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QUANTUM YIELD FOR PHOTOSUBSTITUTION OF A CO GROUP IN CHROMIUM HEXACARBONYL BY PYRIDINE

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Summary

The quantum yield of the photosubstitution of CO by pyridine in cyclohexane has a value of 0.67 ± 0.02 for $[Cr(CO)_6] = 3.10^{-4}$ mol l^{-1} and [pyridine] $= 10^{-2}$ mol l^{-1}.

Introduction

The most widely cited quantum yield in the photochemistry of metal carbonyls is that for the photodissociation of CO from $M(CO)_6$ (M = Cr, Mo, W); it has been repeatedly reported that the value is 1 for all three metal hexacarbonyls [1,2]. On the other hand, the quantum yields for photosubstitution in $M(CO)_5L$ (M = Mo, W) have been published recently [3], and are all appreciably less than unity. This difference in behaviour between the parent hexacarbonyls and their substituted derivatives led us to reexamine the photolysis of $Cr(CO)_6$.

Results

The photochemical reaction:

$$Cr(CO)_6 + C_5H_5N \xrightarrow[\varphi_A]{h\nu} Cr(CO)_5(C_5H_5N) + CO$$

is complicated by the simultaneous absorption of light by the reactants and the product, which makes the selective irradiation of $Cr(CO)_6$ impossible. The mathematical treatment of this inner filter effect has been given by Schläfer [4], and its extension to two absorbing reactants gives relation 1 for the quantum yield ϕ_A of disappearance of the hexacarbonyl:

$$\phi_A = \frac{1}{I_a t}\left[\frac{\epsilon_A + \epsilon_L - \epsilon_B}{\epsilon_A}[B] + \frac{(\epsilon_B - \epsilon_L)[A]_0 - \epsilon_L[L]_0}{\epsilon_A}\ln\left(1 - \frac{[B]}{[A]_0}\right)\right] \qquad (1)$$

I_at is the amount of light absorbed by the sample (einstein l^{-1});

ϵ_A, ϵ_L and ϵ_B are the molar extinction coefficients of $Cr(CO)_6$, pyridine and $Cr(CO)_5$(pyridine), respectively, at the irradiation wavelength.

$[A]_0$, $[L]_0$ are the initial concentrations of $Cr(CO)_6$ and C_5H_5N and $[B]$ is the concentration of $Cr(CO)_5(C_5H_5N)$ at time t.

It has been pointed out, however [5], that such treatment is not sufficient for the system under study because the monosubstituted product can undergo a further photoreaction:

$$Cr(CO)_5(C_5H_5N) + C_5H_5N \xrightarrow[\phi_B]{h\nu} Cr(CO)_4(C_5H_5N)_2 + CO$$

If we call ϕ_B the quantum yield for this reaction, integration for the reaction sequence $A \xrightarrow[\phi_A]{h\nu} B \xrightarrow[\phi_B]{h\nu} C$ gives:

$$[B] = \frac{[A]}{\alpha}\left[\left(\frac{[A]_0}{[A]}\right)^{\alpha} - 1\right] \qquad (2)$$

where α stands for $1 - (\epsilon_B\phi_B/\epsilon_A\phi_A)$.

Equation 2 shows that as the reaction proceeds, the amount of $[B]$ is less than $[A_0] - [A]$ and that the amount of C, calculated from $[C] = [A]_0 - [A] - [B]$ increases steadily. In our case, this results in a production of carbon monoxide

TABLE 1

DEPENDENCE OF THE CONCENTRATIONS (mol l^{-1}) OF REACTANTS AND PRODUCTS WITH THE WAVELENGTH OF IRRADIATION ACCORDING TO EQUATION 2, ASSUMING $\phi_A = 0.7$ AND $\phi_B = 0.2$.

Accurate extinction measurements give (in C_6H_{12}) $\epsilon_A = 3130$ l mol^{-1} cm^{-1} and $\epsilon_B = 3320$ l mol^{-1} cm^{-1} at 313 nm, and $\epsilon_A = 62$ [7] l mol^{-1} cm^{-1} and $\epsilon_B = 4300$ [7] l mol^{-1} cm^{-1} at 366 nm.

$[A]$	$[B]$	$[C]$	$[B]/[C]$	mole of CO produced
313 nm				
$1.000\ 10^{-2}$	0	0	—	0
0.995	$4.99\ 10^{-5}$	$0.01\ 10^{-5}$	499	$5.01\ 10^{-5}$
0.990	9.98	0.02	499	10.02
0.985	14.97	0.03	499	15.03
0.980	19.94	0.06	332	20.06
0.970	29.86	0.14	213	30.14
0.950	49.61	0.39	127	50.39
0.900	98.39	1.61	61	101.61
366 nm				
$1.000\ 10^{-2}$	0	0	—	0
0.995	$4.76\ 10^{-5}$	$0.24\ 10^{-5}$	19.8	$5.24\ 10^{-5}$
0.990	9.07	0.93	9.8	10.93
0.985	12.96	2.14	6.1	17.24
0.980	16.47	3.53	4.7	23.53
0.970	22.49	7.51	3.0	37.51
0.950	31.26	18.74	1.7	68.74
0.900	41.24	58.76	0.7	158.76

TABLE 2

QUANTUM YIELD FOR THE PHOTOSUBSTITUTION IN $Cr(CO)_6$

$[Cr(CO)_6]$ (10^{-4} mol l^{-1})	[pyridine] (10^{-2} mol l^{-1})	ϕ_A	conversion (%)
3.08	0.94	0.65	5.0
3.13	0.94	0.66	1.2
2.83	0.92	0.70	0.8
2.86	0.91	0.66	0.9

which is much larger than that originating from the photolysis of $Cr(CO)_6$ alone. The deviation from a simple stoechiometry for the CO evolution will depend on the irradiation wavelength through the varying values of ϵ_A and ϵ_B which appear in the coefficient α.

