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Photochemical Synthesis of Tris(tetrachloro-*o*-semiquinone) chromium(III) Complex by Oxidative Substitution of $Cr(CO)_6$

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The tris(tetrachloro-*o*-semiquinone)-chromium(III) complex, $Cr(O_2C_6Cl_4)_3$, was described to be formed by refluxing $Cr(CO)_6$ with tetrachloro-*o*-quinone, *o*-$O_2C_6Cl_4$, in benzene for 36 [1] or 12 hours [2]. Our attempts to synthesize this complex by such a procedure failed in spite of a broad variation of such experimental conditions as concentration, material and solvent purity, absence of air and moisture *etc.*

We have found, however, that the reaction of $Cr(CO)_6$ with *o*-$C_2C_6Cl_4$ is a photochemical process which occurs readily even at laboratory temperature. This reaction has shown to be interesting mechanistically as it represents an example of a hitherto not described photochemical reaction of $Cr(CO)_6$ with oxidizing substrate, producing a chromium(III) complex instead of simple substituted derivatives of $Cr(CO)_6$ as in all other cases studied [3–6]. The reaction described is thus a photochemical oxidative-substitution process.

Experimental

Photopreparations were performed by the immersion well technique [9] in an apparatus constructed by Dr. F. Liska, Institute of Chemical Technology, Prague [10]. Water-cooled high pressure mercury arc, light source was used. The light was filtered by the pyrex glass to remove the radiation of wavelengths shorter than approx. 280 nm. Saale-Glass GmbH (GDR) UG 11 filter was used for irradiation within the 280–390 nm spectral range. IR spectra were measured on Perkin Elmer Model 257 grating spectrometer, electronic adsorption spectra were obtained on Unicam SP 800B instrument.

$Cr(CO)_6$ and *o*-$O_2C_6Cl_4$ were used as obtained from Fluka. Benzene was distilled from sodium metal and from Raney nickel.

Results and Discussion

$Cr(O_2C_6Cl_4)_3$ was synthesized as follows: 0.18 g of $Cr(CO)_6$ and 1 g of *o*-$O_2C_6Cl_4$ (*i.e.* molar ratio 1:5) were dissolved in 150 ml of benzene under argon atmosphere and irradiated by the mercury-arc light filtered by pyrex glass for about 2 hours. The orange colour of the solution turned rapidly dark red after the irradiation started. The precipitated dark red solid was filtered off and washed with cold benzene. Yield of the solid was 60–70% based on $Cr(CO)_6$. The obtained product was shown to have identical IR and UV-VIS spectra as $Cr(O_2C_6Cl_4)_3 \cdot 4C_6H_6$ described by Pierpont [1]. It may be recrystallized from CS_2 producing $Cr(O_2C_6Cl_4)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$ species (*cf.* [2]), which was characterized by spectroscopy and by analysis. The described reaction also occurs when the reaction mixture in the pyrex flask is irradiated by direct sunlight. Irradiation by the light of wavelengths 280–390 nm (*i.e.* in the region of LF-absorption of $Cr(CO)_6$) leads also to fast production of $Cr(O_2C_6Cl_4)_3$. No dark reaction between $Cr(CO)_6$ and *o*-$O_2C_6Cl_4$ was observed under any experimental conditions.

The optimum initial molar ratio of $Cr(CO)_6$ and *o*-$O_2C_6Cl_4$ was found to be 1:5. Different values of this ratio significantly decreased the yield of $Cr(O_2C_6Cl_4)_3$. The brown-violet, hitherto not fully characterized product, contaminated by traces of $Cr(O_2C_6Cl_4)_3$, is formed at the ratio 1:1. This product does not contain any CO groups, as proved by IR spectroscopy. High excess of *o*-$O_2C_6Cl_4$ (1:10–15) also decreases the reaction yield, as $Cr(O_2C_6Cl_4)_3$ itself is not photochemically stable in the presence of excess of free *o*-$O_2C_6Cl_4$ producing species absorbing at 710 nm. High excess of *o*-$O_2C_6Cl_4$ also decreases the reaction rate decreasing the number of photons actually absorbed by $Cr(CO)_6$ as the second intense absorption bond of *o*-$O_2C_6Cl_4$ overlaps with the LF-absorption bands of $Cr(CO)_6$.

