

QUANTUM YIELD FOR THE PHOTOSUBSTITUTION OF A CARBONYL GROUP IN MESITYLENECHROMIUM TRICARBONYL BY A MALEIMIDE

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(Received June 2nd, 1975)

Summary

The quantitative study of the photosubstitution of a CO in mesitylenechromium tricarbonyl by *N*-dodecylmaleimide in cyclohexane is hampered by the instability of the reactants and products towards light. In benzene solution, the reaction is clean and the mathematical treatment of the data gives a quantum yield of 0.90 ± 0.09 at 313 nm for the photosubstitution.

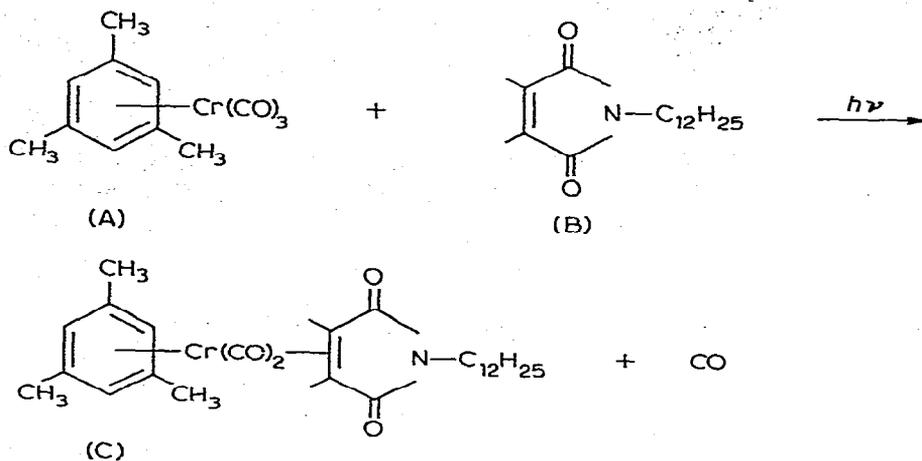
Introduction

The photosubstitution of carbonyl groups in $\text{ArCr}(\text{CO})_3$ complexes in the presence of a ligand L is the most widely used method for the synthesis of the corresponding $\text{ArCr}(\text{CO})_2\text{L}$ [1], but there are no definite* data published on the quantum yield for this process. Quantitative results on such systems are hard to obtain because of (1) the low solubility of most of the components in non-polar solvents, (2) overlapping absorption spectra making selective irradiation impossible and the UV determination on the concentrations difficult, and (3) the relative instability of the products, leading to large errors in estimating the extent of reaction; some $\text{ArCr}(\text{CO})_2(\text{PR}_3)$ complexes are known to be quite stable, but their UV spectra are too similar to those of the parent tricarbonyl to give convenient systems to study.

We have found recently that maleimide and *N*-substituted maleimides (MI) give very stable $\text{ArCr}(\text{CO})_2(\text{MI})$ complexes in yields up to 80% [2]; their solubility in inert solvents can be increased by a proper choice of the *N*-substituent. We report here on the quantum yield of the photosubstitution of a CO group in mesitylenechromium tricarbonyl by *N*-n-dodecylmaleimide.

* M. Wrighton has found a quantum yield of 0.8 for the photosubstitution of CO by pyridine in $(\text{benzene})\text{Cr}(\text{CO})_3$ (private communication; see ref. 24 in Wrighton's review [1]); this had not yet appeared at the time of writing.

The problem of selective irradiation cannot be solved experimentally and has to be overcome by an appropriate mathematical treatment of the data.



Results

The absorption spectra of the three components of the system were measured as accurately as possible; we have found that the major source of scatter in the ϵ values is the inaccuracy of the usual analytical balances for very small quantities. We have used 2 milligram-size samples, weighed to the nearest 10^{-6} g in our microanalytical department affording ϵ values consistent to within less than 1%. The composition of the solutions during the photolysis was calculated by a least-squares treatment of the absorbances at five or even six wavelengths; it was apparent that, when the reaction deviates from the simple $A + B = C$ stoichiometry, spectrophotometric measurements accurate to within 1% can give rise to fluctuations up to a factor of 3 in the concentration of $\text{ArCr}(\text{CO})_2\text{L}$ if estimated at only one wavelength. The photolytic light, selected by a Bausch & Lomb High-Intensity Monochromator, was analyzed with a Hilger & Watts Medium Quartz Spectrograph and found to be nearly pure ($\sim 95\%$) 313 nm light with less than 5% at 366 nm.

