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Photochemical Reactions of Hexachloroiridate(IV) Ion[1]

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The photochemical behaviour of $IrCl_6^{2-}$ has been investigated in acid solutions both in the presence and absence of Cl^- ions. The results show that the complex is little photosensitive and that the nature and the quantum yield of its photoreactions depend on the type of excited state reached upon irradiation. Irradiation with 254-nm light ($\pi \rightarrow e_g$ ligand-to-metal charge transfer transitions) causes two parallel photoreactions, yielding $IrCl_5(H_2O)^{2-}$ and $IrCl_5(H_2O)^-$; the quantum yields of the two processes (but not *their sum) depend on Cl^- concentration, the formation of $IrCl_5(H_2O)^{2-}$ being favoured by the increase of $[Cl^-]$. Irradiation with 313- or 365-nm light (which presumably correspond to $t_{2g} \rightarrow e_g$ ligand field transitions) yields $IrCl_5(H_2O)^-$ in the absence of Cl^- and $IrCl_6^{3-}$ in 1.2 F Cl^-. Finally, irradiation with 433- or 495-nm light ($\pi \rightarrow t_{2g}$ ligand-to-metal charge transfer transitions) does not cause any appreciable reaction. As far as the irradiation at 254 nm is concerned, a photolysis mechanism is proposed which accounts for the detailed experimental results.*

Introduction

Some features make the photochemical investigation of $IrCl_6^{2-}$ attractive. First, the electronic spectrum of this complex is a very peculiar one owing to the presence of narrow charge transfer bands in the visible region. Such bands, which have been thoroughly investigated by Jørgensen[2] since 1956, are due to transitions from "ligand" orbitals to the unfilled t_{2g} "metal" orbitals ($IrCl_6^{2-}$ has a low-spin d^5 electronic configuration). Secondly, both the aquation and one-electron reduction products of $IrCl_6^{2-}$ are known,[3] so that it should be possible to establish whether photoredox, photoaquation or both take place upon excitation in the various spectral regions. A previous investigation[4] on PtX_6^{2-} complexes (X = Br, I) showed that only photoaquation occurred, regardless of the nature of the excited states reached upon irradiation.

While this work was in progress, a short communication has appeared by Sleight and Hare[5] whose results partially disagree with those reported here.

Experimental Section

Preparation of compounds. Commercial $(NH_4)_2[IrCl_6]$ (Fluka A.G., Switzerland) was purified following the indications given in Ref. 6. The compound so obtained did not contain $IrCl_6^{3-}$ since its absorption spectrum did not change upon saturation of the solution with Cl_2.[3] $(NH_4)_2[IrCl_5(H_2O)]$ was obtained by the method of Delépine.[7] Solutions of the $IrCl_5(H_2O)^-$ ion were obtained by oxidizing solutions of $(NH_4)_2[IrCl_5(H_2O)]$ in 2.5 N $HClO_4$ with Cl_2.[3] The electronic absorption spectra of the above compounds (Figure 1) were in agreement with those reported in the literature.[3]

Apparatus. Radiations of 254, 313, and 365 nm were obtained using the radiation equipment previously reported.[8] Narrow spectral bands centered at 433 and 495 nm were isolated from a Philips Attralux Spot 150-W 24-V incandescent lamp by means of interference filters (T_{max}, 50 and 43%; half-width, 20 and 10 nm, respectively). To reduce heating of the interference filters, the light was pre-filtered by a solution of $CuSO_4$ (4% w/v, in 0.1 N H_2SO_4; thickness = 5 cm). Different intensity values of the incident light were obtained by placing uniform-density filters in the optical path. The intensity of the incident light was measured by means of the ferric oxalate actinometer[9] for the radiations of 254, 313, 365, and 433 nm and with the reineckate actinometer[10] for the 495-nm radiations. The absorbance measurements and the recording of the spectra were performed with an Optica CF4 NI spectrophotometer.

Procedure. A weighed amount of the complex was dissolved in 2.5 N $HClO_4$ solutions containing various concentrations of NaCl (0, 0.1, 0.6, and 1.2 F). The

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[1] This work was presented in part at the XI International Conference on Coordination Chemistry, Haifa and Jerusalem, September 1968.

[2] (a) C.K. Jørgensen, *Acta Chem. Scand.*, *10*, 518 (1956); (b) C.K. Jørgensen, *Mol. Phys.*, *2*, 309 (1959); (c) C.K. Jørgensen and W. Preetz, *Z. Naturforschg.*, *22a*, 945 (1967); (d) P. Day and C.K. Jørgensen, *Chem. Phys. Letters*, *1*, 507 (1968).

[3] (a) I. A. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, *84*, 2032 (1962); (b) J. C. Chang and C. S. Garner, *Inorg. Chem.*, *4*, 209 (1965).

[4] V. Balzani, F. Manfrin, and L. Moggi, *Inorg. Chem.*, *6*, 354 (1967).

[5] T. P. Sleight and C. R. Hare, *Inorg. Nuclear Chem. Letters*, *4*, 165 (1968).

[6] G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, *8*, 223 (1966).

[7] M. Delépine, *Bull. soc. chim. France*, [4], *3*, 901 (1908).

