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# INTERACTION OF ARENECARBONYLCHROMIUM π-COMPLEXES WITH LIGHT

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## Summary

Interaction of arenecarbonylchromium π-complexes, $XArCr(CO)_2L$ (L = CO, $PPh_3$ and X = H, $3(CH_3)$, $OCH_3$, $COOCH_3$ and $COCH_3$) with visible light was investigated by measurement of the electronic absorption spectra. These compounds were shown to interact with visible light via photodecay described by first order kinetics. It was shown that $C_6H_6$ and $Cr(CO)_6$ are the products of the photodecay of $C_6H_6Cr(CO)_3$. The substituents in the benzene ring (X = $OCH_3$, $3(CH_3)$, $COOCH_3$ and $COCH_3$) had no essential effect upon the rate of decomposition of the complexes investigated, while substitution of a CO group in $ArCr(CO)_3$ by a $PPh_3$ ligand increased the rate of reaction by about an order of magnitude. The study of the dependence of the rate of reaction on the intensity of the incident light in the course of photodecomposition enabled us to propose a mechanism for the reaction.

## Results and discussion

This paper presents results of the investigation of the interaction of arenecarbonylchromium π-complexes, $XArCr(CO)_3$ and $XArCr(CO)_2PPh_3$ (X = $OCH_3$, $3(CH_3)$, $COOCH_3$, $COCH_3$), with visible light. The electronic absorption spectra were measured for identification of the processes occurring in these compounds under the action of visible light.

The electronic absorption spectra of $XArCr(CO)_3$ and $XArCr(CO)_2PPh_3$ complexes were investigated in the region of 240—700 nm (Fig. 1 and 2) *. In this region the $ArCr(CO)_3$ complexes have two absorption bands with $\lambda_{max}$ 260—270 nm and 315—325 nm (Table 1) while $ArCr(CO)_2PPh_3$ complexes display three bands with $\lambda_{max}$ 227—230, 267—270 and 325—340 nm (Table 2) **.

*(continued on p. 342)*

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* The region of 500—700 nm is not shown in the figure since it showed no absorption bands.

** No detailed investigation of the band with λ max < 220 nm was performed for $ArCr(CO)_3$ since it was beyond our range.

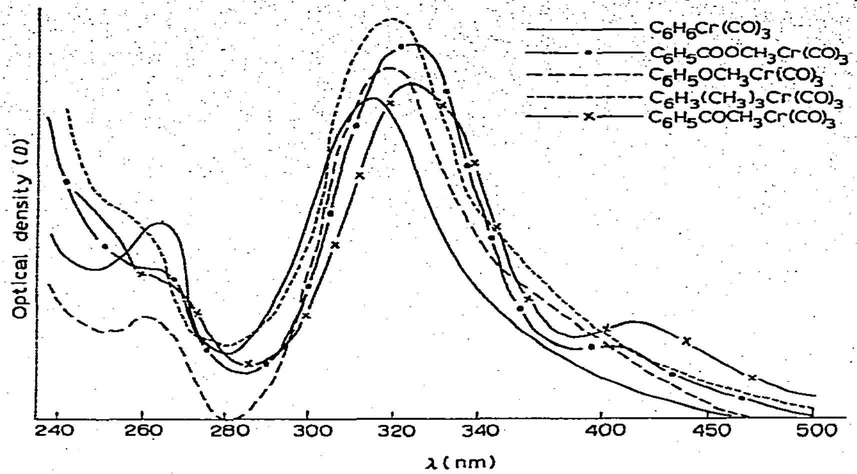


Fig. 1. The electronic absorption spectra of $ArCr(CO)_3$ in cyclohexane solution.