(1) In cyclohexane

The quantum yield ϕ_A for disappearance of mesitylene-chromium tricarbonyl is fluctuating and appreciably larger than the quantum yield ϕ_C for formation of $\text{ArCr}(\text{CO})_2\text{L}$ (NDMI), but always less than 1; the material balance shows erratic decomposition amounting to 10-40%. The results are summarized in Table 1. Control experiments showed indeed that all three components undergo a photodecomposition: $\text{ArCr}(\text{CO})_3$ alone in cyclohexane disappears with ϕ_A close to unity to give transparent products, $\text{ArCr}(\text{CO})_2\text{L}$ with a quantum yield close to 0.2, and the maleimide with a ϕ_B as large as 12. This last result points to a photo-induced polymerization, and we have found actually that 10^{-2} M solutions of *N*-n-dodecylmaleimide in cyclohexane become cloudy on irradiation, even in presence of $\text{ArCr}(\text{CO})_3$ which absorbed 90% of

TABLE I

QUANTUM YIELDS FOR THE PHOTOSUBSTITUTION OF CO BY *N*-DODECYLMALEIMINE IN (MESITYLENE)Cr(CO)₃

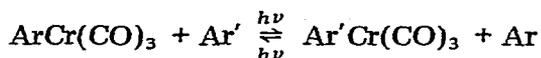
[A]₀ and [B]₀ are the initial concentrations of the arenecromium tricarbonyl and maleimide, respectively; ρ is the chemical yield of the reaction, as determined by UV analysis; φ_A and φ_C are the quantum yields for disappearance of A and for formation of C, respectively.

[A] ₀	[B] ₀	ρ	φ _A	φ _C
Cyclohexane				
1.53 × 10 ⁻³	1.32 × 10 ⁻³	0.94	0.75	0.70
1.40 × 10 ⁻³	1.20 × 10 ⁻³	0.85	0.64	0.54
1.38 × 10 ⁻³	1.58 × 10 ⁻³	0.74	0.58	0.43
1.10 × 10 ⁻³	7.09 × 10 ⁻³	0.68	0.68	0.47
Benzene				
7.49 × 10 ⁻⁴	1.65 × 10 ⁻³	0.91	0.90 ± 0.09	0.81 ± 0.08
1.21 × 10 ⁻³	3.03 × 10 ⁻³	0.84	0.91 ± 0.09	0.76 ± 0.08

the incident light. Acting on the suspicion that this side-reaction was triggered by hydrogen abstraction from the solvent, we turned to benzene, and the results were satisfactory.

(2) In benzene

It has been reported that ArCr(CO)₃ complexes undergo a photochemical exchange [3] according to:



However, the synthetic experiments, and controls during quantum yield measurements, showed no detectable amount of mesitylene-benzene exchange; we have no explanation for this discrepancy with Strohmeier's results. It was checked that ArCr(CO)₃ and *N*-*n*-dodecylmaleimide (even at 10⁻² M concentrations) were stable to light during periods similar to the length of irradiation; the product decomposed quite slowly, with a quantum yield less than 0.1.

When the quantity of product formed was plotted against the amount of starting material consumed, it was found that the points fall on a straight line, but with a slope less than unity, showing that ArCr(CO)₃ undergoes a slight photodecomposition induced by the ligand. The chemical yield being constant along the runs, the discrepancy cannot be due to residual oxygen which should affect the first points much more than later ones, nor to the slight photodecomposition of the product which should show up as a deviation from linearity in the concentration-concentration plot.

In these circumstances, the stoichiometric equation for the system is not A + B = C, but rather A + ρB = ρC, where A is MesCr(CO)₃, B is *N*-*n*-dodecylmaleimide, C is MesCr(CO)₂(NDMI) and ρ the chemical yield of product. The rate equation for such a system is then:

$$-\frac{d[A]}{dt} = \frac{I_a^A \phi_A}{V} = \frac{I_a}{V} \left\{ \frac{\epsilon_A [A]}{\epsilon_A [A] + \epsilon_B [B] + \epsilon_C [C]} \right\} \phi_A \quad (1)$$

where I_a^A is the amount of light absorbed by A (in Einsteins per unit time), I_a is the total amount of light absorbed by the solution and V the volume of the irradiated solution; ϵ_A , ϵ_B , ϵ_C are the extinction coefficients of the components at the irradiation wavelength and $[A]$, $[B]$ and $[C]$ their respective concentrations in moles per unit volume at time t . Equation 1 integrates to

$$\frac{I_a \phi_A t}{V} = \frac{\epsilon_A + \rho(\epsilon_B - \epsilon_C)}{\epsilon_A} ([A]_0 - [A]) + \left\{ \frac{\rho[A]_0(\epsilon_C - \epsilon_B) + \epsilon_B[B]_0}{\epsilon_A} \right\} \ln \frac{[A]_0}{[A]} \quad (2)$$

for the quantum yield ϕ_A for disappearance of A, and

$$\frac{I_a \phi_C t}{V} = \frac{\epsilon_A + \rho(\epsilon_B - \epsilon_C)}{\epsilon_A} [C] + \left\{ \frac{\rho^2[A]_0(\epsilon_C - \epsilon_B) + \rho\epsilon_B[B]_0}{\epsilon_A} \right\} \ln \frac{\rho[A]_0}{[A]_0 - [C]} \quad (3)$$

for the quantum yield ϕ_C for formation of C^* . The quantum yields do not depend on the particular choice of units and are dimensionless if I_a , t , V and the concentrations are expressed in consistent units. The results are summarized in Table 1.

