ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 90 (1995) 31-37

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photochemistry of $IrCl_6^{2-}$ complex in alcohol solutions

E.M. Glebov [a,*], V.F. Plyusnin [a], N.I. Sorokin [a], V.P. Grivin [a], A.B. Venediktov [b],
H. Lemmetyinen [c]

[a] *Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia*
[b] *Institute of Inorganic Chemistry, Novosibirsk 630090, Russia*
[c] *Department of Materials Chemistry, Tampere University of Technology, P.O. Box 589, 33101 Tampere, Finland*

Received 16 November 1994; accepted 10 March 1995

Abstract

Both stationary and laser flash photolysis were used to study the photochemistry of $IrCl_6^{2-}$ in alcohol solutions. The primary photochemical photolysis process at 308 nm was demonstrated to involve electron transfer from the solvent to the excited complex. When the photolysis was performed at 248 nm, the photodissociation of the excited complex, with the elimination of a chlorine atom from the coordination sphere of iridium, was accompanied by electron transfer. At room temperature, the rate constants of the reaction between the primary alcohol radicals and the $IrCl_6^{2-}$ complex were determined to be $(3.2\pm0.1)\times10^9$ M^{-1} s^{-1} for hydroxymethyl and $(2.3\pm0.1)\times10^9$ M^{-1} s^{-1} for α-hydroxyethyl radicals. The dark reactions of the $IrCl_6^{3-}$ complex arising from photolysis are discussed.

Keywords: $IrCl_6^{2-}$; Alcohol solutions; Photolysis; Laser flash photolysis

1. Introduction

The study of $IrCl_6^{2-}$ photochemistry is of major importance in understanding the primary processes in the photochemistry of the chloride complexes of transition metals. The $IrCl_6^{2-}$ complex is a fairly stable particle which is present in solutions containing no free Cl^- ions. The optical spectrum of the $IrCl_6^{2-}$ complex [1,2] consists of intense absorption bands in both the visible and UV regions. The absorption bands in the range 400–500 nm with a maximum extinction coefficient of 4000 M^{-1} cm^{-1} (495 nm) are assigned to the $\pi_{Cl}\rightarrow\pi_{Ir}$ (t_{2g}) transition [1]. A wider and more intense band with a maximum at 232 nm is attributed to the $\sigma_{Cl}\rightarrow\sigma_{Ir}^*$ (e_g) transition. The less intense bands at 306 and 360 nm represent the d–d transitions.

There have been a few reports on the photochemistry of $IrCl_6^{2-}$ in aqueous HCl solutions [3–7] which give rather contradictory data. Thus Sleight and Hare [3] have found that photoaquation is the only process in $IrCl_6^{2-}$ photochemistry. In contrast, Moggi et al. [4] have demonstrated that both photoaquation and photoreduction of $IrCl_6^{2-}$ occur during photolysis. The quantum yield of photoreduction has been found to be wavelength dependent. The following mechanism of photolysis (at 254 nm) has been suggested

$$IrCl_6^{2-} \underset{}{\overset{h\nu}{\rightleftharpoons}} [IrCl_5Cl^{\bullet}]^{2-} \overset{H_2O}{\rightleftharpoons} [IrCl_5(H_2O)Cl^{\bullet}]^{2-} \quad (1)$$

$$[IrCl_5(H_2O)Cl^{\bullet}]^{2-} \rightleftharpoons IrCl_5(H_2O)^{2-} + Cl^{\bullet} \quad (2)$$

$$[IrCl_5(H_2O)Cl^{\bullet}]^{2-} \rightleftharpoons IrCl_5(H_2O)^{-} + Cl^{-} \quad (3)$$

In addition to Ref. [4], Eidem et al. [5] have proposed another pathway of $IrCl_6^{2-}$ photoreduction giving rise to the $IrCl_6^{3-}$ complex

$$(IrCl_6^{2-})^* + Cl^- \longrightarrow IrCl_6^{3-} + Cl^{\bullet} \quad (4)$$

The redox reactions of $IrCl_6^{2-}$ and $IrCl_6^{3-}$ in water solutions have been studied by the method of pulsed radiolysis [6,7]. The rate constants of the reactions of $IrCl_6^{2-}$ with aquated electrons, $H^{\bullet}$ and $^{\bullet}OH$ radicals and the $^{\bullet}O_2^-$ radical ion have been determined.

The photochemistry of $IrCl_6^{2-}$ in organic solvents is unknown. In Ref. [8], the phototransformation of $IrCl_6^{2-}$ was studied in acetonitrile at low temperatures (– 170 °C, – 30 °C).

Previously, we have studied the primary processes of the photochemistry of the chloride complexes of some transition metals (copper, iron, platinum) in simple alcohols [9–14]. Electron transfer from the solvent to the excited complex has been shown to be the primary photochemical process occurring in these systems (reactions (5) and (6))

---

* Corresponding author.

1010-6030/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 1010-6030(95)04070-6

$$MeCl_6^{n-} \overset{h\nu}{\rightleftarrows} (MeCl_6^{n-})^* \quad (5)$$

$$(MeCl_6^{n-})^* + CH_3OH \longrightarrow MeCl_6^{(n+1)-} + {}^{\bullet}CH_2OH + H^+ \quad (6)$$

The primary alcohol radicals can then react with the initial complex.

In this paper, we study the primary processes of $IrCl_6^{2-}$ photoreduction in alcohol solutions using the methods of stationary and laser flash photolysis.

2. Experimental details

Stationary photolysis was performed using radiation from excimer XeCl (308 nm) and KrF (248 nm) lasers or a high-pressure mercury lamp. Optical spectra were recorded on a Specord UV–visible spectrophotometer (Carl Zeiss).

