Mechanism of $Br_2^{•-}$ and $Cl_2^{•-}$ radical anions formation upon $IrCl_6^{2-}$ photoreduction in methanol solutions containing free Br^- and Cl^- ions

E.M. Glebov [a,*], V.F. Plyusnin [a], V.P. Grivin [a], Yu.V. Ivanov [a], N.V. Tkachenko [b], H. Lemmetyinen [b]

[a] Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russian Federation
[b] Institute of Materials Chemistry, Tampere University of Technology, P.O. Box 589, 33101 Tampere, Finland

Abstract

Laser flash photolysis has been used to study the formation of $X_2^{•-}$ radical ions ($X = Br$ and Cl) upon photoreduction of $IrCl_6^{2-}$ complex in methanol solutions, containing free X^- ions. It has been shown that two channels of halogen atom formation are possible. These are the reactions of X^- ions with either the primary radical cation $CH_3OH^{•+}$ which results from single electron transfer from a methanol molecule to the excited complex or the intermediate, arising from transformation of primary light-excited $IrCl_6^{2-}$ complex.   © 1998 Elsevier Science S.A.

Keywords: $IrCl_6^{2-}$; $Br_2^{•-}$; $Cl_2^{•-}$; Radical ions; Methanol solutions; Laser flash photolysis

1. Introduction

The optical absorption of intermediate dihaloid radical ions $X_2^{•-}$ is often recorded in experiments on flash photolysis of the solutions of halide complexes of transition metal ions, containing a free halide ion [1–9]. However, the mechanism of its formation is so far unclear. The precursor of this particle is the halogen atom (X) which in aqueous solutions may arise upon both the dissociation of Me–X bond and the electron transfer from a free X^- ion to the excited complex. The halogen atom reacts then with a diffusion rate constant with a free X^- ion [10–12], thus resulting in $X_2^{•-}$. It is also assumed that $X_2^{•-}$ radical may directly form in the first coordination sphere of the excited complex and then escape into the bulk [8].

Halogen atoms react rather actively with the molecules of organic compounds. However, $X_2^{•-}$ radical ion also was observed upon the photolysis of halide complexes in organic solvents, containing free X^- ions [7,9,13,14]. Previously, electron transfer from the solvent to the excited complex has been shown to be the primary photochemical process occurring upon the photolysis of many halide transition metal complexes in organic solvents (Cu(II) [15,16], Fe(III) [17,18], Pt(IV) [19,20]). The formation of X atom (and, hence, of

the $X_2^{•-}$) in these solvents may be related to the appearance of a competing channel of electron transfer from a free halide ion, located in the second coordination sphere of the excited complex [13,21]. Such an assumption was made in Ref. [22] to explain the dependence of quantum yield on the concentration of Cl^- ions upon stationary $IrCl_6^{2-}$ photolysis in aqueous solutions. Note that the halogen atom may also result from the reaction of X^- ion with the primary particles that arise after electron transfer from the molecules of organic solvent to the excited complex.

It is worth mentioning that the pulse radiolysis of methanol, containing free halide ions, also gives rise to $X_2^{•-}$ radical ions. However, the processes leading to the formation of halogen atoms are also unclear. It has been assumed that Br and I atoms are formed in the reactions of X^- ions with either the primary radical cation $CH_3OH^{•+}$ [23–25] or with the secondary $CH_3O^•$ radicals [26,27].

In this paper, the mechanism of $Br_2^{•-}$ radical ion formation upon photolysis of methanol solutions of $IrCl_6^{2-}$ complex in the presence of free Br^- ions is considered. The stability of $IrCl_6^{2-}$ allows the variation in the concentration of halide ions that determines a choice of this complex in studying the processes of $X_2^{•-}$ radical ion formation. Besides, unlike many other halide complexes of metal ions, $IrCl_6^{2-}$ has an intensive charge transfer bands in the visible region (495 nm [28]) which is not actually overlapped by the absorption bands of

---

* Corresponding author.

$X_2^{\cdot-}$ radical ions. including the band of $Br_2^{\cdot-}$ radical ion (with its maximum at 360 nm [29], Fig. 1). Below we show that this is the key moment because it allows to determine independently the relative yield of $Br_2^{\cdot-}$ and the quantum yield of the initial complex disappearance. The Br^- ion has been chosen as a partner of $IrCl_6^{2-}$ complex because the bromine atom reacts rather slowly with methanol and the reaction of $Br_2^{\cdot-}$ formation successfully competes with this channel of atom disappearance. The second important fact is the use of laser flash photolysis to determine the changes in the system just after a short light pulse.