[8] V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, *7*, 1398 (1968).

[9] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), *A235*, 518 (1956).

[10] E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, *88*, 394 (1966).

ionic strength was maintained constant by adding suitable amounts of $NaClO_4$.[11] The concentration of the complex was 2×10^{-4} or 5×10^{-4} F for the experiments with 254-nm light and 1×10^{-3} F in all the other cases. Under the above conditions, the radiations of 254, 433, and 495 nm were almost completely absorbed by the reactant for the entire irradiation period, while in the case of the 313- and 365-nm radiations, appropriate corrections for the fraction of light absorbed had to be made in order to calculate the quantum yields. In order to avoid secondary photoreactions, only a small per cent of the initial complex concentration was decomposed. The general procedure for the study of the photochemical behaviour of the complex was as follows. Two 1-cm spectrophotometer cells were filled with 3 ml of freshly prepared solution. One of the cells was placed in the thermostated (25°) cell holder of the irradiation equipment. During the irradiation, the solution was stirred by the bubbling of a stream of purified N_2. The other cell was placed in a thermostated cell holder maintained in the dark at the same temperature, in order to provide a control for possible thermal reactions (which, however, did not occur). After a suitable irradiation period, the changes in absorbance caused by irradiation were measured in the range 380-550 nm by the differential spectrophotometric method. No postphotochemical effect could be observed. Afterwards, a stream of chlorine was bubbled through the irradiated and non-irradiated solutions and the differences in absorbance were again measured.

Results

The low-spin d^5 electronic configuration of $IrCl_6^{2-}$ is characterized by a vacancy in the slightly π-antibonding t_{2g} "metal" orbitals. Because of this vacancy, charge transfer transitions from ligand localized orbitals to the t_{2g} "metal" orbitals may also occur, besides the more common ligand → metal charge transfer transitions which involve the higher energy e_g "metal" orbitals. The electronic absorption spectrum of $IrCl_6^{2-}$ is shown in Figure 1. According to Jørgensen,[2b,c] the high intensity band at 232 nm is due to a $\pi_L \rightarrow \sigma_M^*$ (e_g) transition, the shoulder at ~360 nm and, presumably, the band at 306 nm are due to π_M^* (t_{2g})$\rightarrow \sigma_M^*$ (e_g) ligand field transitions, and the bands at 410, 434, 488, and 588 nm to $\pi_L \rightarrow \pi_M^*$ (t_{2g}) transitions.[12]

Thermal Reactions. As previously mentioned, at 25° acid (2.5 N $HClO_4$) solutions of $IrCl_6^{2-}$ did not undergo any appreciable reaction either in the presence or in the absence of added Cl^- ions (up to 1.2 F). At 80°, a slow decomposition reaction took place as evidenced by spectral changes in the visible region. When the solution contained 1.2 F Cl^-, the thermal reaction was clearly a reduction yielding Ir^{III} species, whereas in the absence of Cl^-, some aquation reaction seemed also to occur. The slowness of the thermal reactions of $IrCl_6^{2-}$ and their complicated kinetics were previously pointed out by Martinez.[14]

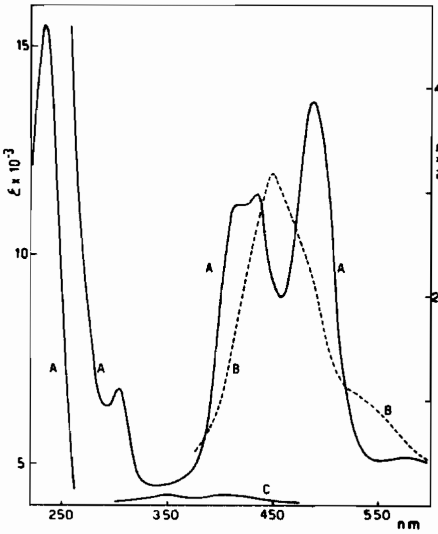

Figure 1. Electronic absorption spectra of: A, $IrCl_6^{2-}$; B, $IrCl_5(H_2O)^-$; C, $IrCl_5(H_2O)^{2-}$.

Irradiation in the $\pi_L \rightarrow \sigma_M^*$ (e_g) Charge Transfer Band (254-nm Light). Upon irradiation with 254-nm light, the spectrum of a *chloride-free solution* of $IrCl_6^{2-}$ changed as shown in Figure 2a. A comparison with the spectra of Figure 1 suggested at first that the following aquation reaction took place:

$$IrCl_6^{2-} + H_2O \xrightarrow{h\nu} IrCl_5(H_2O)^- + Cl^- \qquad (1)$$

However, if only reaction (1) occurred, the isosbestic points should have appeared at 386, 437, 471, and 518 nm, while they actually appeared at 382, 443, 467, and 520 nm. This indicated that some other reaction(s) also occurred. When the irradiated solutions were oxidized by Cl_2, their spectra changed as shown in Figure 2b. By comparing the spectra of Figure 2a with those of Figure 2b, one can observe that the oxidation caused a general increase in absorbance and a displacement of the isosbestic points to 437, 471, and 518 nm, *i.e.* to the values expected for a solution containing *only* $IrCl_6^{2-}$ and $IrCl_5(H_2O)^-$. These results indicated that reaction (1) was accompanied by some redox reaction(s) leading to product(s) which (i) had a low absorbance in the spectral region examined and (ii) was quantitatively oxidized by Cl_2 to $IrCl_6^{2-}$ and/or $IrCl_5(H_2O)^-$. Since it is known[3b] that the Ir^{III} complexes of the $IrCl_x(H_2O)_{6-x}^{3-x}$ type do not appreciably absorb in this spectral region (see, for example, curve C in Figure 1) and are quantitatively oxidized by Cl_2 to the corresponding Ir^{IV} complexes without any stoichiometric change, it was clear that the irradiation, in addition to reaction (1), also caus-