Pulse experiments were carried out using an apparatus for laser flash photolysis with excitation by an XeCl excimer laser (308 nm, 15 ns, 10 mJ) [15,16], as well as a similar instrument with a more powerful (60 mJ) excimer laser [17]. Solutions were placed in optical cuvettes 1–2 mm thick. Excitation and probe beams were passed through the cuvettes at a small angle (2°). In the apparatus using a 60 mJ laser, the excitation and probe beams were passed through a 1 cm cuvette at a right angle.

Oxygen was removed by bubbling of the solutions with argon for 30 min. All the solutions were prepared from spectrally pure reagents. All the experiments were performed using $Na_2IrCl_6 \cdot 6H_20$ prepared as described in Ref. [18].

3. Results and discussion

3.1. Dark reaction of $IrCl_6^{2-}$ with alcohols. Photolysis performed in the visible spectral region

In alcohol solutions, $IrCl_6^{2-}$ is slowly reduced in the dark to $IrCl_6^{3-}$. The value of the rate constant of $IrCl_6^{2-}$ disappearance in pure methanol has been determined from the initial inclination angle of the kinetic curves as $(2.7 \pm 0.3) \times 10^{-5}$ s^{-1} ($[IrCl_6^{2-}] = 3.5 \times 10^{-4}$ M and $T = 299$ K). Previously, the reaction of $IrCl_6^{2-}$ with alcohols was studied in water–alcohol (up to 3 M of alcohol) mixtures [19]. The reaction has been found to be first order with respect to $IrCl_6^{2-}$ and less with respect to alcohols. The data obtained [19] have been explained in terms of the following reaction mechanism (for methanol)

$$IrCl_6^{2-} + CH_3OH \underset{\text{fast}}{\overset{K_7}{\rightleftarrows}} [IrCl_6^{2-}...CH_3OH] \quad (7)$$

$$[IrCl_6^{2-}...CH_3OH] \xrightarrow[\text{slow}]{} IrCl_6^{3-} + {}^{\bullet}CH_2OH + H^+ \quad (8)$$

$$IrCl_6^{2-} + {}^{\bullet}CH_2OH \xrightarrow[\text{fast}]{} IrCl_6^{3-} + H_2CO + H^+ \quad (9)$$

Within the framework of reactions (7)–(9), for low conversion, the observed rate constant of $IrCl_6^{2-}$ reduction is described by expression (10) where K_7 is the equilibrium constant of step (7)

$$k_{\text{eff}} = -\frac{1}{[IrCl_6^{2-}]}\frac{d[IrCl_6^{2-}]}{dt} = 2k_8\frac{K_7[CH_3OH]}{1 + K_7[CH_3OH]} \quad (10)$$

The extrapolation of the Arrhenius plots for k_8 and K_7 obtained in Ref. [19] for our experimental conditions (299 K, pure methanol) gives the value of 1.5×10^{-4} s^{-1} for the observed rate constant of $IrCl_6^{2-}$ reduction. This is five times larger than our result. There are two reasons for the divergence of the data. Firstly, Sen Gupta and Chatterjee [19] have neglected the possibility of peroxide radical formation via reaction (11). The peroxide radicals quickly recombine via reaction (12) without participating in other reactions

$${}^{\bullet}CH_2OH + O_2 \longrightarrow {}^{\bullet}OOCH_2OH \quad (11)$$

$$2{}^{\bullet}OOCH_2OH \longrightarrow \text{molecular products} \quad (12)$$

Sen Gupta and Chatterjee [19] worked with $IrCl_6^{2-}$ concentrations of about $(0.5\text{–}3.5) \times 10^{-4}$ M and a natural content of oxygen (2.5×10^{-4} M in water at 25 °C [20]). In these conditions, reactions (9) and (11) must compete. In methanol, where the solubility of oxygen is an order of magnitude greater than in water (2.6×10^{-3} M at 25 °C [20]), channel (9) is completely switched off and Ir(III) only forms by reaction (8). This leads to a decrease in k_{eff} by a factor of two. Secondly, the decay of the intermediate by reaction (8) in a less polar medium seems to be slower.

Thus the dark reduction of $IrCl_6^{2-}$ is slow and has no effect on the photochemical stages. It should also be noted that the visible charge transfer bands of $IrCl_6^{2-}$ are not photosensitive (photolysis quantum yield is less than 10^{-4}).

3.2. Stationary photolysis of $IrCl_6^{2-}$ complex at 308 nm

Fig. 1(a) shows the changes in the optical spectrum of $IrCl_6^{2-}$ in methanol solution irradiated with an XeCl laser (308 nm) at room temperature. On photolysis, a new absorption band with a maximum at 209 nm is observed with an isosbestic point at 223 nm. The isosbestic point has been used to determine the extinction coefficient of the new band as 28 500 M^{-1} cm^{-1}. This band can be attributed to Ir(III) ($IrCl_6^{3-}$ complex). In water solutions, the absorption band of the complex exhibits a maximum at 211 nm with an extinction coefficient of 28 200 M^{-1} cm^{-1} and weak d–d bands in the visible region ($\lambda_{\max} = 560$, 415 and 356 nm, $\epsilon = 10$, 76 and 64 M^{-1} cm^{-1} respectively) [5].