Table 1 lists the results derived for two different irradiation wavelengths 366 nm and 313 nm with $\phi_A = 0.7$* and $\phi_B = 0.2$ [6].

It appears quite clear that for photolysis at 366 nm, 2% disappearance of $Cr(CO)_6$ leads to 17.6% excess of CO, but only to 0.3% excess at 313 nm. The apparent quantum yield estimated from the amount of CO evolved is thus larger than the quantum yield ϕ_A for the first photodecarbonylation.

In the light of these preliminary observations, we irradiated chromium hexacarbonyl at 313 nm in carefully degassed cyclohexane, keeping the conversion below 1-2%. Table 2 lists the results of several runs. The mean value obtained is $\phi = 0.67 \pm 0.02$ with $[Cr(CO)_6] \sim 3 \times 10^{-4}$ mol l^{-1} and [pyridine] $\sim 10^{-2}$ mol l^{-1}.

It was confirmed that (a) there is no dark reaction between $Cr(CO)_6$ and C_5H_5N if the temperature is kept below 35°C, (b) the back reaction, $Cr(CO)_5$-(C_5H_5N) + CO, is negligible in the dark, even under 380 Torr of carbon monoxide, and (c) pyridine gives no stable photoproducts during irradiation times longer than those used in this work.

It is noteworthy that Schläfer [4], taking into account the inner filter effect, calculated a quantum yield $\phi_A = 0.72$ from one of Strohmeier's experiments in which the progress of reaction was monitored by the evolution of CO.

Our final result for ϕ_A is thus definitely less than unity, demonstrating the existence of radiationless processes competing with the photodissociation. These aspects of the photochemistry of $Cr(CO)_6$ will be considered further in forthcoming publications.

Experimental

Products

Chromium hexacarbonyl was sublimed; pyridine was distilled over zinc powder and purified by GLC. Spectrochemical grade cyclohexane was used as supplied. Chromium pentacarbonyl pyridine was synthesized photochemically and sublimed [8], m.p. 96-97°C [9] (lit. 96°C).

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* This work.

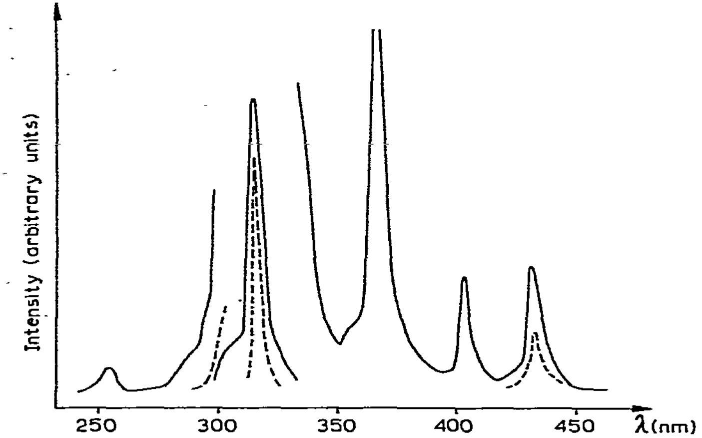

Fig. 1. Spectrophotometric distribution of the photolytic light. Solid line: monochromator output when set at 313 nm; dashed line: same, with the naphthalene + 9-methylanthracene filter. The response of the photomultiplier was attenuated by a factor of 100 between 300 and 340 nm.

Analytical procedures

The changes in the system were followed by UV-vis spectrophotometry (Unicam SP 1800), which required an accurate knowledge of the extinction coefficients. This was achieved by using mg-size samples, weighed to the nearest 10^{-6} g in our microanalytical department, affording ϵ values with a scatter less than 1%. For $Cr(CO)_5$(pyridine), the value of ϵ_{max} at 394 nm was found to be 5460.

Irradiation

The solution, contained in a cylindrical 100 ml flask fitted with sidearms leading to a 1.000 cm and a 5.000 cm pathlength spectrophotometer quartz cuvettes (Helma QS), was thoroughly degassed by successive freeze-pump-thaw cycles down to a residual pressure less than 5×10^{-4} Torr and then transferred to the irradiation cells. The length of the cell was such as to ensure total absorption of the light (absorbence >2).

Light from an Osram HBO 200W mercury arc passed through a Bausch and Lomb high intensity grating monochromator set at 313 nm and the resulting ray was filtered by a benzene solution of naphthalene + 9-methylanthracene followed by an aqueous solution of nickel sulfate. Fig. 1 gives the spectral distribution of the emerging light. The photolysing light was split by a quartz window to allow actinometry with potassium ferrioxalate [10]. The solutions were vigorously stirred with a glass coated iron rod actuated by a rapidly rotating magnet.

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