The primary photoprocess of $IrCl_6^{2-}$ complex in methanol is the electron transfer from a solvent molecule to the excited complex [30,31]

$$IrCl_6^{2-} \overset{h\nu}{\rightleftarrows} (IrCl_6^{2-})^* \overset{CH_3OH}{\rightarrow} IrCl_6^{3-} + \cdot CH_2OH + H^+ \qquad (1)$$
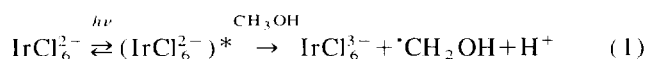
In oxygen-free solutions, $\cdot CH_2OH$ radical reacts with the initial complex

$$\cdot CH_2OH + IrCl_6^{2-} \rightarrow IrCl_6^{3-} + CH_2O + H^+ \qquad (2)$$
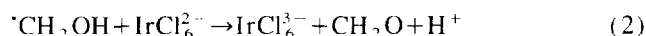
In the presence of oxygen, $\cdot CH_2OH$ radical transforms with a diffusion rate into peroxide radical $\cdot(OO)CH_2OH$ which does not participate in subsequent transformations of iridium complexes. Therefore, most of experiments were performed in the presence of oxygen.

2. Experimental details

$IrCl_6^{2-}$ solutions were prepared using $Na_2IrCl_6 \cdot 6H_2O$ (Aldrich). NaBr and LiCl (Aldrich) were employed as the sources of bromide- and chloride-ions, respectively. Optically pure alcohols (Merck) were used to prepare solutions. The optical absorption spectra were recorded on UNICAM 8735/50 or Specord UV–Vis (Carl Zeiss) spectrophotometers. Stationary photolysis was performed using radiation of a high-pressure mercury lamp with glass filters for the separation of necessary wavelengths. Sometimes, a pulsed XeCl laser (308 nm) was used as a source of light. In this case, the identity of changes in the absorption spectra powdered by lamp and laser irradiation was controlled.

The ionic strength of methanol solutions of NaBr was estimated using the Shedlovsky approximation method [32] for the calculation of thermodynamic dissociation constant K_{NaBr}. Mean activity coefficients of the corresponding ions and concentration dependence of equivalent conductivity were taken from Refs. [33,34]. K_{NaBr} was calculated to be 0.32 M. So, taking into account the values of mean activity coefficients, the degree of NaBr dissociation was found to be about unity at used range of concentrations (0.83 in 1 M solution). The dissociation constant of LiCl in methanol is equal to 0.018 M [35].

A setup for laser flash photolysis [36] consisted of an XeCl excimer laser (308 nm, 20 ns) for excitation, xenon arc lamp with a monochromator as a source of probing light and mono-
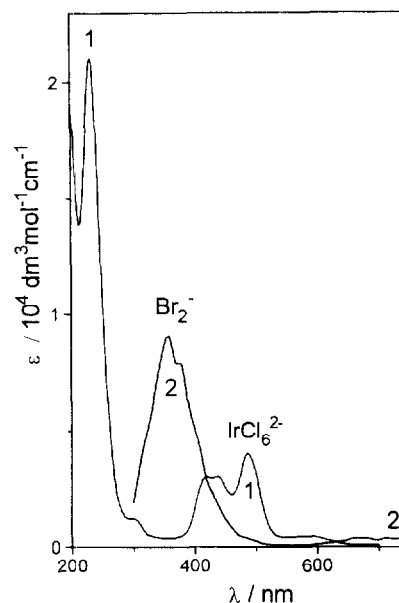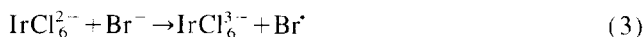

Fig. 1. Optical absorption spectrum of $IrCl_6^{2-}$ complex (curve 1) according to Ref. [28], and of $Br_2^{\cdot-}$ radical ion (curve 2) according to Ref. [12].

chromator with photomultiplier in a measuring channel. The signal, produced by photomultiplier was recorded using a digital Tektronix 7912AD oscillograph, connected to an IBM computer. In some experiments we used a similar (in parameters) setup for laser flash photolysis, described in Ref. [20].