The formation of $IrCl_6^{3-}$ with a 100% yield confirms that electron transfer from the solvent to the excited complex is the primary process of $IrCl_6^{2-}$ photochemistry (reactions (5) and (6)). The primary product is the radical of the solvent (${}^{\bullet}CH_2OH$ for methanol) which can react with $IrCl_6^{2-}$ (reaction (9)) and with oxygen (reaction (11)). Competition between these reactions will lead to the dependence of

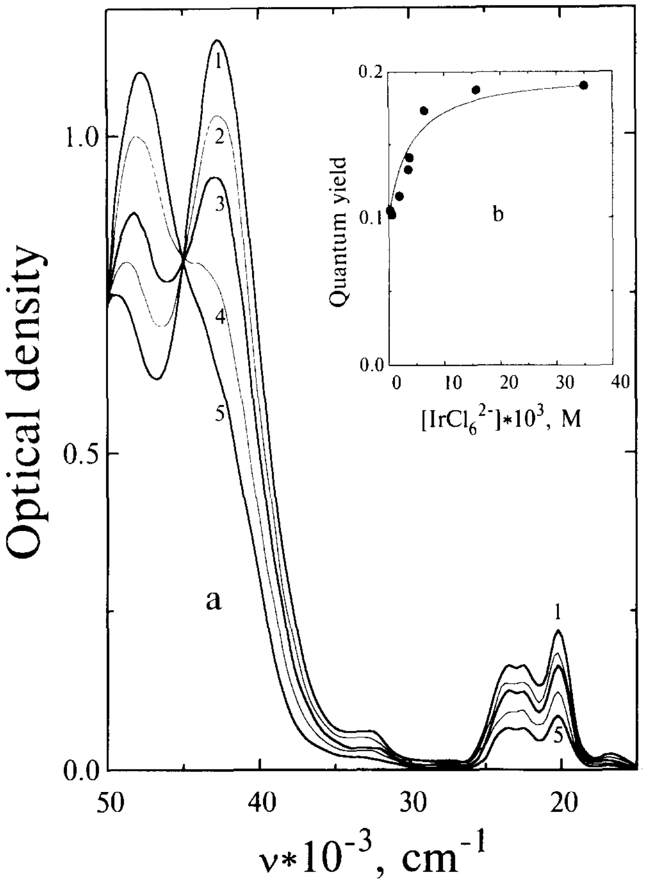

Fig. 1. $IrCl_6^{2-}$ photolysis (308 nm, XeCl excimer laser) in methanol at 300 K. (a) Change in the optical spectrum (cuvette thickness, 0.086 cm; $IrCl_6^{2-}$ concentration, 5.4×10^{-4} M; natural content of oxygen; energy, 17.5 mJ per pulse): curves 1–5 denote 0, 35, 70, 160 and 260 pulses respectively. (b) Dependence of the quantum yield of $IrCl_6^{2-}$ disappearance on its concentration: full line, calculation by Eq. (13) using parameters $\phi_0=0.1$, $k_9=3.2\times10^9\ M^{-1}\ s^{-1}$, $k_{11}=5.0\times10^9\ M^{-1}\ s^{-1}$.

the quantum yield on the $IrCl_6^{2-}$ concentration according to

$$\phi=\phi_0\left[1+\frac{1}{1+(k_{11}[O_2])/(k_{10}[IrCl_6^{2-}])}\right] \qquad (13)$$

where ϕ_0 is the quantum yield at low concentrations of the initial complex. Fig. 1(b) confirms this dependence. The rate constant of interaction between the $^{\bullet}CH_2OH$ radical and oxygen is $5\times10^9\ M^{-1}\ s^{-1}$ [21] and for the reaction of $^{\bullet}CH_2OH$ with the initial $IrCl_6^{2-}$ complex is given in Section 3.3. At low $IrCl_6^{2-}$ concentration (less than 10^{-3} M), the quantum yield is 0.1. If the concentration exceeds the content of oxygen dissolved in methanol, the quantum yield almost doubles. In developing Eq. (13) we have neglected the opportunity of $^{\bullet}CH_2OH$ radical recombination. The validity of this approximation is discussed below.

Therefore it is assumed that, at low $IrCl_6^{2-}$ concentrations, the removal of oxygen from the solution must have the same effect as an increase in the concentration of the initial complex, i.e. a doubling of the quantum yield. This is observed in pulse experiments as shown in the next section.

3.3. Flash photolysis of $IrCl_6^{2-}$ complex at 308 nm

Fig. 2(a) shows the characteristic shape of the kinetic curves on laser flash photolysis of $IrCl_6^{2-}$ in methanol. When the oxygen content is normal, we observe bleaching after the laser pulse (Fig. 2(a), curve 1) whose spectrum coincides with that of $IrCl_6^{2-}$ (Fig. 2(b)). In argon-saturated solutions, the magnitude of bleaching increases about twofold during a few microseconds (Fig. 2(a), curve 2). This is attributed to the reaction of the alcohol radical with the initial complex (reaction (9)) because the observed first-order rate constant linearly depends on the concentration of $IrCl_6^{2-}$ (Fig. 2(c)). The slope of the straight lines have been used to determine the rate constants of the reactions of $IrCl_6^{2-}$ with $^{\bullet}CH_2OH$ and $CH_3{}^{\bullet}CHOH$ radicals: $(3.2\pm0.1)\times10^9$ and $(2.3\pm0.1)\times10^9\ M^{-1}\ s^{-1}$ respectively. The flash photolysis data are in fair agreement with the dependence of the quantum yield of stationary photolysis on the $IrCl_6^{2-}$ concentration.