TABLE 1

THE ELECTRONIC ABSORPTION SPECTRA OF ARENECARBONYLCHROMIUM COMPLEXES $ArCr(CO)_3$

| No. | Compound | $\lambda^1_{max}$ (nm) | $\epsilon^1$ (l mol$^{-1}$ cm$^{-1}$) | $\Delta\nu^1_{1/2}$ (cm$^{-1}$) | $\lambda^2_{max}$ (nm) | $\epsilon^2$ (l mol$^{-1}$ cm$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | $C_6H_6Cr(CO)_3$ | 220 | — | — | 263 | 7430 |
| 2 | $C_6H_6OCH_3Cr(CO)_3$ | 220 | — | — | 258—262 | 4100 |
| 3 | 1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$ | 220 | — | — | 260 [a] | 6400 |
| 4 | $C_6H_5COOCH_3Cr(CO)_3$ | 223 [a] | 17600 | 2600 | 263 | 4800 |
| 5 | $C_6H_5COCH_3Cr(CO)_3$ | 220 | — | — | 267 | 5900 |

[a] Wavelength at the middle reflection point.

TABLE 2

THE ELECTRONIC ABSORPTION SPECTRA OF ARENECARBONYLCHROMIUM COMPLEXES $ArCr(CO)_2PPh_3$

| No. | Compound | $\lambda^1_{max}$ (nm) | $\epsilon^1$ (l mol$^{-1}$ cm$^{-1}$) | $\Delta\nu^1_{1/2}$ (cm$^{-1}$) | $\lambda^2_{max}$ (nm) | $\epsilon^2$ (l mol$^{-1}$ cm$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | $C_6H_6Cr(CO)_2P(C_6H_5)_3$ | 227 [a] | 28100 | 3200 | 268 | 8200 |
| 2 | $C_6H_5OCH_3Cr(CO)_2P(C_6H_5)_3$ | 229 [a] | 17500 | 2500 | 267 | 7400 |
| 3 | 1,3,5-$C_6H_3(CH_3)_3Cr(CO)_2P(C_6H_5)_3$ | 230 [a] | 25600 | 2600 | 267 | 4500 |
| 4 | $C_6H_5COOCH_3Cr(CO)_2P(C_6H_5)_3$ | 230 [a] | 24000 | 1200 | 268 | 5700 |
| 5 | $C_6H_5COCH_3Cr(CO)_2P(C_6H_5)_3$ | [b] | [b] | [b] | 270 [a] | 6500 |

[a] Wavelength at the middle inflection point. [b] Wavelength is so intensive that we failed to determine $\lambda_{max}$ and $\epsilon$ at the given concentration. Dilution caused very fast decomposition and decreased accuracy of and $\epsilon$ determination.

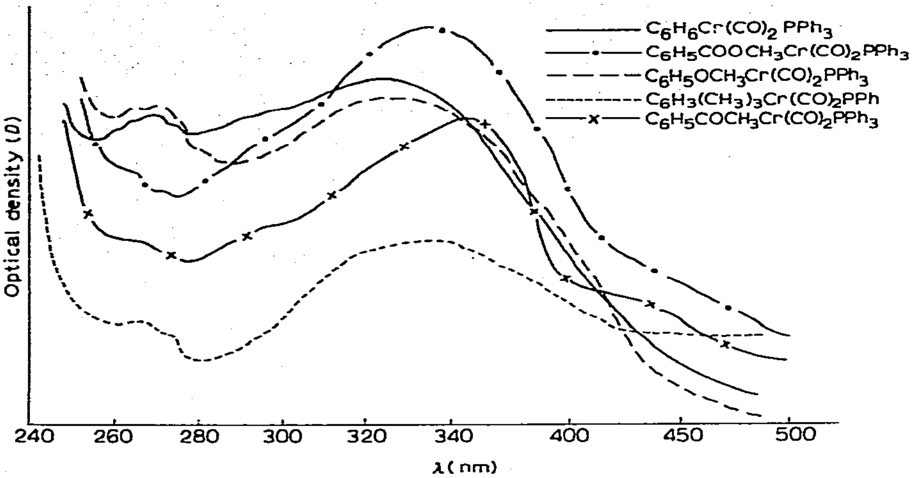


Fig. 2. The electronic absorption spectra of $ArCr(CO)_2PPh_3$ in cyclohexane solution.