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[11] Such a reaction medium was used because the aquo-product, $IrCl_5(H_2O)^{2-}$, apparently undergoes olation reactions in solutions of lower acidity and ionic strength.[3a]

[12] Actually, the bands at 232 and 488 nm are due to transitions from (π+σ) ligand orbitals rather than from pure π ligand orbitals.[2c] For a recent discussion of the $IrCl_6^{2-}$ spectrum, see also Ref. 13.

[13] T. P. Sleight and C. R. Hare, *J. Phys. Chem.*, *72*, 2207 (1968).

[14] M. R. Martinez, Ph. D. Thesis, University of California, Los Angeles, 1958.

ed the formation of $IrCl_6^{3-}$ and/or $IrCl_5(H_2O)^{2-}$. By means of a quantitative analysis of the spectrophotometric data, it was then possible to establish that $IrCl_5(H_2O)^{2-}$ was the main product of the photoredox process (reaction 2) and it was also possible to determine the quantum yields of formation of $IrCl_5(H_2O)^-$ and $IrCl_5(H_2O)^{2-}$.

$$IrCl_6^{2-} + H_2O \xrightarrow{h\nu} IrCl_5(H_2O)^{2-} + Cl \qquad (2)$$

Such an analysis was carried out as follows.

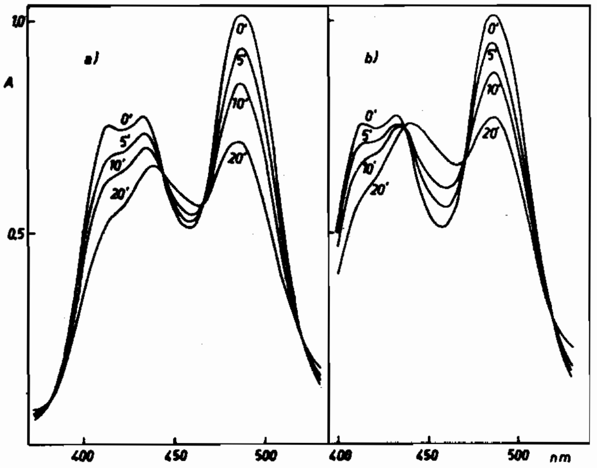

Figure 2. Absorption spectra of: *a*) chloride-free 2×10^{-4} F $IrCl_6^{2-}$ solutions after various irradiation periods with 254-nm light (3×10^{-7} einstein/min); *b*) the same solutions as in *a*), after oxidation with Cl_2. Note that the presence of Cl_2 in the oxidized solutions prevents reliable spectrophotometric measurements below 400 nm.

In a 1-cm cell, the absorbance of the irradiated solution *before the oxidation,* A, is given by

$$A = C_r\varepsilon_r + C_{aq}\varepsilon_{aq} + C_{red}\varepsilon_{red} \qquad (3)$$

where C_r, C_{aq}, and C_{red} and ε_r, ε_{aq}, and ε_{red} are the concentrations and the extinction coefficients of the reactant, photoaquation product, and photoredox product, respectively. In eq. 3, the third term of the summation may be neglected since the chloro-aquo complexes of Ir^{III} are known[3b] to have extinction coefficients at least 10^2 times lower than the corresponding Ir^{IV} complexes in the spectral range of interest (400-550 nm) (see, for example, Figure 1). Therefore, eq. 3 may be written as follows:

$$A = C_r\varepsilon_r + C_{aq}\varepsilon_{aq} \qquad (4)$$

The absorbance of the irradiated solution *after the oxidation,* A′, will obviously depend on the actual nature of the redox product. If this is $IrCl_6^{3-}$, after oxidation we should have

$$A' = C_r\varepsilon_r + C_{aq}\varepsilon_{aq} + C_{red}\varepsilon_r \qquad (5)$$

Combining eqs. 4 and 5, one obtains:

$$A'-A = C_{red}\varepsilon_r \qquad (6)$$

If the reduction product is $IrCl_5(H_2O)^{2-}$, after oxidation we should have

$$A' = C_r\varepsilon_r + C_{aq}\varepsilon_{aq} + C_{red}\varepsilon_{aq} \qquad (7)$$

Combining eqs. 4 and 7, one obtains:

$$A'-A = C_{red}\varepsilon_{aq} \qquad (8)$$

Now, the experimental A′-A values obtained at several wavelengths fit well with eq. 8, whereas they do not fit with eq. 6. This also appears evident when the spectra A and B of Figure 1 are compared with Figure 3, where the A′-A values for a typical experiment have been reported. Thus, we may conclude that, under the experimental conditions used, $IrCl_5(H_2O)^{2-}$ is by far the predominant product of the photoredox reaction of $IrCl_6^{2-}$.