3. Results and discussion

3.1. Dark reaction of $IrCl_6^{2}$ with bromide ions in methanol

The existence of a free Br^- ion in methanol solution of $IrCl_6^{2-}$ leads to a dark reaction of its reduction resulting in the appearance of a new UV absorption band with a maximum at 263 nm (Fig. 2) which belongs to the Br_3^- ion. The latter results from the following reaction sequence

$$IrCl_6^{2-} + Br^- \rightarrow IrCl_6^{3-} + Br^\cdot \qquad (3)$$

$$Br^\cdot + Br^- \rightarrow Br_2^{\cdot-} \qquad (4)$$

$$Br_2^{\cdot-} + Br_2^{\cdot-} \rightarrow Br^- + Br_3^- \qquad (5)$$

In aqueous solutions, Br_3^- ion has the absorption band with a maximum at 270 nm and the extinction coefficient of 36 000 $dm^3 \ mol^{-1} \ cm^{-1}$ [37]. Two $IrCl_6^{2-}$ complexes are used to form one Br_3^- ion. Therefore the effective extinction coefficient of the arising band must be 18 000 $dm^3 \ mol^{-1} \ cm^{-1}$. The experimental value of the effective extinction coefficient is about 13 500 $dm^3 \ mol^{-1} \ cm^{-1}$ which is explained by the disappearance of a part of Br atoms and of $Br_2^{\cdot-}$ radicals in reactions with methanol [12,24]. The shift of band maximum from 270 to 263 nm is caused by the use of water instead of methanol as a solvent.
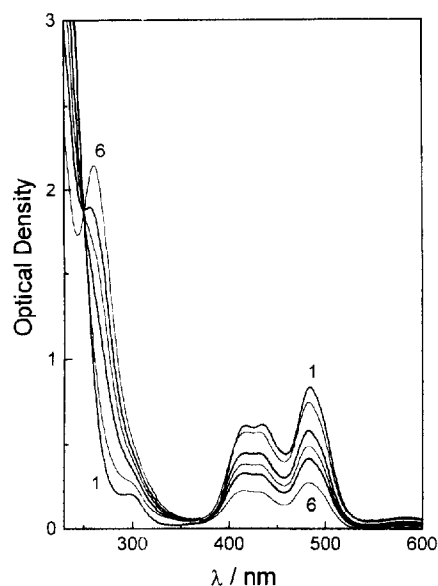
Fig. 2. Dark reaction between $IrCl_6^{2-}$ and NaBr in methanol. Change in the optical absorption spectrum (cuvette thickness, 1 cm; $[IrCl_6^{2-}]$ = 2.3×10^{-4} M; [NaBr] = 0.5 M; T = 295 K). Curve 1—initial spectrum of $IrCl_6^{2-}$; curves 2–6 denote 1, 6, 11, 16, 31 min after addition of NaBr respectively.

The appearance of Br_3^- ion may distort the results on flash photolysis because it has absorption at the wavelength of laser radiation (308 nm) and is subjected to photodissociation into Br atom and $Br_2^{\cdot-}$ radical ion [38]. The rate constant of reaction (3) is found to be $(1.1 \pm 0.1) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. Therefore, at 293 K, a characteristic reaction time at $[Br^-]$ = 0.5 M, is more than 30 min and reaches four hours with temperature drops to 280 K. The time between the preparation of the sample and the beginning of experiment on flash photolysis was not greater than 1 min. So, the dark reaction did not disturb the results of photochemical experiments.

3.2. Laser flash photolysis of $IrCl_6^{2-}$ in methanol solutions with the presence of free Br^- ions

Just after the laser pulse, in $IrCl_6^{2-}$ methanol solutions, containing free bromide ions, the intermediate absorption bands with maxima at 365 and 670 nm appear (Fig. 3). These bands belong to $Br_2^{\cdot-}$ radical ion (ε = 9000 and 200 dm^3 mol^{-1} cm^{-1}, respectively [29]). The spectrum of a decrease in the optical density after complete disappearance of $Br_2^{\cdot-}$ absorption coincides with that of $IrCl_6^{2-}$ complex and its amplitude depends linearly on the laser pulse intensity.