| $\Delta\nu^2_{1/2}$ (cm$^{-1}$) | $\lambda^3_{max}$ (nm) | $\epsilon^3$ (l mol$^{-1}$ cm$^{-1}$) | $\Delta\nu^3_{1/2}$ (cm$^{-1}$) | $\lambda^4_{max}$ (nm) | $\epsilon^4$ (l mol$^{-1}$ cm$^{-1}$) | $\Delta\nu^4_{1/2}$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| 2100 | 315 | 9870 | 2200 | — | — | — |
| 1400 | 318 | 12000 | 2000 | — | — | — |
| 1700 | 318 | 15000 | 2300 | — | — | — |
| 1900 | 323 | 11000 | 2100 | 386—404 | 2100 | 2100 |
| 1800 | 325 | 13200 | 2200 | 412—416 | 3400 | 2000 |

| $\Delta\nu^2_{1/2}$ (cm$^{-1}$) | $\lambda^3_{max}$ (nm) | $\epsilon^3$ (l mol$^{-1}$ cm$^{-1}$) | $\Delta\nu^3_{1/2}$ (cm$^{-1}$) | $\lambda^4_{max}$ (nm) | $\epsilon^4$ (l mol$^{-1}$ cm$^{-1}$) | $\Delta\nu^4_{1/2}$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| 2100 | 325 | 9500 | 3600 | — | — | — |
| 4000 | 327 | 8300 | 2400 | — | — | — |
| 2300 | 332 | 8600 | 3700 | — | — | — |
| 2900 | 335 | 8000 | 1500 | $420^a$ | 2300 | 2000 |
| 3700 | 340 | 9800 | 2700 | $420^a$ | 3000 | 2600 |

Moreover when X = $COOCH_3$ and $COCH_3$ the spectra of $XArCr(CO)_3$ and $XArCr(CO)_2PPh_3$ exhibit an additional band or inflection point at $\lambda_{max}$ 400—420 nm.

It should be noted that in $ArCr(CO)_2PPh_3$ the band with $\lambda_{max}$ 267—270 nm is slightly structured owing to the presence of the triphenylphosphine group. Triphenylphosphine itself has a similar structure in the spectrum.

After illumination of $ArCr(CO)_2L$ complexes (L = CO, $PPh_3$) in solution with visible light, their electronic adsorption spectra changed considerably independent of whether they were treated with sunlight or with an incandescent lamp, in air or under an inert atmosphere. The change of conditions only affected the rate of decomposition.

It is quite significant that the intensity of the band with $\lambda_{max}$ 315—340 nm decreased to zero in the course of illumination (Fig. 3). This allows us to conclude that this band is due to the starting complexes, i.e. in this region the decomposition products do not contribute essentially to the spectrum of the investigated system. Assuming that this band belongs only to the starting complexes it was employed in computing the rate constant of decomposition of the compounds investigated. It was found that the decomposition of $ArCr(CO)_2L$ complexes (L = CO, $PPh_3$) is described by a first order kinetic equation (eq. 1), where $k$

$$k = \frac{\ln D_0/D}{t} \qquad (1)$$

is the rate constant of decomposition; $D_0$ is the optical density of undecomposed complex at a wavelength $\lambda$; $D$ is the optical density of the complex during decomposition at the same wavelength.