The photochemical reaction between $Cr(CO)_6$ and *o*-$O_2C_6Cl_4$ was also followed by IR spectroscopy in the ν-CO region and by UV-VIS spectroscopy. Under all experimental conditions described above, the ν(CO) IR-band at 1985 cm^{-1} simply decreases when the solution is irradiated. Interruption of irradiation stops the reaction, which starts again immediately after the irradiation is switched on (Fig. 1). When the solutions of $Cr(CO)_6$ were irradiated in the absence of *o*-$O_2C_6Cl_4$, the decrease of ν(CO) band was much slower (Fig. 1). Formation of any intermediate containing CO-ligands was never observed, regardless of the value of the molar ratio of the reactants. UV-VIS spectroscopy proved that Cr-

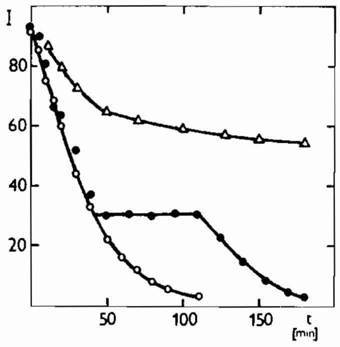

Fig. 1. Dependence of the intensity (I) of the ν(CO) band at 1980 cm^{-1} on the irradiation time. Solution of 64 mg of $Cr(CO)_6$ and 430 mg of o-$O_2C_6Cl_4$ in 100 ml of benzene. ○: continuous irradiation, ●: irradiation interrupted at t = 50 min and switched on at t = 110 min. △: continuous irradiation of $Cr(CO)_6$ solution in absence of o-$O_2C_6Cl_4$. (Intensity in arbitrary units.)

$(O_2C_6Cl_4)_3$ is the only product formed in the course of the reaction.

From the experimental data outlined above, it may be concluded that

1) $Cr(O_2C_6Cl_4)_3$ complex is formed by a photochemical reaction:

$$Cr(CO)_6 + 3\ o\text{-}O_2C_6Cl_4 \xrightarrow[h\nu]{} Cr(O_2C_6Cl_4)_3 + 6CO \qquad (1)$$

This reaction is solely a photochemical process which does not occur as a thermal one.

2) No reaction intermediates could be prepared or detected spectroscopically within the time frame of the overall reaction, *i.e.* the primary reaction step has to be the rate determining one.

3) Neither $[Cr(CO)_2(O_2C_6Cl_4)_2]$ nor $[Cr(CO)_4(O_2C_6Cl_4)]$ species are formed as intermediates of reaction (1), or by the irradiation of the benzene solutions of $Cr(CO)_6$ and o-$O_2C_6Cl_4$ in the molar ratio 1:1 or 1:2.

Chromium hexacarbonyl is well known to undergo a wide variety of photosubstitution reactions producing mono- or di-substituted derivatives $Cr(CO)_5L$ or $Cr(CO)_4(L{-}L)$ [3–6], without change of the formal oxidation number of chromium atom. Photosubstitution of more than two carbonyl ligands is a very slow process which occurs only with strong π-acids capable to stabilize the zerovalent metal oxidation state [4, 11, 12], such as PF_3, $PF_2(OP_r^n)$, $PF(OMe)_2$. Further substitution of $Cr(CO)_4L_2$ complexes needs usually very long irradiation [11–13]; formation of CrL_6 and $Cr(CO)L_5$ requires irradiations even for 6–20 days [11]. Moreover, mixtures of various $M(CO)_{6-n}L_n$ derivatives are usually formed [12].

Contrary to these results, photosubstitution of all CO-ligands in $Cr(CO)_6$ by o-$O_2C_6Cl_4$ is completed under mild conditions within approximately two hours without any apparent formation of $[Cr(CO)_4(O_2O_6Cl_4)]$ and/or $[Cr(CO)_2(O_2C_6Cl_4)_2]$ intermediates. It was proved [7, 8] that the product, $Cr(O_2C_6Cl_4)_3$, is a chromium(III)-tris-o-semiquinone complex. Reaction (1) thus represents a hitherto undescribed photoactivation of $Cr(CO)_6$ for oxidative addition. The overall reaction may thus be regarded as a *photochemical oxidative substitution* of all CO-ligands in $Cr(CO)_6$. We suggest the following mechanism for this reaction: photoexcitation produces $Cr(CO)_5$ as a primary photoproduct [3–6] which reacts very rapidly with o-$O_2C_6Cl_4$ *via* one- or two-electron oxidative addition, producing $[Cr^I(CO)_4(o\text{-semiquinone})]$ or $[Cr^{II}(CO)_4(\text{catecholate})]$ complex respectively. Such redox processes results in a strong destabilization of all remaining Cr–CO bonds as they diminish the Cr → CO π-back bonding due to the removal of electrons from chromium t_{2g} orbitals. The primary intermediate, $Cr(CO)_4(O_2C_6Cl_2)$, has therefore to be an unstable species, reacting very rapidly with further o-$O_2C_6Cl_4$ molecules producing the final $Cr(III)(o\text{-semiquinone})_3$ complex. The suggested mechanism may be a more general one and photolysis of $M(CO)_6$ (M = Cr, Mo, W) in the presence of oxidizing ligands can produce a wide variety of new compounds. Several systems are under investigation in this laboratory.

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