The main process of $Br_2^{\cdot-}$ radical ion disappearance is determined by the reaction of disproportionation (5) because the effective rate constant depends linearly on the initial absorption amplitude, i.e. on the initial radical concentration (Fig. 4a). The rate constant, determined using the slope of this dependence is found to be $(5.0 \pm 0.1) \times 10^8$ dm^3 mol^{-1} s^{-1} (295 K) which is close to the published data (k_5 = $(5.4 \pm 0.2) \times 10^8$ dm^3 mol^{-1} s^{-1} in the mixture of
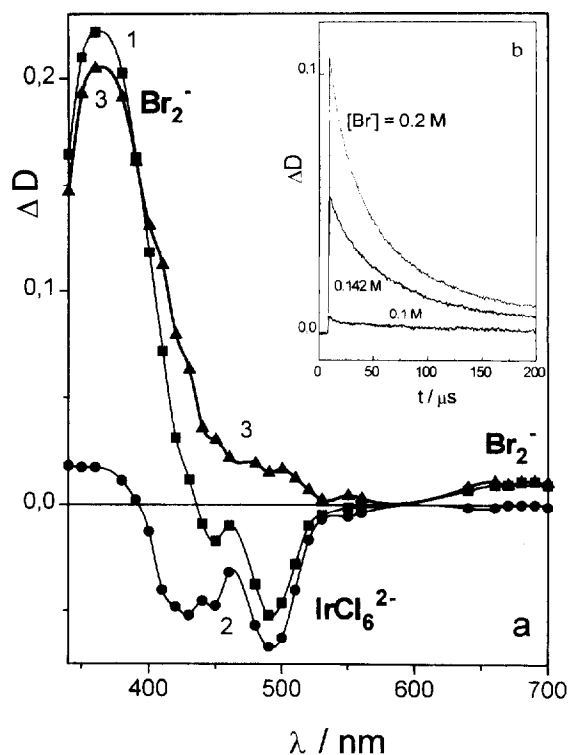

Fig. 3. Laser flash photolysis of $IrCl_6^{2-}$ in methanol with 0.2 M of NaBr (cuvette thickness, 1 cm; $[IrCl_6^{2-}]$ = 2.2×10^{-4} M). (a) Changes in the optical density: just after a laser pulse (curve 1); 180 μs after laser pulse (curve 2); difference between spectra (1) and (2) (curve 3)—$Br_2^{\cdot-}$ spectrum. (b) Kinetic curve of $Br_2^{\cdot-}$ radical-ion disappearance (recording at 360 nm).

methanol with diethyl ether [17]). The formation of Br_3^- ion in reaction (5) is confirmed by the appearance of absorption band (λ_{max} = 263 nm) of this ion upon the stationary photolysis of $IrCl_6^{2-}$ in the presence of Br^- (Fig. 4b).

The kinetics of $Br_2^{\cdot-}$ disproportionation has been studied in methanol solutions containing 0.082–0.25 M NaBr. So, the ionic strength of the solution was changed in the range of 0.08–0.23 (at lower concentration of salt the $Br_2^{\cdot-}$ doesn't occur). The effect of ionic strength on the rate constant of ionic reaction has been taken into account using the Brönsted–Bjerrum theory combined with the extended Debye–Huckel theory (Eq. (6) [40]):

$$f = \log \frac{k_\mu}{k_0} = \alpha \sqrt{\mu} \left\{ \frac{(Z_a + Z_b)^2}{1 + d_{act} \beta \sqrt{\mu}} - \frac{Z_a^2}{1 + d_a \beta \sqrt{\mu}} - \frac{Z_b^2}{1 + d_b \beta \sqrt{\mu}} \right\} \quad (6)$$

where d_a, d_b and d_{act} are the mean effective diameters (in Angstrom) of reacting ions and activated complex respectively; Z_a and Z_b are the charges of ions; μ is the ionic strength; α = 1.825×10^6 $(\varepsilon T)^{-3/2}$; β = $5.03 \times 10^9 (\varepsilon T)^{-1/2}$; ε is the dielectric permeability of the medium.