We now discuss the reliability of the earlier assumption of the negligibly small influence of the recombination of alcohol radicals on photolysis. In flash photolysis experiments, the

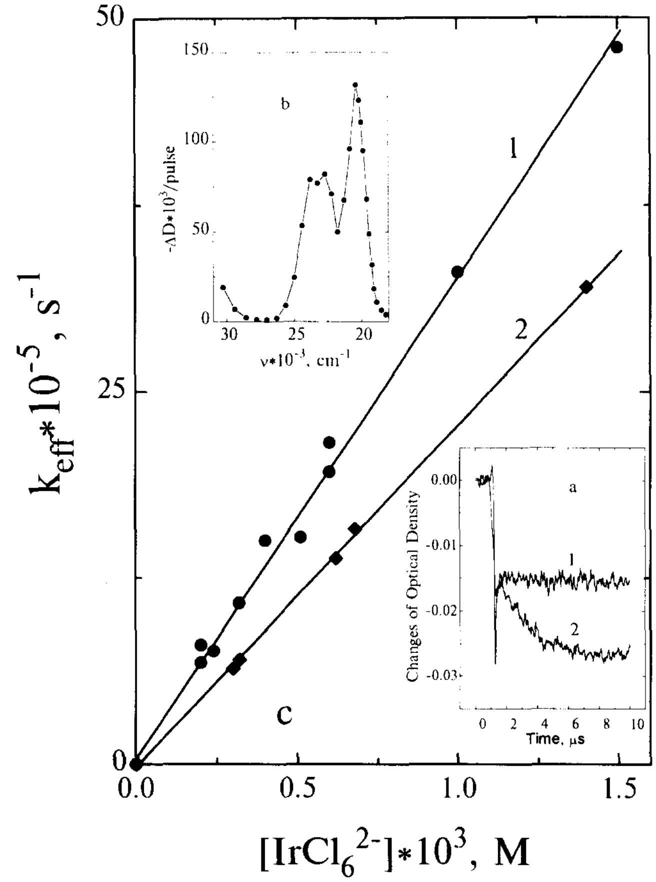

Fig. 2. Laser flash photolysis of $IrCl_6^{2-}$ at 308 nm. (a) Kinetic curves in methanol ($T=300$ K; recording at 500 nm; $[IrCl_6^{2-}]=1.03\times10^{-4}$ M; 1 cm cuvette): curve 1, natural content of oxygen; curve 2, without oxygen. (b) Changes in the optical density in methanol just after a laser pulse: full line, $IrCl_6^{2-}$ spectrum. (c) Dependence of the observed rate constant of $IrCl_6^{2-}$ decay in methanol (curve 1) and ethanol (curve 2) on the concentration of this complex.

decrease in the $IrCl_6^{2-}$ concentration is about 3×10^{-6} M per pulse. The concentration of the $^{\bullet}CH_2OH$ radicals is of the same order. Assuming the recombination rate constant of the $^{\bullet}CH_2OH$ radicals to be 1.4×10^9 M^{-1} s^{-1} [22], the characteristic time of radical disappearance in the recombination reaction would be about 100 μs. The characteristic time of reaction between the radical and the initial complex in our experiments varies from 0.2 to 3 μs. In stationary photolysis experiments, the maximum change in the radical concentration per laser pulse is no more than 3×10^{-6} M. Therefore it is concluded that the role of $^{\bullet}CH_2OH$ radical recombination in all our experiments is small.

3.4. Stationary photolysis of $IrCl_6^{2-}$ complex at 248 nm

Fig. 3 shows the change in the optical spectrum of $IrCl_6^{2-}$ irradiated with a KrF excimer laser (248 nm). On photolysis to rather large (50%) conversions, the isosbestic point is preserved at 219 nm (instead of 223 nm as on irradiation at 308 nm). Further irradiation disturbs the isosbestic point. Compared with photolysis performed at 308 nm the observed band has a smaller optical density and its maximum is shifted towards deeper UV regions. Photolysis performed with mercury lamp irradiation in the region of 253 nm causes the same spectral changes. When the $IrCl_6^{2-}$ concentration is much lower than that of dissolved oxygen, the photolysis quantum yield is 0.1.

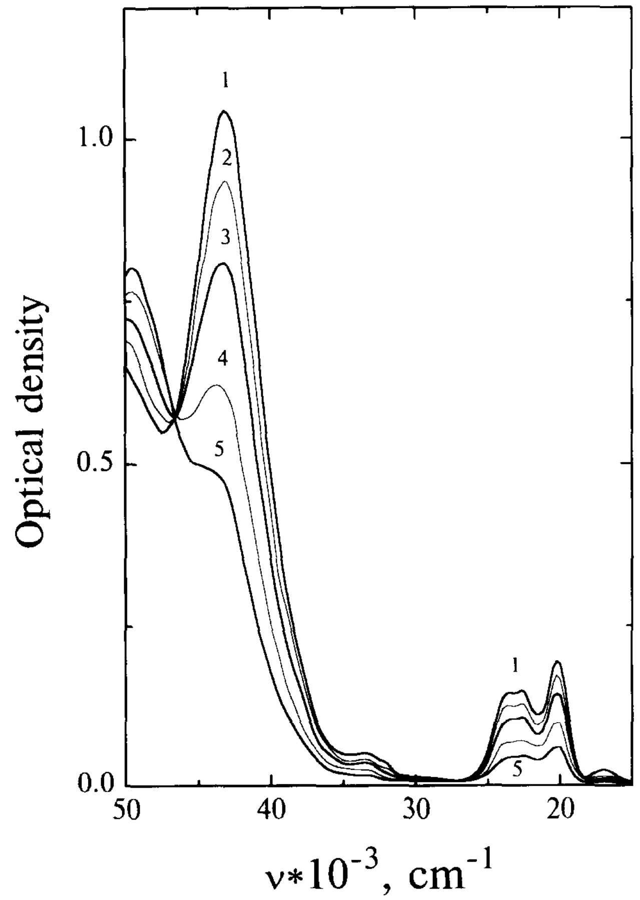

Fig. 3. $IrCl_6^{2-}$ photolysis in methanol at 300 K (irradiation at 248 nm (KrF excimer laser); cuvette thickness, 0.086 cm; $IrCl_6^{2-}$ concentration, 5.3×10^{-4} M; natural content of oxygen; energy, 3.7 mJ per pulse): curves 1–5 denote 0, 30, 80, 170 and 270 pulses respectively.