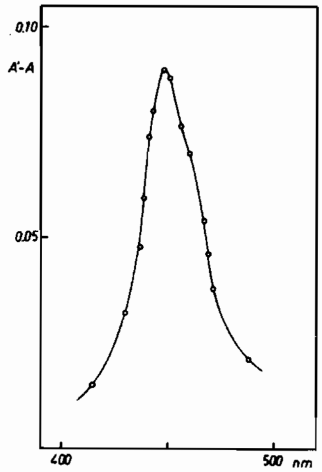

Figure 3. Increase in the absorbance of an irradiated $IrCl_6^{2-}$ solution due to the oxidation with Cl_2. $[IrCl_6^{2-}] = 5 \times 10^{-4}$, irradiation at 254 nm for 20 min with 6×10^{-7} einstein/min

Quantitative data concerning the formation of the redox product were obtained from eq. 8 or, independently, by measuring the decrease in absorbance at 386, 437, 471, and 517 nm (*i.e.,* at the isosbestic points between reactant and its aquation product); at these wavelengths, in fact, if A° is the initial (zero-time) value of the absorbance and A is the absorbance value after a certain period of irradiation, the concentration of the redox product formed in that period is given by:

$$C_{red} = (A^\circ - A)/(\varepsilon_r - \varepsilon_{red}) \qquad (9)$$

The C_{red} values obtained from eqs. 8 and 9 are in fair agreement (see below). The concentration of the aquo-product, $IrCl_5(H_2O)^-$, was then obtained by measuring the change in absorbance at wavelengths other than those of the isosbestic points:

$$C_{aq} = \frac{(A^\circ - A) - C_{red}(\varepsilon_r - \varepsilon_{red})}{(\varepsilon_r - \varepsilon_{aq})} \qquad (10)$$

The total amount of $IrCl_6^{2-}$ decomposed (*i.e.,* $C_{aq} +$

C_{red}) was obtained independently from the following equation:

$$C_t = C_{aq}+C_{red} = (A^o-A')/(\varepsilon_r-\varepsilon_{aq}) \qquad (11)$$

Mean values of C_{aq}, C_t, and C_{red} (from eq. 8) were obtained for each run, using absorbance measurements at 10 different wavelengths in the range 400-550 nm; in the case of the C_{red} values obtained from eq. 9, only the four wavelengths corresponding to the isosbestic points were, of course, used. As an example, we report here the concentration values obtained for a 5×10^{-4} F solution of $IrCl_6^{2-}$ irradiated for 30 minutes with a light intensity of 3×10^{-7} einstein/min:

C_{red} (from eq. 8) = $(0.81\pm0.05)\times10^{-5}$ mole/l
C_{red} (from eq. 9) = $(0.79\pm0.2\ )\times10^{-5}$ mole/l
C_{aq} (from eq. 10) = $(7.9\ \pm0.4\ )\times10^{-5}$ mole/l
C_t (from eq. 11) = $(8.8\ \pm0.2\ )\times10^{-5}$ mole/l

Linear plots of the absorbance variations (and, as a consequence, of C_{aq} and C_{red}) versus irradiation time were obtained at each wavelength in the region 400-550 nm. *This indicated that both $IrCl_5(H_2O)^-$ and $IrCl_5(H_2O)^{2-}$ were formed by parallel, zero-order reactions.* The quantum yields for the production of $IrCl_5(H_2O)^-$ (Φ_{aq}) and $IrCl_5(H_2O)^{2-}$ (Φ_{red}) and the total quantum yield of $IrCl_6^{2-}$ disappearance ($\Phi_t=\Phi_{aq}+\Phi_{red}$) are reported in Table I. They were found to be independent of light intensity (3×10^{-7}–6×10^{-7} einstein/min) and reactant concentration (2×10^{-4}–5×10^{-4} F).

Table I. Quantum Yield Values for the Photoreactions of $IrCl_6^{2-}$ at 254 nm [a]

$[Cl^-]$	$\Phi_{aq}\times10^2$	$\Phi_{red}\times10^2$	$\Phi_t\times10^2$
0	2.50 ± 0.15	0.45 ± 0.15	2.90 ± 0.20
0.1	1.85 ± 0.20 [b]	1.15 ± 0.20 [b]	2.95 ± 0.20
0.6	1.30 ± 0.15 [b]	1.50 ± 0.20 [b]	2.90 ± 0.15
1.2	0.80 ± 0.10 [b]	2.15 ± 0.20 [b]	2.90 ± 0.20

[a] Φ_{aq} = quantum yield for $IrCl_5(H_2O)^-$ formation; Φ_{red} = quantum yield for $IrCl_5(H_2O)^{2-}$ formation; $\Phi_t = \Phi_{aq}+\Phi_{red}$.
[b] zero-time value (see text).