The results of the calculation of the ionic strength on the rate constant of the reaction (5) (k_5), using Eq. (6) with
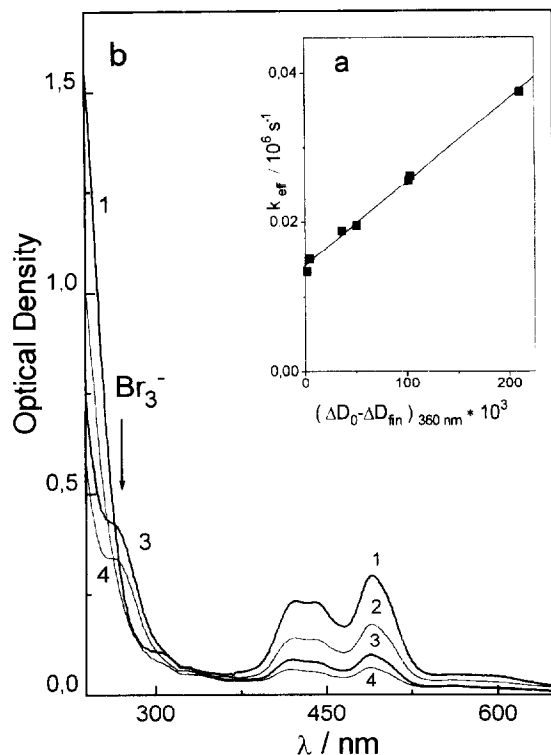
Fig. 4. Disappearance of $Br_2^{\bullet-}$ radical ions and appearance of Br_3^- ions upon $IrCl_6^{2-}$ photolysis (308 nm, XeCl excimer laser) in methanol with addition of NaBr (cuvette thickness, 1 cm; $T = 295$ K). (a) Dependence of the effective initial first-order rate constant of $Br_2^{\bullet-}$ disappearance on its initial optical density (360 nm) upon laser flash photolysis. (b) Change in the optical absorption spectrum due to laser irradiation (measured in a spectrophotometer): $[IrCl_6^{2-}] = 8 \times 10^{-5}$ M; $[NaBr] = 0.2$ M. Curves 1–4 denote 0, 50, 150, 500 laser pulses.

Fig. 5. Ionic strength effect on the rate constants of the reactions between ions. Calculated using Eq. (6). Curve 1—$Br_2^{\bullet-} + Br_2^{\bullet-}$ (reaction (5), with parameters: $d_a = d_b = 6.7$ A, $d_{act} = 2d_a$); curve 2— $[IrCl_6^{3-}...CH_3OH^{+\bullet}]^{2-} + Br^-$ (reaction (12a), with parameters: $d_a = 12.7$ A, $d_b = 3.9$ A, $d_{act} = 15.1$ A); curve 3—$(IrCl_6^{2-})^{*\#} + Br^-$ (see reaction (20), parameters: $d_a = 8.4$ A, $d_b = 3.9$ A, $d_{act} = 12.3$ A).

parameters $d_a = d_b = 6.7$ A [41], $d_{act} = 2d_a$ are shown on Fig. 5 (curve 1). When μ is in the range of 0.08–0.23, the change of the rate constant is not more that 20%, that could be included to the experimental error of k_5 ($k_5 = (5.0 \pm 0.5) \times 10^8$ M^{-1} c^{-1}). Extrapolation to zero ionic strength, according to Fig. 5 gives the value of $k_5^0 = 1 \times 10^8$ dm^3 mol^{-1} s^{-1}. In water solutions the rate constant of $Br_2^{-\bullet}$ disproportionation is 4–6-fold higher (at comparable ionic strength) [39], which is assigned to the influence of dielectric permeability of solvent on the reaction of the equally charged particles.

The intercept of a straight line in Fig. 4a is determined by the reaction of $Br_2^{\bullet-}$ radical ion with methanol. The rate constant of this reaction is $k = (5.8 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1} which substantially differs from the value of 4.4×10^3 dm^3 mol^{-1} s^{-1} measured in Ref. [24] by the method of pulse radiolysis. This difference is, probably, due to the fact that the authors of Ref. [24] neglected the possibility of $Br_2^{\bullet-}$ radical ions recombination.

A relative yield of $Br_2^{\bullet-}$ radical ion, depending on Br^- ion concentration in methanol (having regard to the degree of dissociation of NaBr), is shown in Fig. 6b. It is determined by a change in the optical density just after laser pulse at 360
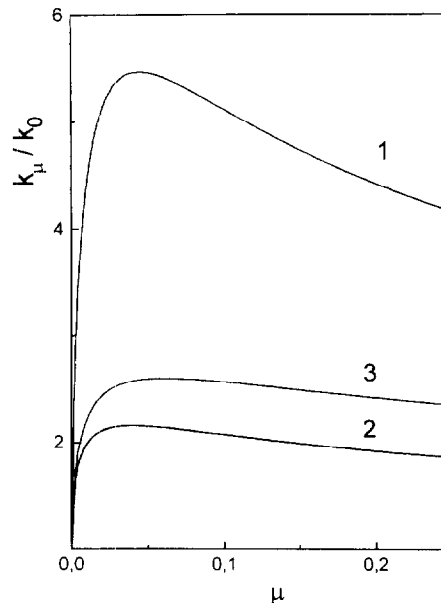
and 495 nm (the maxima of the absorption bands of $Br_2^{\bullet-}$ and initial $IrCl_6^{2-}$ complex, Fig. 3a). Note that a relative yield of $Br_2^{\bullet-}$ has the S-type dependence on $[Br^-]$ (Fig. 6c). When the Br^- concentrations is lower than 0.08 M, this radical ion does not actually form. The bromine atom is the $Br_2^{\bullet-}$ radical ion precursor and the S-type dependence of the relative $Br_2^{\bullet-}$ yield is assigned to the fact that the bromine atom arises near the $IrCl_6^{2-}$ complex. The Onzager radius ($R_0 = 2e^2/4\pi\varepsilon_0\varepsilon kT$) for the $IrCl_6^{2-}$-Br^- pair in methanol is 34 A. Therefore, Br^- ion may appear near the complex only with increasing ionic strength μ (actually, NaBr concentration) when the counter-ion screening decreases the Coulomb repulsion and the radius of ionic atmosphere $R_i = (\varepsilon_0\varepsilon kT/e^2\mu)^{1/2}$ tends to the total radius of partners (≈ 6 A).

