ArH^* \longrightarrow ArH + \text{heat} \quad (14)$$

Since the reaction $2Cl^\cdot \rightarrow Cl_2$ in light is reversible and the chlorine atom reacts slowly with acetic acid, the reaction of $Cl^\cdot$ with an Au(II) complex (5), which also explains the high resistance of $HAuCl_4$ to irradiation of its solutions in acetic acid in the absence of a hydrocarbon, should exist. The rather rapid reaction (6) becomes possible when a hydrocarbon is introduced into the system.

After this, the resulting radical $R^\cdot$ reacts with Au(III). This reaction evidently proceeds rapidly, since the introduction into the system of oxygen, which is an alkyl-radical trap ($R^\cdot + O_2 \rightarrow RO_2^\cdot$), changes the rate of reduction of Au(III) only slightly and does not change the composition of the products of oxidation of the alkane. For example, when oxygen is bubbled through the reaction solution during irradiation, the conversion of $HAuCl_4$ in the presence of cyclohexane after 1 h is 40%, as compared with 60% in a closed flask (Fig. 1). Correspondingly, $0.9 \cdot 10^{-4}$ and $1.1 \cdot 10^{-4}$ mole of cyclohexyl chloride are formed. The reaction of $R^\cdot$ with Au(III) may proceed differently as, for example, in analogy with complexes of some other metals [9], via a mechanism involving ligand transfer (detachment of a Cl atom) (7) or through the intermediate formation of a σ-alkyl complex of gold (8) (see [10, 11]). The resulting carbonium ion $R^+$ may react with $Cl^-$ ions to give RCl or add $CH_3COO^-$ or $OH^-$ to give the corresponding oxygen-containing products. Finally, the formation of an olefin is possible when $H^+$ splits out.

The Au(II) compounds formed as a result of the one-electron reduction are unstable [12] and undergo disproportionation, just like the resulting Au(I) complex: (9)-(11). Reaction (12) is also possible.

Let us note that Au(I) is capable of giving colorless π complexes with olefins. In fact, we found that olefins (for example, 1-hexene) react rapidly with $AuCl_4^-$ upon irradiation with light (Fig. 1, curve 6). Thus the amount of $AuCl_4^-$ decreases to 63% in the first 20 min of irradiation of the solution, at the same time that deposition of metallic gold still does not occur. During this period a significant part of the gold evidently exists in solution in the form of an olefin π complex of Au(I), which does not absorb in the visible part of the spectrum. After this period, deposition of metallic gold is observed, and the reaction slows down.

The above-presented order of the hydrocarbons with respect to the decrease in their activity in the reduction of Au(III) corresponds to the decrease in the rate of the reaction of the chlorine atom with these hydrocarbons. Thus Au(III) is reduced by cyclohexane more rapidly than by ethylbenzene and toluene by factors of 3.5 and 7, respectively, which are close to the ratios of the rate constants for the reaction of $Cl^{\cdot}$ with cyclohexane and these hydrocarbons (2.5 and 8, respectively, at 40°C [13]).

The role of benzene in the system is somewhat unusual. The introduction of this hydrocarbon together with cyclohexane leads to a certain decrease in the rate of reduction of Au(III) as compared with the reaction that occurs in the bsence of benzene. This is evidently associated with the fact that aromatic compounds, due to energy transfer from $Au(III)^*$, may actually catalyze the conversion of the energy of the excited state to heat: (13) and (14).

The addition of small amounts of LiCl or $H_2SO_4$ to the system does not lead to an appreciable slowing down of the reduction of Au(III) by hexane; slowing down of the reaction is therefore evidently not caused by $H^+$ or $Cl^-$ ions but rather by some other products such as, for example, Au(II) derivatives or a π-olefin complex of Au(I).

## EXPERIMENTAL

All of the reactions were carried out with vigorous stirring of the solution with a magnetic stirrer in air (if not specially stipulated) in a cylindrical quartz flask with a diameter of 2 cm with a jacket cooled with running water (~15°C) with illumination with the total light of a DRSh-1000 high-pressure mercury lamp (1000 W). The volume of the solution was 6 ml. The metallic gold that deposited on the walls of the flask was mechanically removed periodically with a glass rod. The $AuCl_4^-$ concentrations was determined spectrophotometrically (Specord UV-Vis) from the absorption in the visible region. The concentrations of the products of oxidation of the organic substrates were determined by GLC. For this, after the reaction was complete, a small amount of water was added to the solution, and the hydrocarbon layer was separated and washed with water and $NaHCO_3$ solution. The products were analyzed with a Biokhrom-1 chromatograph with a flame-ionization detector. The products of oxidation of cyclohexane (cyclohexanol, cyclohexanone, cyclohexyl acetate, cyclohexyl chloride) were analyzed with a 4-m long column packed with 15% Carbowax-20M on Chromaton N-AW-DMCS (column diameter 3 mm). The isomeric alkyl chlorides were analyzed with a 3-m-long column (diameter 3 mm) packed with 5% XE-60 silicone on Chromaton N-AW-DMCS; the selectivities of attack at the C—H bonds were determined as the ratios of the areas of the corresponding peaks of the chloroalkanes with allowance for the numbers of primary, secondary, and tertiary bonds in the starting hydrocarbon.

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## CONCLUSIONS

Irradiation of solutions of $HAuCl_4$ and a hydrocarbon (alkane, alkylarene, or benzene) in acetic acid with light leads to the formation of metallic gold and alkyl or aryl chlorides. A reaction mechanism that includes attack by a free Cl atom on the saturated C—H bond of the hydrocarbon is proposed.

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