When the experiments were carried out in *the presence of Cl^-* (0.1, 0.6, or 1.2 F NaCl), in the first irradiation periods the absorbance decreased in the entire spectral range between 380 and 550 nm; for longer irradiation periods, however, the absorbance increased at certain wavelengths (Figure 4a). After oxidation of the irradiated solutions by Cl_2, the absorbance increased and the resulting spectra were quite similar to those of Figure 2b. Calculations as those described above showed that $IrCl_5(H_2O)^-$ and $IrCl_5(H_2O)^{2-}$ were again the main products of the photochemical reactions. The plots of absorbance versus irradiation time were nonlinear for the absorbance values measured before the oxidation (Figure 4a), while they were linear for the values measured after the oxidation (Figure 4b). Accordingly, plots such as those of Figure 5 were obtained for C_{aq} and C_{red} ($C_{aq}=[IrCl_5(H_2O)^-]$, $C_{red}=[IrCl_5(H_2O)^{2-}]$), while the sum of $C_{aq}+C_{red}$ was found to be a linear function of the irradiation time. *The differential quantum yields*[15] for the production of $IrCl_5(H_2O)^-$ and $IrCl_5(H_2O)^{2-}$ at various irradiation times were calculated from the slopes of the tangents of concentration *vs.* time plots. These differential quantum yields showed a linear dependence on the irradiation time (Figure 6), with slopes which increased with increasing Cl^- concentration. The extrapolation of these plots to zero-time of irradiation gave the quantum yields which have been summarized in Table I together with the quantum

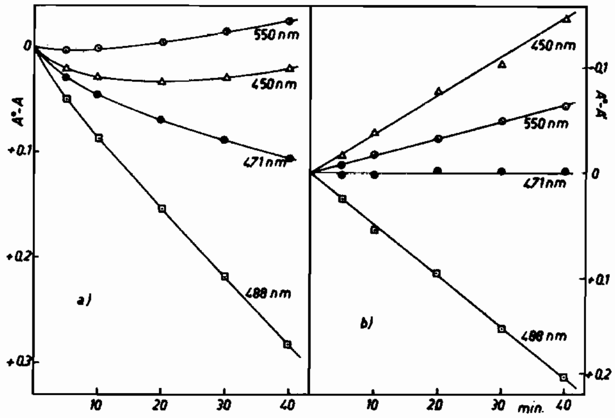

Figure 4. *a*) Absorbance variations caused by 254-nm irradiation on 5×10^{-4} F $IrCl_6^{2-}$ solutions containing 1.2 F Cl^- (3×10^{-7} einstein/min); *b*) absorbance variations for the same solutions as in *a*), but measured after oxidation with Cl_2.

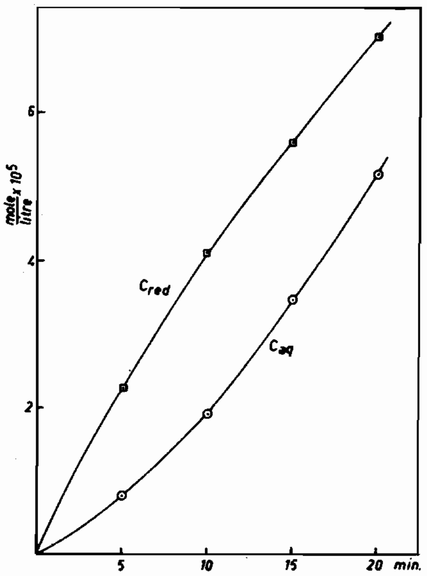

Figure 5. Concentrations of the photoproducts $IrCl_5(H_2O)^-$ (C_{aq}) and $IrCl_5(H_2O)^{2-}$ (C_{red}) after various irradiation periods. $[IrCl_6^{2-}]=5\times10^{-4}$, $[Cl^-]=1.2$, $\lambda=254$ nm, einstein/min = 6×10^{-7}.

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(15) For a discussion concerning the *differential* quantum yields in photochemical experiments, see H. Mauser, Z. *Naturforschg.*, *22b*, 367 (1967).

yields obtained in the absence of Cl^-. Changes in light intensity (3×10^{-7}–6×10^{-7} einstein/min) and reactant concentration (2×10^{-4}–5×10^{-4} F) did not have any effect.

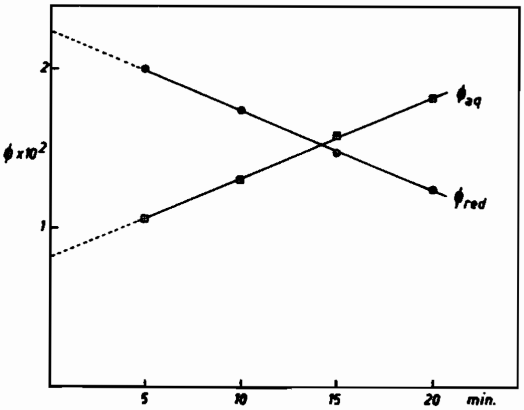


Figure 6. Dependence of the differential quantum yields on irradiation time. $[IrCl_6^{2-}]=5\times10^{-4}$, $[Cl^-]=1.2$, einstein/min $=6\times10^{-7}$.