To check the connection between the S-type dependence of the relative $Br_2^{\bullet-}$ yield and the ionic strength of the solvent, we have performed experiments in methanol solution of $IrCl_6^{2-}$ with addition of 1 M LiCl which, for the dissociation constant of 0.0158 M [35], gives the ionic strength of 0.11. The photolysis of this solution without NaBr does not result in a signal of intermediate absorption in the region of 360 nm (which may be assigned to the $Cl_2^{\bullet-}$ radical ion [10]). Adding 0.05 M NaBr to the solution results in the appearance of the $Br_2^{\bullet-}$ signal. In the absence of LiCl the absorption of $Br_2^{\bullet-}$ at this concentration of NaBr is not recorded.

Fig. 6a shows the dependence of the quantum yield of $IrCl_6^{2-}$ disappearance on the Br^- content in solution. It is observed to increase by not more than 5% in the studied concentration range of Br^- ion (0–1 M).
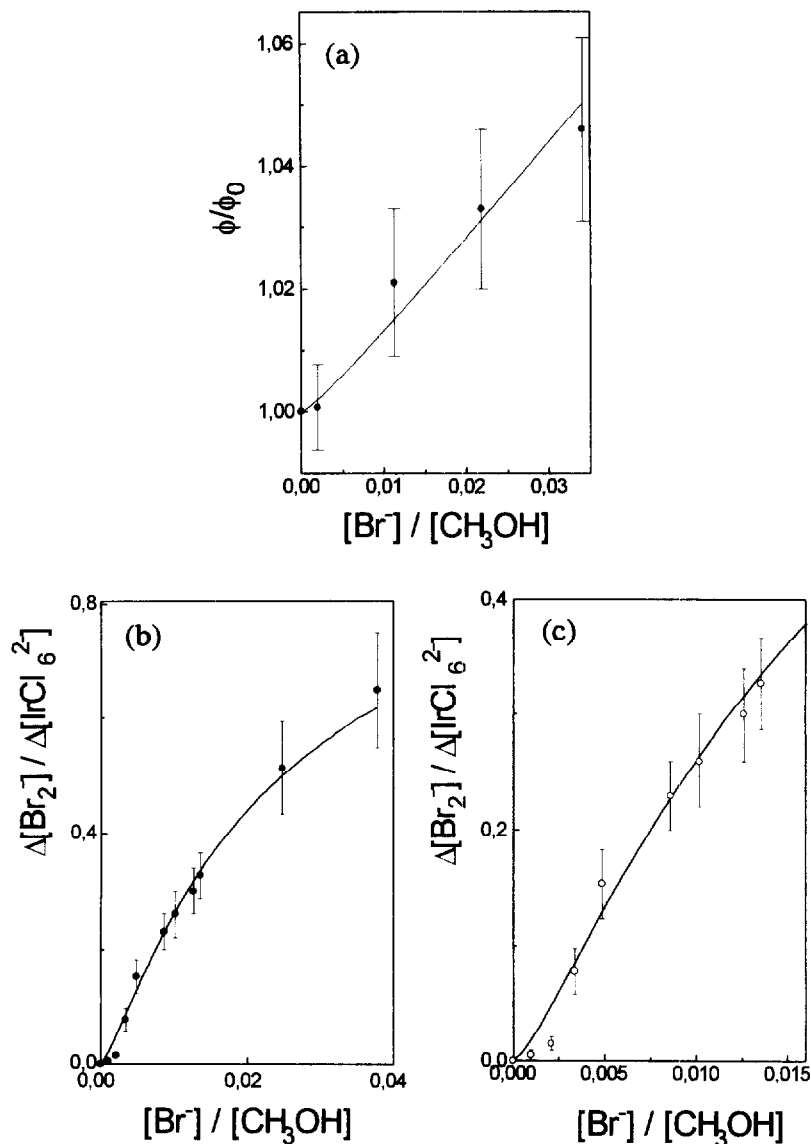
Fig. 6. Laser flash photolysis of $IrCl_6^{2-}$ in methanol with addition of NaBr. (a) Dependence of a relative quantum yield of $IrCl_6^{2-}$ disappearance on Br^- ions concentration: experimental points and approximation within the framework of Eq. (14) with parameters $\varphi_0 = 0.1$, $\alpha_0 = 1.8$ (factor f is calculated from Eq. (6) with parameters $d_a = 12.7$ A, $d_b = 3.9$ A, $d_{act} = 15.1$ A). (b) Dependence of Br_2^{--} relative yield on relative concentration of bromine ions $[Br^-]/[CH_3OH]$: experimental points and approximation within the framework of Eq. (17b) with parameters $\beta = 1 \times 10^4$; $\gamma_0 = 42$ (factor f is calculated like in the previous case). (c) Initial part of (b).