In the spectra of complexes $XArCr(CO)_2L$ (L = CO, $PPh_3$ and X = $COOCH_3$ and $COCH_3$) the additional band intensity with $\lambda_{max}$ 400—420 nm also decreased

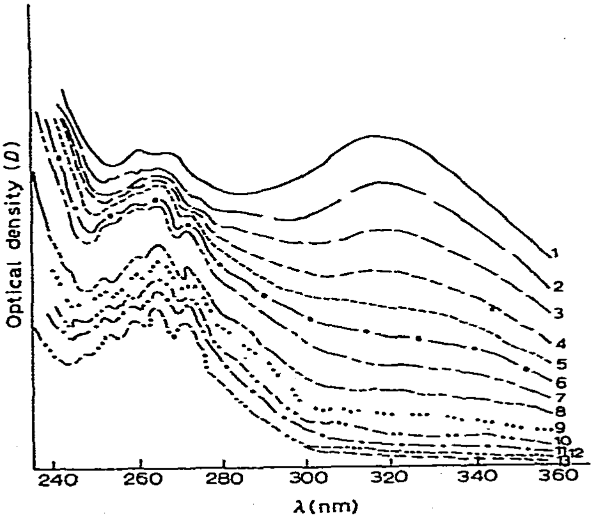


Fig. 3. The change of the electronic absorption spectra of $C_6H_6Cr(CO)_2PPh_3$ in cyclohexane solution upon its illumination with a lamp. 1; the spectrum of initial complex—13; the spectrum of decomposed complex.

during decomposition. The decomposition rate constants computed from this band were equal to those obtained with $\lambda_{max}$ 315—340 nm. Thus this band is due only to the starting complex.

Table 3 shows the decomposition rate constants of $XArCr(CO)_2L$ complexes, computed from the measured optical density of the band with $\lambda_{max}$ 315—340 nm. Statistical treatment of the constants obtained [4] provides the basis for the conclusion, that at the value of $\alpha$ 0.05%, a replacement of one CO group in $XArCr(CO)_3$ by a $PPh_3$ ligand increases the rate of decomposition by an order of magnitude. The electron donor substituents, $X = OCH_3$, $3(CH_3)$, facilitate the decomposition of the complexes, while electron attracting groups, $X = COOCH_3$ and $COCH_3$, cause a slight decrease in the rate. If, for example $C_6H_6Cr(CO)_2PPh_3$ has a decomposition rate 4.4 times greater than $C_6H_6Cr(CO)_3$ then the decomposition rates of $1,3,5\text{-}C_6H_3(CH_3)_3Cr(CO)_2PPh_3$ and $C_6H_5COOCH_3Cr(CO)_2PPh_3$ are respectively 8- and 3-fold those of the tricarbonyl complexes.

We found that substituents in the benzene ring do not essentially affect the rate of decomposition of the investigated complexes (Tables 4 and 5). However, when $\alpha$ 0.05% one may ascertain that the rate of decomposition of $XArCr(CO)_3$ complexes is higher when $X = COOCH_3$ and $3(CH_3)$ whereas the rate of decomposition of $XArCr(CO)_2PPh_3$ complexes is higher when $X = OCH_3$ and $(CH_3)_3$. It should be noted that an increase in the rate of decomposition of arenecarbonylchromium complexes with introduction of a triphenylphosphine ligand cannot be explained solely by their higher extinction coefficient $\epsilon$ resulting from introduction of the ligand. Similar conclusions may be drawn for the change of rate of decomposition of these complexes with their coefficients upon introduction of substituents into the benzene ring.

Fig. 3 shows that the structuring of the band at $\lambda_{max}$ 260—270 nm is enhanced during the course of decomposition of the complexes. We have shown that enhancement of this band structuring is due to formation of the free aromatic compound in the course of decomposition [1]. For $C_6H_6Cr(CO)_3$, treatment of spectral data was performed which revealed that its decomposition affords benzene and one other product, $Cr(CO)_6$. Assuming that in the region of 260—320 nm among the decomposition products of $C_6H_6Cr(CO)_3$ only three components,

