Phase-Transfer Photolysis of Metal Hexacarbonyls
Horst Kunkely and Arnd Vogler*
Institut für Anorganische Chemie der Universität Regensburg, Universitätssstrasse 31,
D-8400 Regensburg, Germany
Received June 4, 1992

Summary: The photochemical conversion of M(CO)₆ (M = Cr, Mo, W) to M(CO)ₓX⁻ (X = halogen) across a hexane/water interface leads to a separation of the reactant and product. This process may be of general importance for synthetic applications. Under suitable conditions inner-filter effects and secondary photolysis can be avoided.

Photochemical reactions in microheterogeneous media have been investigated extensively.¹² In particular excited-state electron transfer of metal complexes has been

(2) Thomas, J. K. The Chemistry of Excitation at Interfaces; ACS Monograph 151; American Chemical Society: Washington, DC, 1984.

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studied in order to achieve an efficient charge separation by a spatial isolation of reactants and products.\(^1\) Recently, excited-state electron transfer from a metal complex to an organic acceptor across a macroscopic liquid/liquid interface was also accomplished.\(^4\) Such systems may be useful not only for mechanistic studies but also for synthetic applications. We explored this possibility and selected the photo substitution of chromium, molybdenum, and tungsten carbonyls by halide anions for the present investigations.\(^5\) While the photolysis was carried out in hexane solutions, the product formation took place in water. This phase-transfer photolysis is based on the different solubilities of reactant and product in both immiscible solvents. The carbonyls dissolve only in the nonpolar alkane, and the substituted carbonyl anions are soluble only in water.

The photolysis was performed in a very simple setup. An optical cell contained both immiscible solutions in two separate layers. In typical experiments the photolysis cell was filled with 2.6 mL of 0.1 M alkali halide in water and 0.5 mL of 5 \(\times\) 10\(^{-4}\) M M(CO)\(_6\) in n-hexane. Both solutions were saturated with argon. From high-pressure lamp (Osram HBO 100 W/2 or Hanovia 1-kW 977 B-1) passed suitable glass or interference filters, entered the optical cell vertically from the bottom, passed the aqueous solution, and was absorbed by the metal carbonyl in the hexane layer.

The photolysis leads to the well-known dissociation of the hexacarbonyl.\(^6,7\)

\[
M(CO)\_6 \rightarrow M(CO)\_5 + CO
\]

The M(CO)\(_5\) fragment recombines with CO or diffuses to the interface where it reacts with halide:

\[
M(CO)\_5 + X^- \rightarrow M(CO)\_5X^-
\]

Since M(CO)\(_5\)X\(^-\) does not dissolve in hexane, it accumulates in the aqueous phase.

The progress of the photolysis was monitored by absorption spectroscopy. The optical cell was adjusted to a position which enabled the analyzing light beam of the spectrometer to pass only the aqueous layer. The spectral variations which accompanied the irradiation confirmed the formation of M(CO)\(_5\)X\(^-\) in each experiment (Table 1).

<table>
<thead>
<tr>
<th>reactants</th>
<th>(\lambda_m (nm))</th>
<th>product</th>
<th>(\lambda_{max} (\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)(_5) + NaBr</td>
<td>290-370</td>
<td>Cr(CO)(_5)Br(^-)</td>
<td>443 (840), 424 (24000)</td>
</tr>
<tr>
<td>Cr(CO)(_5) + NaI</td>
<td>366</td>
<td>Cr(CO)(_5)I(^-)</td>
<td>438 (10000), 348 (300)</td>
</tr>
<tr>
<td>Mo(CO)(_5) + NaCl</td>
<td>290-370</td>
<td>Mo(CO)(_5)Cl(^-)</td>
<td>407 (2150), 268 (25000)</td>
</tr>
<tr>
<td>Mo(CO)(_5) + NaBr</td>
<td>290-370</td>
<td>Mo(CO)(_5)Br(^-)</td>
<td>406 (2150), 252 (30000)</td>
</tr>
<tr>
<td>Mo(CO)(_5) + NaI</td>
<td>333</td>
<td>Mo(CO)(_5)I(^-)</td>
<td>408 (1500), 290 (200)</td>
</tr>
<tr>
<td>W(CO)(_5) + NaCl</td>
<td>310-380</td>
<td>W(CO)(_5)Cl(^-)</td>
<td>416 (3100), 246 (60000)</td>
</tr>
<tr>
<td>W(CO)(_5) + NaBr</td>
<td>333</td>
<td>W(CO)(_5)Br(^-)</td>
<td>416 (3500), 247 (70000)</td>
</tr>
<tr>
<td>W(CO)(_5) + NaI</td>
<td>290-370</td>
<td>W(CO)(_5)I(^-)</td>
<td>406 (2750), 333 (14000)</td>
</tr>
</tbody>
</table>

* M(CO)\(_5\) in hexane and NaX in water. * M(CO)\(_5\)X\(^-\) in water. \(\lambda_{max}\) (nm) and \(\epsilon (\text{M}^{-1} \text{cm}^{-1})\); see ref 8.