3.3. Origin of processes, producing a bromine atom

A bromine atom may result from a direct outersphere electron transfer from a free Br^- ion to the excited $IrCl_6^{2-}$ complex

$$IrCl_6^{2-} \xrightarrow{h\nu} (IrCl_6^{2-})^* \xrightarrow{Br^-} IrCl_6^{3-} + Br^\bullet \qquad (7)$$
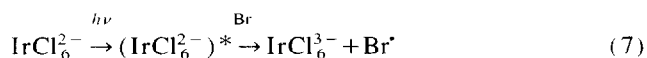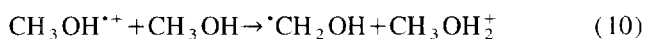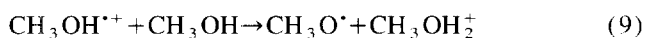
Another mechanism of bromine atom formation may be determined by the oxidation of bromide ion by one of the primary intermediates, arising in the early stages after the electron transfer from an alcohol molecule to the light-excited $IrCl_6^{2-}$ complex. It is known that one of the primary particles upon radiolysis of liquid methanol is $CH_3OH^{\bullet+}$ radical cation

[26,27] which can also appear upon $IrCl_6^{2-}$ complex photoreduction

$$IrCl_6^{2-} \xrightarrow[CH_3OH]{h\nu} (IrCl_6^{2-})^* \rightarrow IrCl_6^{3-} + CH_3OH^{\bullet+} \qquad (8)$$
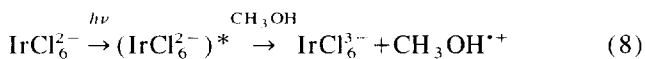
The primary $CH_3OH^{\bullet+}$ radical cation transfer proton to methanol molecule, transforming thus into either $CH_3O^\bullet$ or $^\bullet CH_2OH$ radicals [42]

$$CH_3OH^{\bullet+} + CH_3OH \rightarrow CH_3O^\bullet + CH_3OH_2^+ \qquad (9)$$

$$CH_3OH^{\bullet+} + CH_3OH \rightarrow {^\bullet}CH_2OH + CH_3OH_2^+ \qquad (10)$$

Due to reaction with methanol, the methoxy radical gives the hydroxymethyl radical

$$CH_3O^\bullet + CH_3OH \rightarrow {^\bullet}CH_2OH + CH_3OH \qquad (11)$$
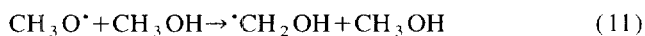
$CH_3OH^{\cdot+}$ radical cation and $CH_3O^{\cdot}$ radical display the oxidative properties and their reactions with Br^- ion may be an alternative source of bromine atoms

$$CH_3OH^{\cdot+}+Br^-\rightarrow CH_3OH+Br^{\cdot} \tag{12}$$

$$CH_3O^{\cdot}+Br^-\rightarrow CH_3O^-+Br^{\cdot} \tag{13}$$
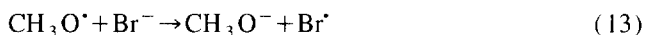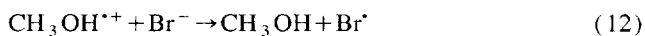
3.3.1. Direct electron transfer from Br^- ion to excited complex