TABLE 3

DECOMPOSITION RATE CONSTANTS FOR $XArCr(CO)_2L$ COMPLEXES

| No. | Compound | $k \times 10^3$ $(min^{-1})$ | $k_{PPh_3}/k_{(CO)_3}$ |
|---|---|---|---|
| 1 | $C_6H_6Cr(CO)_2P(C_6H_5)_3$ | 4.5 | 4.4 |
| 2 | $C_6H_6Cr(CO)_3$ | 1.1 | |
| 3 | $C_6H_5COOCH_3Cr(CO)_2P(C_6H_5)_3$ | 4.5 | 3.0 |
| 4 | $C_6H_5COOCH_3Cr(CO)_3$ | 1.5 | |
| 5 | $C_6H_5COCH_3Cr(CO)_2P(C_6H_5)_3$ | 3.8 | 3.2 |
| 6 | $C_6H_5COCH_3Cr(CO)_3$ | 1.2 | |
| 7 | $C_6H_5OCH_3Cr(CO)_2P(C_6H_5)_3$ | 6.1 | 6.1 |
| 8 | $C_6H_5OCH_3Cr(CO)_3$ | 1.0 | |
| 9 | $1,3,5\text{-}C_6H_3(CH_3)_3Cr(CO)_2P(C_6H_5)_3$ | 12.5 | 8.3 |
| 10 | $1,3,5\text{-}C_6H_3(CH_3)_3Cr(CO)_3$ | 1.5 | |

TABLE 4

DECOMPOSITION RATE CONSTANTS FOR XArCr(CO)3 COMPLEXES

| No. | Compound | $k \times 10^3$ (min$^{-1}$) | $k_n/k_1$ |
|---|---|---|---|
| 1 | $C_6H_6Cr(CO)_3$ | 1.1 | 1.0 |
| 2 | $C_6H_5COOCH_3Cr(CO)_3$ | 1.5 | 1.3 |
| 3 | $C_6H_5COCH_3Cr(CO)_3$ | 1.2 | 1.1 |
| 4 | $C_6H_5OCH_3Cr(CO)_3$ | 1.0 | 0.9 |
| 5 | 1,3,5-$C_6H_3(CH_3)_3Cr(CO)_3$ | 1.5 | 1.3 |

$C_6H_6$, $C_6H_6Cr(CO)_3$ and $Cr(CO)_6$ contribute to the electronic absorption spectra of investigated solution [2] we computed their concentrations from the system of simultaneous equations $D = (\epsilon_B c_B + \epsilon_C c_C + \epsilon_H c_H)d$ for three wavelengths: 261, 307 and 314 nm, where $D$ is an optical density of solution; $\epsilon_B$, $\epsilon_C$, $\epsilon_H$ are the extinction coefficients of $C_6H_6$, $C_6H_6Cr(CO)_3$ and $Cr(CO)_6$ respectively, $c_H$, $c_B$, $c_C$ are the concentrations of $Cr(CO)_6$, $C_6H_6$ and $C_6H_6Cr(CO)_3$ respectively; and $d$ is the thickness of absorbing layer. Fig. 4 shows two absorption spectra. One was measured in the course of $C_6H_6Cr(CO)_3$ decomposition while the other is the spectrum of the three-component system prepared from the computed concentrations, it can be seen that the spectra are practically identical. Coincidence of computed and experimental data suggests that $C_6H_6$ and $Cr(CO)_6$ are the decomposition products of $C_6H_6Cr(CO)_3$ in cyclohexane solution upon its illumination with visible light.

We found that photodecomposition takes place during interaction of arene-carbonylchromium complexes with visible light. Fig. 5 presents the change of the decomposition rate constant $k$ upon batch illumination of the solution. The parts parallel to the abscissa axis correspond to the dark periods while parts c, e, g, i, l correspond to periods of illumination. It is quite obvious that the decomposition takes place mainly upon illumination. This is most distinctly seen under stationary conditions i.e. starting from the e part. Here the reaction rate at the dark parts is zero, i.e. the reaction does not occur. The experimental data available, however, provide no conclusion on the decomposition mechanism for the initial part of reaction. We also studied the time dependence of the rate of decomposition at various temperatures. It was shown that in darkness, even at 70° C, practically no decomposition occurred for several days. These data cer-