![Figure 1](image1.png)

Figure 1. Spectral changes during the photochemical formation of Mo(CO)\(_5\)Br\(^-\) in water in the presence of 0.1 M NaBr by phase-transfer photolysis of 5 \(\times\) 10\(^{-3}\) M Mo(CO)\(_6\) in n-hexane at (a) 0 and (f) 40 min irradiation time, with 290 nm < \(\lambda_{irr}\) < 370 nm and a 1-cm cell.

![Figure 2](image2.png)

Figure 2. Spectral changes during the photochemical formation of W(CO)\(_5\)Cl\(^-\) in water in the presence of 0.1 M NaCl by phase-transfer photolysis of 5 \(\times\) 10\(^{-3}\) M W(CO)\(_6\) in n-hexane at (a) 0 and (e) 30 min irradiation time, with 310 nm < \(\lambda_{irr}\) < 380 nm and a 1-cm cell.

1. At the beginning, the alkali halide is the only absorbing species in the aqueous phase while the absorption spectrum of M(CO)\(_5\)X\(^-\) develops during the photolysis. Figures 1 and 2 show typical examples. After 30 min irradiation time approximately 30% of W(CO)\(_5\)Br\(^-\) was converted to W(CO)\(_5\)Br\(^-\) (spectrum e, Figure 2).

With the arrangement described above, the electronic excitation and the photodissociation of the metal carbonyl occur close to the interface of both layers. This situation favors the product formation since the diffusion of the M(CO)\(_5\) fragment to the interface has to compete with the regeneration of M(CO)\(_6\). However, for synthetic applications it can be a disadvantage that the photolyzing light passes the aqueous layer first since the photoproduce may cause inner-filter effects and can undergo secondary photoreactions. Owing to the rather long lifetime of the M(CO)\(_5\) fragment, a modification of the experimental conditions circumvents these complications. If the irradiating light enters the hexane layer horizontally, the light is immediately absorbed by the hexacarbonyl while the aqueous phase can be kept in the dark.\(^8\) Detrimental inner-filter effects and secondary photoreactions are thus avoided. This procedure was successfully applied to the photochemical conversion of M(CO)\(_5\) to M(CO)\(_5\)I\(^-\) with M = Mo and W. However, it must be emphasized that this procedure may not be applicable if a short-lived intermediate or an electronically excited molecule has to reach the interface. Owing to the short lifetime, the electronic excitation must take place very close to the interface. This can be accomplished best when the light hits the interface according to the arrangement described first. Such a simple setup was also used to study the excited-state
Summary: Phenylacetylene at 100 °C in the presence of catalytic amounts of the triangulo cluster $\text{Co}_3(\mu_2-H)(\mu_2-\text{CO})_3(\text{PMe}_3)_6$ is transformed into a linear trimer with high regioselectivity and stereoselectivity. Crystals of the new dienyne (Figure 3) in X-ray structure study are shown to contain molecules in the most stable conformation as expected from MNDO calculations.

Homogeneous catalysis with transition-metal cluster molecules is a promising route to new forms of catalytic activity. While there is no convincing argument against the suspicion that undetected mononuclear intermediates may act as effective catalysts, cluster catalysis continues to supply efficient synthetics that do not succeed without clusters.

Investigating trimethylphosphine complexes of low-valent cobalt and nickel, we found an easy access to molecular clusters of the triangulo type. Irradiation of freely soluble mononuclear compounds of Co(0) and Ni(0) in toluene over 3 h at 80 °C resulted in deposition of the sparingly soluble title compound in 45% yield. Under these conditions no nickel is incorporated (e.g. from Ni(CO)(PMe3)3 as a convenient source of carbonyl ligands).

$$2 \text{Co}(\text{C}_2\text{H}_4)(\text{PMe}_3)_3 + \text{Ni}(\text{CO})(\text{PMe}_3)_3 \xrightarrow{\text{hv}} \text{Co}_3(\text{H})(\text{CO})_3(\text{PMe}_3)_6$$