The differences between the spectral changes on irradiation at 248 and 308 nm are probably connected with a new route of $IrCl_6^{2-}$ phototransformation on irradiation at 248 nm which competes with electron transfer. This new channel may be $IrCl_6^{2-}$ photosolvation. However, in this case, the resulting $IrCl_5(CH_3OH)^-$ complex should display intense absorption bands in the visible region similar to those of the $IrCl_5(H_2O)^-$ complex [4,23]. The change in mechanism and products under the influence of two-quantum processes can also be excluded because a decrease in the intensity of the excitation light by about nine orders of magnitude (transition from pulse laser to stationary mercury lamp) has no effect on the position of the isosbestic point at 219 nm.

It remains to suggest that, on irradiation at 248 nm, electron transfer competes with the elimination of a chlorine atom from the coordination sphere of excited $IrCl_6^{2-}$ which leads to the formation of the $IrCl_5(CH_3OH)^{2-}$ complex. This is similar to processes (1) and (2) occurring in water solutions. The decrease in the extinction coefficient of the observed band and the resulting shift in the isosbestic point (from 223 to 219 nm) indicate that the absorption band of the $IrCl_5(CH_3OH)^{2-}$ complex is significantly less intense than that of $IrCl_6^{3-}$. Fig. 4 shows the process of separation of the $IrCl_5(CH_3OH)^{2-}$ absorption band under the assumption that only the $IrCl_6^{2-}$ and $IrCl_6^{3-}$ complexes absorb at 45 000 cm^{-1} (222 nm) and the longer wavelength part of the spectrum. This assumption allows the $IrCl_5(CH_3OH)^{2-}$ spectrum to be restored and the contribution of photodissociation to the overall photoreaction to be estimated. It appears that about two- thirds of the photolysed $IrCl_6^{2-}$ complex forms $IrCl_6^{3-}$ and only one-third gives rise to $IrCl_5(CH_3OH)^{2-}$.

In order to verify the formation of $IrCl_5(CH_3OH)^{2-}$, an irradiated solution of $IrCl_6^{2-}$ was bubbled with molecular chlorine. The fast oxidation of the Ir(III) ion by chlorine is unlikely to cause changes in its coordination sphere [4]. The solution, bleached after irradiation, is rapidly coloured as a result of Ir(III) oxidation to Ir(IV). As shown in Fig. 5(a), when chlorine is passed through the sample irradiated at 308 nm, the spectrum of the initial $IrCl_6^{2-}$ complex is almost completely restored. When chlorine is passed through the sample irradiated at 248 nm, the appearance of a maximum at 450 nm (Fig. 5(b)) testifies to the formation of the $IrCl_5(CH_3OH)^-$ complex, the spectrum of which must be similar to that of $IrCl_5(H_2O)^-$. Thus the assumption of two methods of $IrCl_6^{2-}$ photoreduction and the formation of two products from the photolysis performed at 248 nm is confirmed by experiments on the oxidation of the photoreaction products. The disturbance of the isosbestic point at large $IrCl_6^{2-}$ conversions is caused by photolysis of the $IrCl_6^{3-}$ formed which displays a noticeable ($\epsilon=2000$ M^{-1} cm^{-1}) absorption at 248 nm (for details, see Section 3.6).

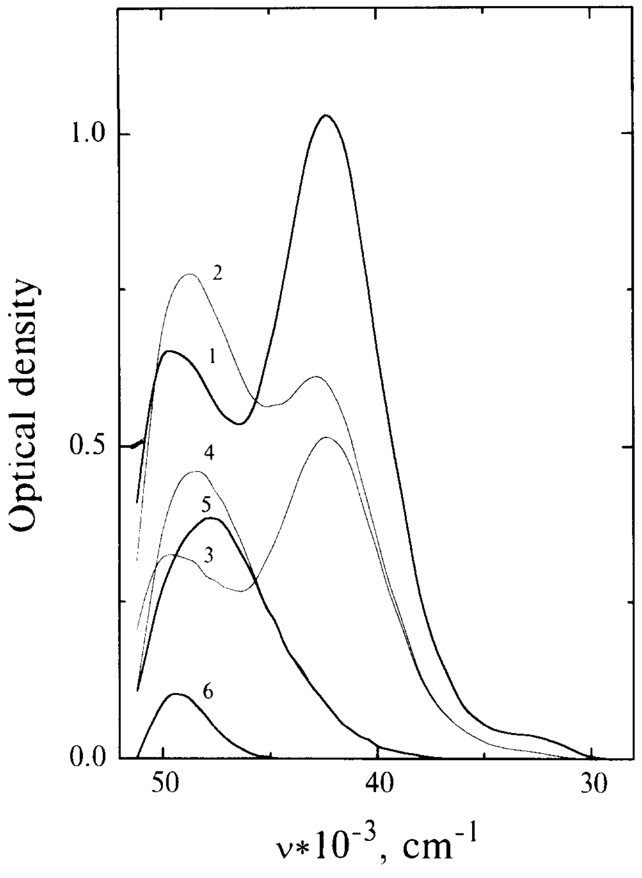

Fig. 4. Reconstruction of the spectrum of the $IrCl_5(CH_3OH)^{2-}$ complex formed from $IrCl_6{}^{2-}$ photolysis at 248 nm: 1, $IrCl_6{}^{2-}$ spectrum (5.3×10^{-4} M in a cuvette 0.086 cm thick); 2, spectrum after 170 pulses (3.7 mJ per pulse); 3, spectrum of remaining $IrCl_6{}^{2-}$ (50%); 4, difference between spectra (2) and (3); 5, $IrCl_6{}^{3-}$ spectrum restored by the tail of curve 4 (33% of the initial complex concentration); 6, difference between spectra (4) and (5) (the $IrCl_5(CH_3OH)^{2-}$ spectrum).