TABLE 5

DECOMPOSITION RATE CONSTANTS FOR XArCr(CO)2L COMPLEXES

| No. | Compound | $k \times 10^3$ (min$^{-1}$) | $k_n/k_1$ |
|---|---|---|---|
| 1 | $C_6H_6Cr(CO)_2P(C_6H_5)_3$ | 4.5 | 1.0 |
| 2 | $C_6H_5COOCH_3Cr(CO)_2P(C_6H_5)_3$ | 4.5 | 1.0 |
| 3 | $C_6H_5COCH_3Cr(CO)_2P(C_6H_5)_3$ | 3.8 | 0.8 |
| 4 | $C_6H_5OCH_3Cr(CO)_2P(C_6H_5)_3$ | 6.1 | 1.4 |
| 5 | 1,3,5-$C_6H_3(CH_3)_3Cr(CO)_2P(C_6H_5)_3$ | 12.5 | 2.7 |

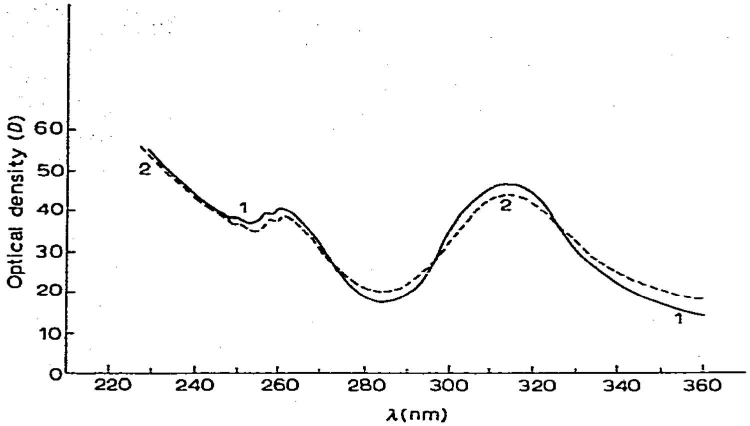


Fig. 4. Absorption spectra; (1) the spectrum of partially decomposed $C_6H_6Cr(CO)_3$ at time $t_k$; (2) the spectrum of the three-component system $C_6H_6$ + $Cr(CO)_6$ + $C_6H_6Cr(CO)_3$ at time $t_k$.

tainly support the photochemical nature of the decomposition of the complexes investigated.

The decomposition rate vs. incident light intensity has been studied for $C_6H_6$-$Cr(CO)_3$ [3]. The obtained dependence (Fig. 6) demonstrates that the decomposition process is multistep and is rather complicated. Some intensities of incident

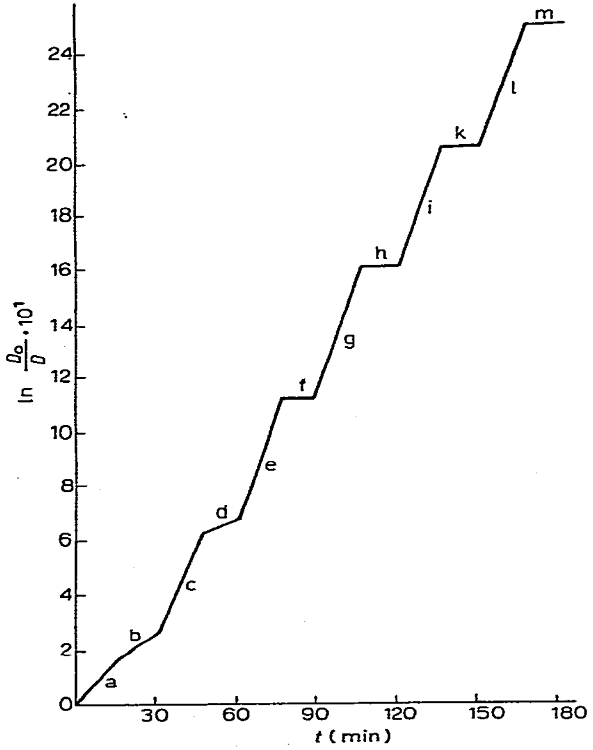
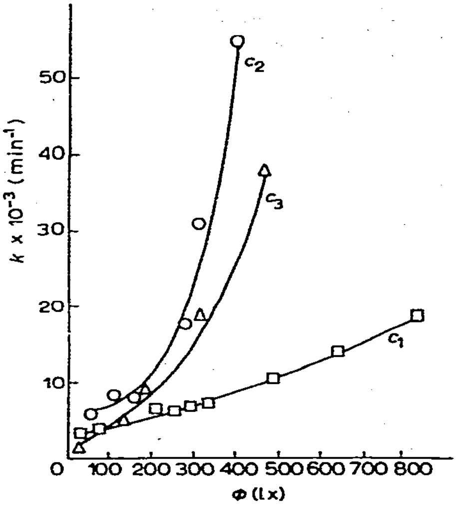