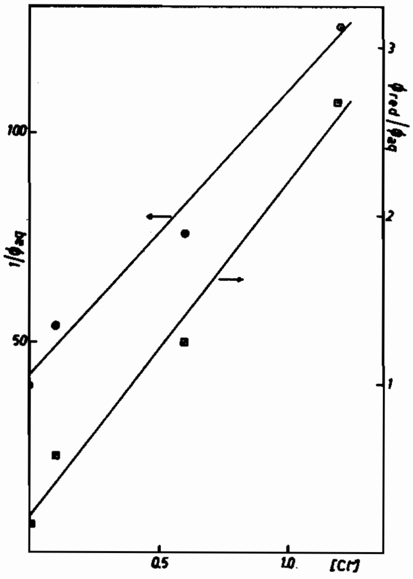


Figure 7. Dependence of the (extrapolated) quantum yields on Cl^- concentration (excitation with 254-nm light).

It can be easily verified that the quantum yields of Table I fit with the following equations (see Figure 7):

$$1/\Phi_{aq} = A+B[Cl^-] \qquad (12)$$

$$\Phi_{red}/\Phi_{aq} = C+D[Cl^-] \qquad (13)$$

where A=42, B=67 mole^{-1}, C=0.22, and D=1.98 mole^{-1}. Note that $D/B=2.9\times10^{-2}$, which is the experimental value of Φ_t.

Irradiation in the Ligand Field Bands (313- and 365-nm Light). Upon irradiation with 313- or 365-nm light, which probably corresponds to ligand field bands,[2,13] the spectrum of *chloride-free solutions* of $IrCl_6^{2-}$ changed, but isosbestic points were present at 386, 437, 471, and 518 nm. Since these isosbestic points are just those expected for a mixture of $IrCl_6^{2-}$ and $IrCl_5(H_2O)^-$ (Figure 1), one can conclude that only a photoaquation reaction was observable under these conditions. The quantum yield of this reaction was 1×10^{-2} at 313 nm and 1×10^{-3} at 365 nm.

When the experiments were carried out *in the presence of 1.2 F Cl^-*, the absorbance decreased in the entire spectral region examined; when the irradiated solutions were oxidized by Cl_2, their spectra came back to the zero-time spectrum, thus indicating that the photochemical product had to be $IrCl_6^{3-}$. The quantum yield of $IrCl_6^{3-}$ formation was 2×10^{-2} at 313 nm and 5×10^{-3} at 365 nm.

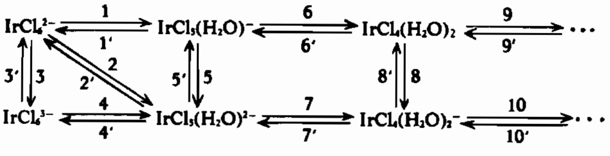
Irradiation in the $\pi_L\rightarrow\pi_M^*$ (t_{2g}) Charge Transfer Bands (433- and 495-nm Light). The complex proved to be almost insensitive to photoexcitation in this spectral region. For chloride-free solutions, no change in absorbance could be observed, even after very long irradiation periods. For solutions containing 1.2 F Cl^-, no spectral change was observed upon 459-nm irradiation, but a small decrease in absorbance was obtained with 433-nm light; this indicated that some redox reaction occurred, with a very low efficiency ($\Phi\sim1\times10^{-4}$). The nature of the reduced product was not investigated.

A summary of the experimental results obtained at the various wavelengths is given in Table II.

Finally, we would like to note that our results are in disagreement with those reported in a preliminary communication by Sleight and Hare.[5] These authors claimed that only an aquation reaction occurred when hydrochloric or water solutions of $IrCl_6^{2-}$ were irradiated with 254- or 360-nm light.

Discussion

Photochemical Reactions and Thermal Secondary Reactions. The processes which *might* take place in our system are represented in Scheme 1. Under the experimental conditions used in this work (light absorbed only by the reactant $IrCl_6^{2-}$, T = 25°, irradiation for less than 1 hour, $0\leqslant[Cl^-]\leqslant1.2$), most of the processes shown in this scheme may be neglected.



Scheme 1. Processes which might occur upon irradiation of $IrCl_6^{2-}$. For the sake of clearness, only the Ir-containing species are shown.

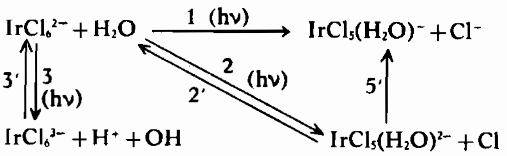
Specifically: (i) the only possible photoreactions are those which originate from $IrCl_6^{2-}$; (ii) no thermal reactions of $IrCl_6^{2-}$ occur (see Results); (iii) the aquations of $IrCl_6^{3-}$,[3a] $IrCl_5(H_2O)^{2-}$ [3b] and $IrCl_5$-

Table II. Quantum Yield Values for the Formation of Various Photochemical Products of $IrCl_6^{2-}$.