3.5. Dark reactions occurring after $IrCl_6{}^{2-}$ photolysis

The intensity of the absorption band of $IrCl_6{}^{3-}$, arising from photolysis, decreases rather slowly (tens of minutes). The rate of disappearance depends on the concentration of O_2. Fig. 6(a) shows the changes in the $IrCl_6{}^{3-}$ spectrum resulting from $IrCl_6{}^{2-}$ photolysis in argon-saturated solutions. As no absorption is observed in the visible region, there is no regeneration of Ir(IV). It is probable that $IrCl_6{}^{3-}$ disappears by solvation (Eq. (14))

$$IrCl_6{}^{3-} + CH_3OH \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} IrCl_5(CH_3OH)^{2-} + Cl^- \qquad (14)$$

Fig. 6(b) (curve 1) displays the kinetics of the decrease in $IrCl_6{}^{3-}$ optical density at 209 nm. Curve 2 in this figure is calculated within the framework of reaction (14).

The initial slope of the kinetic curve can be used to estimate the magnitude of $k_{14}=2.5\times10^{-4}$ s^{-1}. The magnitude of x_0/x_∞ (where x_0 is the initial concentration of $IrCl_6{}^{3-}$ and x_∞ is its concentration at infinity) is used to determine the ratio $k_{14}/k_{-14}=8\times10^{-5}$ M and $k_{-14}=3.125$ M^{-1} s^{-1}. These parameters testify that a Cl^- concentration in the region 1–10^{-2} M would significantly shift equilibrium (14) to the left and fully break the decrease in the intensity of the $IrCl_6{}^{3-}$ band. However, the addition of 1.6 M LiCl (when the dissociation constant of LiCl in methanol is 0.0158 M [20], this gives a free Cl^- concentration of 0.15 M) slows down the rate of $IrCl_6{}^{3-}$ disappearance by about a factor of four and fails to stop the reaction (curve 3, Fig. 6(b)). Thus the process of $IrCl_6{}^{3-}$ solvation must be accompanied by a complementary reaction of disappearance. The nature of this reaction may be conditioned by the existence of the products of methanol decomposition photosensitized by $IrCl_6{}^{2-}$ (e.g. formaldehyde).

It must be emphasized that the data for the solvation of the $IrCl_6{}^{3-}$ complex differ markedly from the data for aquation. The rate constant of $IrCl_6{}^{3-}$ aquation

$$IrCl_6{}^{3-} + H_2O \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} IrCl_5(H_2O)^{2-} + Cl^- \qquad (15)$$

determined in Ref. [24], is 3.4×10^{-5} s^{-1} and the equilibrium constant k_{15}/k_{-15} is 25 M (25 °C). Ref. [23] gives values of $k_{15}=9.4\times10^{-6}$ s^{-1} (25 °C) and $k_{15}/k_{-15}=6$ M

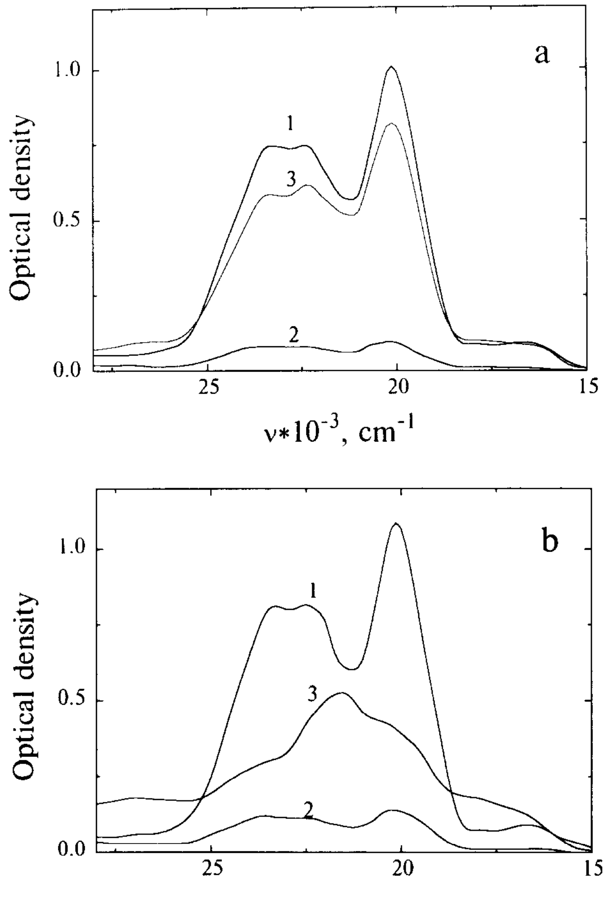

Fig. 5. Oxidation of $IrCl_6{}^{2-}$ photolysis products by molecular chlorine in methanol: (a) photolysis at 308 nm (1, initial spectrum of $IrCl_6{}^{2-}$; 2, spectrum after irradiation; 3, spectrum of irradiated solution bubbled with Cl_2 for 6 s); (b) photolysis at 248 nm (1, initial spectrum; 2, spectrum after irradiation; 3, spectrum of irradiated solution bubbled with Cl_2 for 6 s).