Discussion

The quantum yield for photosubstitution of a carbonyl group in $\text{MesCr}(\text{CO})_3$ by NDMI is high, but may be less than 1. The complexity of the system precludes, unfortunately, a systematic study of the entering ligand concentration. We feel however that the observed result is the quantum yield for photodissociation, because it is highly improbable that maleimide would be able to quench an excited state or react with it. There is only one result in the literature suggesting a bimolecular process on an electronically excited transition metal carbonyl complex: Keeton and Basolo [6] have found that the quantum yield for substitution of a CO in $\text{Mn}(\text{NO})(\text{CO})_3$ by $\text{P}(\text{C}_6\text{H}_5)_3$ rises with increasing ligand concentration but we feel that this result might be due to the presence of traces of triphenylphosphine oxide, which are exceedingly difficult to remove and which show unexpected catalytic effects in ligand substitution reactions [7]. So far all attempts to detect an excited state at room temperature in other transition-metal carbonyl complexes have failed and, if we assume a lifetime as long as 10^{-8} sec for such a species and a diffusion rate constant of $10^9 \text{ M}^{-1} \text{ sec}^{-1}$, ligand concentrations as low as $3 \times 10^{-3} \text{ M}$ will be able to affect only 3% of the excited states.

The origin of the quantum deficit of 0.1 ± 0.1 is not known; it is clear, however, that some radiationless decay should operate since no luminescence

* Equations 2 and 3 are similar to those given by Schläfer [4] for the inner filter effect and by Wagner [5] for multiple stoichiometry, extended to the case where two absorbing species react to give one absorbing product.

TABLE 2

 ϵ VALUES FOR THE COMPONENTS IN BENZENE AND CYCLOHEXANE

Benzene λ nm	285	299	305	313	319	347	
MesCr(CO) ₃	2570	5200	6960	9470	10125 ^a	4700	
NDMI	665	700 ^a	675	620	550	110	
MesCr(CO) ₂ (NDMI)	7270 ^a	5920	5755	6000	7200	12800 ^a	
Cyclohexane λ (nm)	250	285	299	305	313	319	347
MesCr(CO) ₃	760	2630	5230	7385	10120	10720 ^a	4700
NDMI	130	670	700	735 ^a	650	550	110
MesCr(CO) ₂ (NDMI)	5290	6875 ^a	5920	5625	5770	6835	11930 ^a

^a ϵ_{\max} values.

from ArCr(CO)₃ has ever been observed, even at 77 K. Our experiments give no information on the multiplicity of the excited state leading to dissociation.

Apart from the quantum yield of 1 [8]* for the photodissociation of M(CO)₆ (M = Cr, Mo, W), the efficiency for the photocleavage of MesCr(CO)₃ is apparently one of the highest yet reported in transition metal carbonyl derivatives [1].

Experimental

N-n-dodecylmaleimide. 37 g (202 mmol) n-dodecylamine dissolved in the minimum amount of glacial acetic acid are added to a solution of 19.6 g (200 mmol) maleic anhydride dissolved in the minimum amount of acetic acid [10]. The resulting mixture is heated under reflux for 2 h, cooled, poured on ice and neutralised with potassium carbonate. Ether is then added, and the aqueous layer is repeatedly extracted with additional portions of ether. The combined organic fractions are evaporated to dryness, leaving a brown oil which soon solidifies. Elution with chloroform through alumina gives then a fairly pure (TLC) and clearer product. Crystallisation from EtOH/H₂O proved rather tricky because of the low melting point of the product: 54-54.5°C after four recrystallisations.

Mesitylenechromium dicarbonyl-N dodecylmaleimide was made photochemically according to our previous procedure [2]. Analysis found: C, 65.7; H, 8.0; N, 2.9. C₃₇H₃₉O₄NCr, C, 65.7; H, 8.0; N, 2.8%.

Quantum yields were run in a special set-up consisting of a 200 ml flask to which two quartz cells were sealed, one 2 cm long and the other 0.1 cm, for irradiation and UV analysis respectively. The flask was used for degassing by successive freeze-pump-thaw cycles down to a residual pressure less than 3×10^{-4} Torr; the solution could then be transferred to the photolysis or to the analytical cuvette by tilting. Light from an Osram 200 W high-pressure mercury arc was selected with a Bausch & Lomb High-Intensity monochromator; a beam-splitter facilitated actinometry with potassium ferrioxalate. During

* We have redetermined this quantum yield and found it to be definitely less than 1 [9].

the photolysis, the solutions were stirred with a glass-coated iron rod actuated by a fast rotating magnet. A Unicam SP 1800 spectrometer was used for the spectrophotometric estimation. Table 2 collects the useful ϵ values in benzene and in cyclohexane.

Acknowledgements

We thank Professor E. Van der Donckt and Dr. L. Wilputte for interesting discussions. We are grateful to Dr. M. Benedek, from the microanalytical department, for accurate weighings. One of us (O.D.) acknowledges a fellowship from the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture.

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