Type of irradiation (λ of excitation)	Experiments without added Cl^-			Experiments in the presence of 1.2 F Cl^-		
	$IrCl_5(H_2O)^-$	$IrCl_5(H_2O)^{2-}$	$IrCl_6^{3-}$	$IrCl_5(H_2O)^-$	$IrCl_5(H_2O)^{2-}$	$IrCl_6^{3-}$
$\pi_L(t_{1u})\rightarrow\sigma_M^*(e_g)$ (254 nm)	2.5×10^{-2}	4.5×10^{-3}	$(<1 . 10^{-4})$ [a]	8.0×10^{-3}	2.2×10^{-2}	$(<1\times10^{-4})$ [a]
$\pi_M^*(t_{2g})\rightarrow\sigma_M^*(e_g)$ (313 nm)	1×10^{-2}	$(<2\times10^{-4})$ [a]		$(<4\times10^{-3})$ [a]		2×10^{-2}
$\pi_M^*(t_{2g})\rightarrow\sigma_M^*(e_g)$ (365 nm)	1×10^{-3}	$(<4\times10^{-5})$ [a]		$(<1\times10^{-5})$ [a]		5×10^{-3}
$\pi_L(t_{2u})\rightarrow\pi_M^*(t_{2g})$ (433 nm)	$(<5\times10^{-5})$ [a]	$(<3\times10^{-5})$ [a]		$(<5\times10^{-5})$ [a]	$\sim1\times10^{-4}$	
$\pi_L(t_{1u})\rightarrow\pi_M^*(t_{2g})$ (495 nm)	$(<5\times10^{-5})$ [a]	$(<3\times10^{-5})$ [a]		$(<5\times10^{-5})$ [a]	$(<3\times10^{-5})$ [a]	

[a] Upper limit values, as evaluated on the basis of the experimental errors involved in the absorbance measurements.

$(H_2O)^-$,[14,16] and the anations of $IrCl_5(H_2O)^{2-}$ [3b] and $IrCl_5(H_2O)^-$ [14,16] are very slow processes and thus they may be neglected; (iv) $IrCl_5(H_2O)^-$ is kinetically stable towards reduction to $IrCl_5(H_2O)^{2-}$.[16] It follows that the above scheme reduces to Scheme 2, where processes 1, 2 and 3 may only occur photochemically and processes 2′, 3′ and 5′ may only occur thermally.

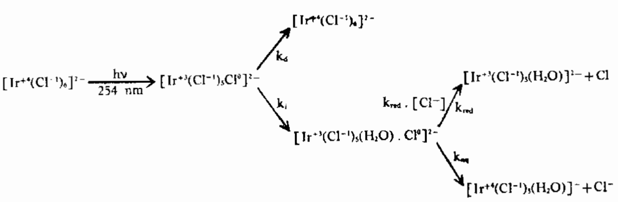


Scheme 2. Photochemical and thermal reactions which *can* occur upon irradiation of $IrCl_6^{2-}$.

The experimental results (Table II) show that all of the three possible photoproducts of $IrCl_6^{2-}$ may be obtained (although not all together). From Scheme 2, it follows that $IrCl_5(H_2O)^{2-}$ and $IrCl_6^{3-}$ must originate directly from $IrCl_6^{2-}$ through processes 2 and 3, respectively. On the contrary, $IrCl_5(H_2O)^-$ could originate either directly from $IrCl_6^{2-}$ by means of a photoaquation reaction (process 1) or indirectly by photoreduction of $IrCl_6^{2-}$ to $IrCl_5(H_2O)^{2-}$, followed by thermal re-oxidation of this last compound (processes 2+5′). It should be noted, however, that *in the absence of Cl^- ions* both $IrCl_5(H_2O)^{2-}$ and $IrCl_5(H_2O)^-$ are produced with zero-order rate law upon 254-nm irradiation (see Results). This means that $IrCl_5(H_2O)^-$ *cannot* be formed through the consecutive processes 2 and 5′. Therefore, $IrCl_5(H_2O)^-$ must be produced by process 1. Note, however, that reaction 5′ becomes important when Cl^- ions are present in the irradiated solutions, as shown by the plots in Figure 5.

Photolysis Mechanisms. The results obtained (Table II) show that $IrCl_6^{2-}$ is little photosensitive and that the nature and the quantum yield of its photoreactions *depend* on the wavelength of irradiation. This spectrospecificity suggests that the nature of the excited states directly reached by irradiation plays a preponderant role in determining the photochemical behaviour of $IrCl_6^{2-}$, contrary to what happens for $PtBr_6^{2-}$ which was found to undergo the same photoreaction (*i.e.*, a photoaquation) with a constant quantum yield (0.4), regardless of the charge-transfer or ligand-field nature of the excited states reached by irradiation.[4] It is also worth noting the great difference in photoreactivity between the $\pi_L\rightarrow\sigma_M^*$ (e_g) and $\pi_L\rightarrow\pi_M^*$ (t_{2g}) excited states of $IrCl_6^{2-}$. Such a difference may reflect the greater antibonding character of the $\sigma^*(e_g)$ « metal » orbitals with respect to the $\pi^*(t_{2g})$ ones.[17]