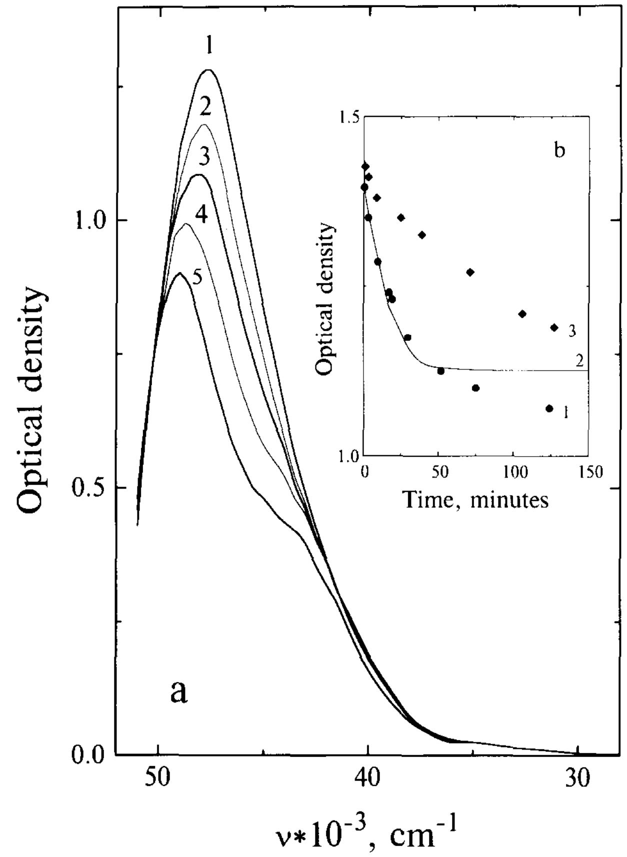

Fig. 6. Dark reactions after $IrCl_6^{2-}$ photolysis (308 nm) in oxygen-free methanol solution (initial $IrCl_6^{2-}$ concentration, 6.4×10^{-4} M; cuvette thickness, 0.086 cm). (a) Change in the optical spectrum of $IrCl_6^{3-}$: 1, initial spectrum; 2, spectrum after irradiation; 3–5, 24, 43, 83 and 224 min in the dark respectively. (b) Time dependence of the optical density change at 209.4 nm: 1, experimental kinetic curve; 2, calculations within the framework of Eq. (14) with parameters $K_{14}=8\times10^{-5}$ M, $k_{14}=2.5\times10^{-4}$ s^{-1} (extinction coefficients of $IrCl_6^{3-}$ and $IrCl_5(CH_3OH)^{2-}$, 25 640 and 8300 M^{-1} cm^{-1} respectively); 3, experimental kinetic curve after addition of 1.6 M LiCl.

(50 °C). The higher value of the equilibrium constant for water solution is probably connected with the more powerful coordination ability of water compared with methanol.

The existence of oxygen in solution leads to the oxidation of Ir(III) to Ir(IV) (recorded by the appearance of the $IrCl_6^{2-}$ bands in the visible spectral region, Fig. 7(a)) in addition to the above-mentioned reactions. The rise of the additional band displayed at 450 nm (due to the $IrCl_5(CH_3OH)^-$ complex) indicates that the solvated complex of trivalent iridium, $IrCl_5(CH_3OH)^{2-}$, is also oxidized. The initial rate of increase in $IrCl_6^{2-}$ concentration is proportional to the $IrCl_6^{3-}$ content (Fig. 7(b)).

However, it seems probable that the oxidation of Ir(III) to Ir(IV) is not a result of the immediate reaction with oxygen. This is evident from the fact that the $IrCl_6^{3-}$ complex, photochemically obtained in oxygen-free solution, is completely unoxidizable during subsequent bubbling with oxygen. Oxidation is assumed to be due to the reaction of Ir(III) with the products of methanol decomposition, photosensitized by $IrCl_6^{2-}$, in the presence of oxygen, most probably peroxides [25]. Formaldehyde, also formed as a result of methanol photodecomposition, should be excluded from the list of possible oxidizers, because the bubbling of photolysed solutions by formaldehyde does not lead to the oxidation of Ir(III) to Ir(IV) (on the contrary, in alcohol solutions, formaldehyde reduces Ir(IV) to Ir(III)).

3.6. Photosolvation of the $IrCl_6^{3-}$ complex

It has been assumed (Section 3.4) that the disturbance of the isosbestic point on extended photoirradiation of $IrCl_6^{2-}$ at 248 nm is caused by the secondary photodecomposition of the trivalent iridium complex formed: $IrCl_6^{3-}$. This is supported by the following experiment. An argon-saturated sample was primarily irradiated at 308 nm to transform $IrCl_6^{2-}$ into $IrCl_6^{3-}$. This sample was then irradiated using the light of a KrF laser at 248 nm, falling within the $IrCl_6^{3-}$ absorption band. The spectral changes are the same as those caused by the dark reaction of $IrCl_6^{3-}$ solvation. Therefore it can be assumed that irradiation at 248 nm leads to the photosolvation of $IrCl_6^{3-}$ with a quantum yield of about 0.25. It should be noted that the availability of both thermal and photochemical