Fig. 5. The plot ln $D_0/D$ = f(t) for $C_6H_6Cr(CO)_3$ solution; parts a, c, e, g, i, l correspond to illumination; parts b, d, f, h, k, m correspond to the dark periods.



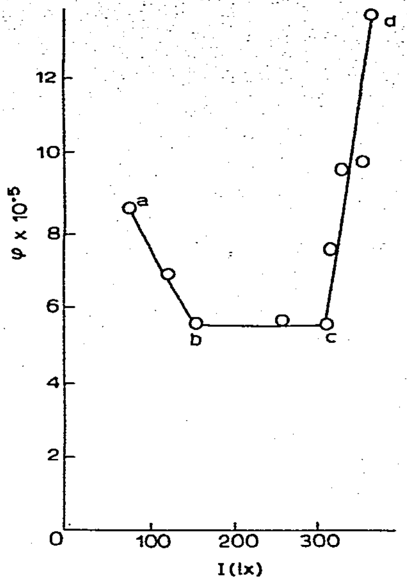


Fig. 6. The decomposition rate constant of $C_6H_6Cr(CO)_3$ solution in cyclohexane vs. the incident light intensity at various concentrations: $c_1 = 10^{-4}$ mol/l, $c_2 = 10^{-5}$ mol/l, $c_3 = 5 \times 10^{-5}$ mol/l.

Fig. 7. The quantum yield of decomposition of $C_6H_6Cr(CO)_3$ solution in cyclohexane vs. the incident light intensity concentration $c_2 = 10^{-5}$ mol/l.

light cause the so-called "break", i.e. the decomposition step occurs with a sharp increase in the rate constant. At higher concentrations the break occurs at greater intensities of incident light.

To specify quantitatively the characteristics of the photochemical decomposition of $C_6H_6Cr(CO)_3$, we used the quantum yield of this reaction. The dependence of the quantum yield of decomposition on the incident light intensity shows that in this case the photodecay is a complex process (Fig. 7). The dependence obtained enabled us to conclude that three simultaneous processes take place in the course of photodecay and that they have different dependencies on the intensity of the incident light.

The total decomposition rate may be given by eq. 2, where $A$ is the initial con-

$$W = k'A\sqrt[n]{I} + k''AI + k'''AI^2 \qquad (2)$$

centration of starting product; $I$ is incident light intensity; $n$ is the parameter providing a weak dependence of $W$ on $I$ in the region of incident light of low intensity; $k'$, $k''$, $k'''$ are the rate constants of the three simultaneous reactions. In this case the quantum yield of reaction is defined by eq. 3, where p is the pro-

$$\varphi = \mathrm{p}A\left|\frac{k'}{\sqrt[n]{I^{n-1}}} + k'' + k'''I\right| \qquad (3)$$

portionality coefficient accounting for the energy of incident quanta applied to the solution. The following kinetic schemes may be proposed for these reactions:

1. $\mathrm{A} \xrightarrow[k']{h\nu}$ decomposition products (part a—b, Fig. 6).