The best results obtained in this work concerned the irradiation with 254-nm light and thereby, we shall dedicate our discussion to them. As we have seen, the irradiation of $IrCl_6^{2-}$ solutions with 254-nm light causes two parallel photoreactions, namely a photoaquation leading to $IrCl_5(H_2O)^-$ and an intramolecular photoreduction yielding $IrCl_5(H_2O)^{2-}$. The results obtained show that, when Cl^- ions are present in the irradiated solutions, not only a secondary dark reaction occurs which partially converts $IrCl_5(H_2O)^{2-}$ into $IrCl_5(H_2O)^-$ (see the discussion above), *but the relative importance of the two photoreactions also changes.* Specifically, photoaquation is the predominant reaction mode at low Cl^- concentration, whereas at high Cl^- concentration, the main photoreaction is the photoreduction (Table I). It should also be pointed out that the sum of Φ_{aq} and Φ_{red} does *not* change with varying $[Cl^-]$. This means that $[Cl^-]$ only affects the competition between the two reaction modes without influencing the competition between physical and chemical deactivation. In other words, $IrCl_5(H_2O)^-$ and $IrCl_5(H_2O)^{2-}$ seem to originate from a common intermediate which (i) cannot be converted back to the reactant $IrCl_6^{2-}$ and (ii) is preferentially transformed into $IrCl_5(H_2O)^{2-}$ (rather than into $IrCl_5(H_2O)^-$) when Cl^- ions are present in the solution. A speculative reaction mechanism which seems to interpret these experimental results is that represented in Scheme 3, where $[Ir^{+3}$-



Scheme 3. Proposed mechanism for the photolysis of $IrCl_6^{2-}$.

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(16) We have verified that at 25° the spectrum of an $IrCl_5(H_2O)^-$ solution does not show any change for at least 1 hour, regardless of the presence of Cl^- (up to 1.2 F).

$(Cl^{-1})_5(H_2O)\cdot Cl^{\circ}]^{2-}$ represents an intermediate in which a Cl atom is definitively detached from the central metal atom, although it is still contained in the solvent cage of the parent complex. From such an intermediate, a net redox reaction will result if Cl succeeds in escaping from the solvent cage. Alternatively, Cl will reoxidize its cage partner to $IrCl_5(H_2O)^-$ and diffuse away as Cl^-; in this case, a net aquation reaction will result.[19] The increasing importance of the redox process with increasing $[Cl^-]$ could be due to an easier Cl escaping *via* an electron transfer from an « outer » Cl^- to the Cl atom in the cage.

On the common assumption that the excited molecules and the intermediate rapidly reach a stationary concentration, the kinetic development of the above mechanism leads to the following equations (the processes which the kinetic constants refer to are those shown in Scheme 3):

$$\Phi_t = \frac{k_i}{k_d + k_i} \tag{14}$$

$$\Phi_{aq} = \frac{k_i}{k_d + k_i} \cdot \frac{k_{aq}}{k_{aq} + k_{red} + k'_{red}[Cl^-]} = \Phi_t \cdot \frac{k_{aq}}{k_{aq} + k_{red} + k'_{red}[Cl^-]} \tag{15}$$

$$\frac{1}{\Phi_{aq}} = \frac{1}{\Phi_t} \cdot \frac{k_{red} + k_{aq}}{k_{aq}} + \frac{1}{\Phi_t} \ \frac{k'_{red}}{k_{aq}}[Cl^-] \tag{16}$$

$$\Phi_{red} = \frac{k_i}{k_i + k_d} \cdot \frac{k_{red} + k'_{red}[Cl^-]}{k_{aq} + k_{red} + k'_{red}[Cl^-]} = \Phi_t \cdot \frac{k_{red} + k'_{red}[Cl^-]}{k_{aq} + k_{red} + k'_{red}[Cl^-]} \tag{17}$$

$$\frac{\Phi_{red}}{\Phi_{aq}} = \frac{k_{red}}{k_{aq}} + \frac{k'_{red}}{k_{aq}}[Cl^-] \tag{18}$$

The experimental results showed that: (i) $\Phi_t = \Phi_{aq} + \Phi_{red}$ was independent of $[Cl^-]$, light intensity and complex concentration; (ii) Φ_{aq} and Φ_{red} were independent of light intensity and complex concentration, but they depended in a rather complex way on $[Cl^-]$ (see eqs. 12 and 13). It can be easily verified that *all* of these results are consistent with eqs. 14 to 18. In particular, compare eq. 12 with eq. 16 and eq. 13 with eq. 18; from these last two equations one can also obtain the following ratios for the kinetic constants involved:

$k'_{red}/k_{aq} = 1.98$ mole^{-1} $\qquad k_{red}/k_{aq} = 0.22$

Acknowledgments. The authors are grateful to Prof. V. Carassiti for his interest in this work.

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[17] This difference in the antibonding character is also reflected in the band width of the two ligand metal charge transfer transitions.[18]

[18] C. K. Jørgensen, « Absorption Spectra and Chemical Bonding in Complexes », Pergamon Press, Oxford, 1962.

[19] We would like to point out that the above mechanism is very similar to the one proposed by Adamson[20] for explaining some features of the photochemistry of Co^{III} complexes; for a complete discussion of Adamson's mechanism, see Ref. 21.

[20] A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, *80*, 3865 (1958).

[21] V. Balzani, L. Moggi, F. Scandola, and V. Carassiti, *Inorg. Chim.. Acta Rev.*, *1*, 7 (1967).