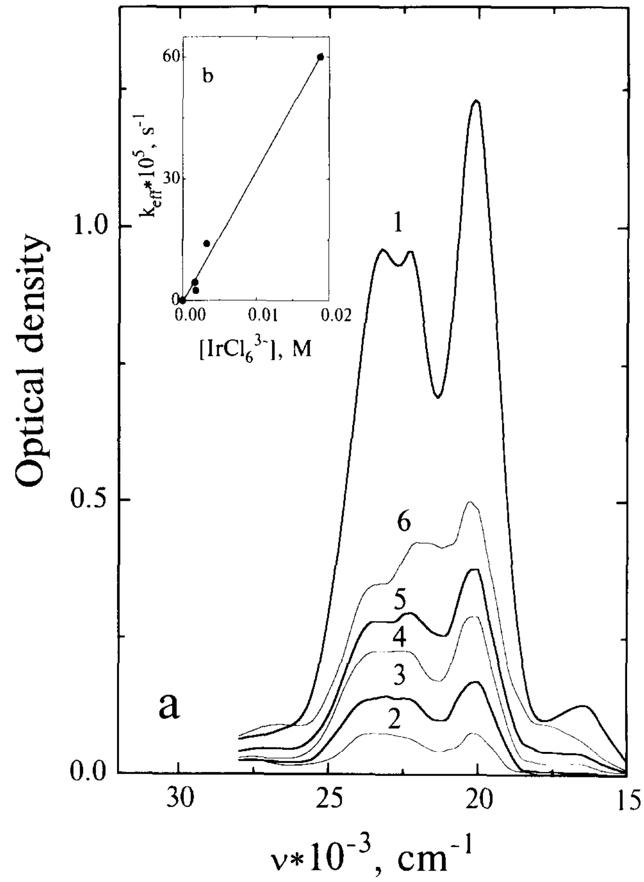

Fig. 7. Dark reactions after $IrCl_6^{2-}$ photolysis (308 nm) in methanol solution with a natural content of oxygen. (a) Change in the optical spectrum in the visible region (1, initial spectrum of $IrCl_6^{2-}$ (3.5×10^{-3} M) in cuvette 0.086 cm thick; 2–6, spectra 0, 12, 31, 57 and 300 min after photolysis). (b) Dependence of the observed rate constant of the reverse appearance of the $IrCl_6^{2-}$ complex on the initial concentration of $IrCl_6^{3-}$.

solvation is also characteristic of the trivalent platinum complex: $PtCl_6^{3-}$ [16].

4. Conclusions

The photochemistry of $IrCl_6^{2-}$ in simple alcohols confirms that electron transfer from the solvent to the excited complex is the main primary photochemical process in similar systems. The photodissociation of the initial complex, with the elimination of a chlorine atom from the coordination sphere, observed during photolysis at 248 nm, is responsible for 30% of the photodecomposed complex. It will be of interest to study this process by the method of laser flash photolysis.

Acknowledgement

The financial support of the Russian Foundation for Fundamental Research is gratefully acknowledged (Research Grant No. 94-03-08933).

References

[1] C.K. Jorgensen, *Mol. Phys.*, 2 (1959) 309.

[2] P. Day and C.K. Jorgensen, *Chem. Phys. Lett.*, *1* (1968) 507.

[3] T.P. Sleight and C.R. Hare, *Inorg. Nucl. Chem. Lett.*, *4* (1968) 165.

[4] L. Moggi, G. Varani, M.F. Manfrin and V. Balzani, *Inorg. Chim. Acta*, *4* (1970) 335.

[5] P.K. Eidem, A.W. Maverick and H.B. Gray, *Inorg. Chim. Acta, 50* (1981) 59.

[6] R.K. Broszkewicz, *J. Chem. Soc., Dalton Trans.*, *17* (1973) 1799.

[7] C.L. Crawford, M.R. Cholani, S.L. Roberts and R.J. Hanrahan, *Radiat. Phys. Chem.*, *40* (1992) 205.

[8] S. Fukuzumi and J.K. Kochi, *Inorg. Chem.*, *19* (1980) 3022.

[9] V.F. Plyusnin, N.M. Bazhin and O.B. Kiseleva, *Zh. Fiz. Khim.*, *54* (1980) 672.

[10] N.M. Bazhin, V.V. Korolev and V.F. Plyusnin, *Khim. Vys. Energ.*, *14* (1980) 255.

[11] N.P. Gritsan, V.F. Plyusnin and N.M. Bazhin, *Teor. Eksp. Khim.*, *22* (1986) 39.

[12] I.V. Khmelinski, V.F. Plyusnin, N.P. Gritsan and N.M. Bazhin, *Zh. Khim. Fiz.*, *4* (1989) 2770.

[13] I.V. Khmelinski, V.F. Plyusnin and V.P. Grivin, *Zh. Fiz. Khim.*, *53* (1989) 2722.

[14] V.P. Grivin, I.V. Khmelinski and V.F. Plyusnin, *J. Photochem. Photobiol. A: Chem.*, *59* (1991) 153.

[15] V.P. Grivin, V.F. Plyusnin, I.V. Khmelinski, N.M. Bazhin, M. Mitewa and P.R. Bontchev, *J. Photochem. Photobiol. A: Chem.*, *51* (1990) 371.

[16] V.P. Grivin, I.V. Khmelinski, V.F. Plyusnin, I.I. Blinov and K.P. Balashev, *J. Photochem. Photobiol. A: Chem.*, *51* (1990) 167.

[17] J. Niiranen, K. Nieminen and H. Lemmetyinen, *J. Photochem. Photobiol. A: Chem.*, *56* (1991) 43.

[18] E.N. Sloth and C.S. Garner, *J. Am. Chem. Soc.*, *77* (1955) 1440.

[19] K.K. Sen Gupta and U. Chatterjee, *J. Inorg. Nucl. Chem.*, *43* (1981) 2491.

[20] B.P. Nikolskii (ed.), *Spravochnik Khimika (Handbook of Chemist)*, Vol. 3, Nauka, Leningrad, 1965, pp. 316–333, 674.

[21] G.E. Adams and R.L. Wilson, *Trans. Faraday Soc.*, *65* (1969) 2981.

[22] D.W. Johnson and G.A. Salmon, *Can. Chem. J.*, *55* (1977) 2030.

[23] I.A. Poulsen and C.S. Garner, *J. Am. Chem. Soc.*, *84* (1962) 2032.

[24] A.J.P. Domingos, A.M.T.S. Domingos and J.M. Peroxito Cabral, *J. Inorg. Nucl. Chem.*, *31* (1969) 2563.

[25] E.T. Denisov, N.I. Mitskevich and V.E. Agabekov, *Mekhanizm Zhidkofaznogo Okisleniya Kislorodsoderzhashchikh Soedinenii (The Mechanism of Liquid Phase Oxidation of Oxygen Containing Compounds)*, Nauka i Tekhnika, Minsk, 1975, p. 334.