This dependence cannot be explained in terms of the available experimental data.

2. A $\xrightarrow[k'']{h\nu}$ decomposition products (part b—c).

This part of the plot $\varphi = \mathrm{f}(I)$ is parallel to the abscissa axis i.e. it is a monoquantum process.
3. In this case the plot $\varphi = \mathrm{f}(I)$ suggests a biquantum reaction. We assume one of the possible mechanisms.

$$\begin{tikzcd}
 & & \text{deactivation of an excited molecule of the initial compound.} \\
\mathrm{A} \arrow[r, "h\nu", "k_1"'] & \mathrm{A}^* \arrow[ur, "+\mathrm{M}\ (\mathrm{M} = \mathrm{A} + \mathrm{B})", "k_2"'] \arrow[dr, "h\nu", "k_3"'] & \\
 & & \text{decomposition products.}
\end{tikzcd}$$

(part c—d)

However the nature of this mechanism is not clear. Compound B is one of decomposition products which should play the role of inhibitor. Investigation shows that $\mathrm{Cr(CO)_6}$ may play such a role. Assuming that the rate of accumulation of excited particles in reaction 3 is zero, the stationary state can be expressed by eq. 4.

$$\frac{\mathrm{d}A^*}{\mathrm{d}t} = k_1AI - k_2A^*\mathrm{M} - k_3A^*I = 0 \tag{4}$$

In eq. 4 the term $k_1AI$ specifies the accumulation of excited particles $A^*$ by absorption of a quantum $h\nu$ by the nonexcited molecules $A$. Then the particles $A^*$ may undergo deactivation via collision with nonexcited molecules $A$ or inhibitor B (the term $k_2A^*\mathrm{M}$) or absorb the secondary quantum $h\nu$ giving the decomposition products (the term $K_3A^*I$). $k_1$, $k_2$, $k_3$ are the rate constants of these processes It follows from eq. 4 that

$$A = \frac{k_1AI}{k_2\mathrm{M} + k_3I} \tag{5}$$

Then the reaction rate has the form given in eq. 6 and the reaction rate constant

$$W = k'''AI^2 = k_3A^*I = \frac{k_1k_3AI^2}{k_2\mathrm{M} + k_3I} \tag{6}$$

is given by eq. 7.

$$k''' = \frac{k_1k_3}{k_2\mathrm{M} + k_3I} \tag{7}$$

when $k_3I < k_2\mathrm{M}$ the third term in eq. 3 describes an experimental dependence $\varphi = \mathrm{f}(I)$.

From eq. 3 it follows that at low intensities the decomposition which has negligible dependence on the incident light intensity, will be most probable (part a—b, Fig. 6). The monoquantum decomposition of complex A is most probable at the mean intensities (part b—c). At high incident light intensities the decomposition of the initial compound is determined by deactivation of the excited molecule A* and by a biquantum photodecay (part c—d).

## Experimental

The solutions of $XArCr(CO)_2L$ ($L = CO$, $PPh_3$; $X = H$, $3(CH_3)$, $OCH_3$, $COOCH_3$, $COCH_3$) were prepared in darkness in a hermetically sealed camera under an inert gas atmosphere ($N_2$, Ar). The illumination of the solution was performed with 15—500 W lamps. The incident light intensity was registered by means of a photodiode. The illuminated solution was thermostatted (25°C ± 0.5). The samples for spectral investigation were taken with a syringe through an airtight packing. The spectra were recorded on a Hitachi EPS-3T registrating spectrophotometer in the 220—700 nm region. Cyclohexane was used as solvent for all compounds. The starting compound concentration varied within $10^{-4}$—$10^{-5}$ mol/l.

Arenechromiumtricarbonyls were prepared by method [5], arenechromiumdicarbonyltriphenylphosphines were obtained from arenechromiumtricarbonyls and triphenylphosphine under UV illumination [6]. The purity of prepared compounds was checked by means of IR, NMR, mass-spectroscopy and melting-point data.

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