Upon direct electron transfer, the quantum yield of $IrCl_6^{2-}$ disappearance is determined by competition of various channels of the relaxation of electron excitation of the complex

$$\varphi=\frac{k_1[CH_3OH]+k_2[Br^-]}{k_0+k_1[CH_3OH]+k_2[Br^-]} \tag{14}$$

$$=\varphi_0\frac{1+10^f\alpha_0x}{1+\varphi_0 10^f\alpha_0 x},$$

where k_0, k_1 and k_2 are the rate constants of radiationless transition into the ground state and of electron transfer from solvent molecule and Br^- ion to $(IrCl_6^{2-})^*$; $k_2/k_1=10^f\times\alpha_0$; $\alpha_0=k_2/k_1$ is the ratio of the rate constants of electron transfer at zero ionic strength; f is a function of ionic strength determined by Eq. (6); $x=[Br^-]/[CH_3OH]$; and $\varphi_0=k_1[CH_3OH]/(k_0+k_1[CH_3OH])$ is the initial quantum yield for solutions without Br^-. According to Ref. [30], $\varphi_0=0.1$.

A relative yield of $Br_2^{\cdot-}$ radical-ions is determined by the product of the probability of Br atom appearance by the probability of its reaction with Br^-. With allowance made for the ionic strength of the solution, it is determined by Eq. (15)

$$\frac{\Delta[Br_2^{\cdot-}]}{\Delta[IrCl_6^{2-}]}=\frac{10^f\alpha_0x}{1+10^f\alpha_0x}\times\frac{\beta x}{1+\beta x}, \tag{15}$$

where $\beta=k_{Br^-}/k_{CH_3OH}$ is the ratio of the rate constants of the reaction of Br atom with both Br^- ion and methanol. The reaction of a bromine atom with Br^- proceeds with almost diffusion rate constant ($k_{Br^-}=1.6\times10^{10}$ dm^3 mol^{-1} s^{-1} in acetonitrile [12], 9×10^9 dm^3 mol^{-1} s^{-1} in water [11]). The reaction of Br atom with methanol is much slower ($k_{CH_3OH}=0.93\times10^6$ dm^3 mol^{-1} s^{-1} [12]) which determines the efficiency of Br^- ion as a trap of Br atom ($\beta=k_{Br^-}/k_{CH_3OH}\approx10^4$). When $\beta\approx10^4$, the factor $\beta x/(1+\beta x)$ in Eq. (14) is close to unity already at $x>10^{-3}$, i.e. for Br^- concentrations of greater than 0.024 M.

Thus, in the case of direct electron transfer from Br^- ion to excited complex, the concentration dependencies of both the quantum yield and relative $Br_2^{\cdot-}$ radical ion yield must be actually determined by the only parameter α_0. The values of parameters $d_a=8.4$ A (diameter of the $IrCl_6^{2-}$ ion [43]), $d_b=3.9$ A (diameter of the Br^- ion [43]), and $d_{act}=d_a+d_b$ allow one to calculate the f factor (Eq. (6)) for different concentrations of Br^- and, then, to use it in Eq. (15). The experimental values of relative yield for Br^- concentrations greater than 0.1 M fit in the curve, determined by Eq. (15)

with $\alpha_0^{(Br)}=45\pm4$. The quantum yield of $IrCl_6^{2-}$ disappearance, determined 50 ns after laser pulse (Fig. 6a), demonstrates only a weak dependence on Br^- concentration ($\alpha_0^{(\varphi)}\approx1.8\pm0.3$). Thus, the model of direct electron transfer disagrees with the concentration dependencies of the quantum yield of $IrCl_6^{2-}$ disappearance and of the relative yield of $Br_2^{\cdot-}$. The contribution of the direct electron transfer into the general process of Br atom appearance cannot exceed 4% ($\alpha_\varphi^{(0)}/\alpha_{Br}^{(0)}=1.8/45=0.04$).

3.3.2. Bromine atom appearance in the reaction of intermediates with Br^-

Consider now the possibility of bromine atom appearance in the reaction with one of the primary intermediates of photolysis (reactions (12) or (13)). In this case, the quantum yield of $IrCl_6^{2-}$ disappearance must be completely independent of Br^- concentration which is in fair agreement with the experimental data (Fig. 6a). The relative yield of bromine atom, in the case of the reaction of the $CH_3O^{\cdot}$ radical, is equal to

$$\frac{\Delta[Br^{\cdot}]}{\Delta[IrCl_6^{2-}]}=\frac{\gamma x}{1+\gamma x}, \tag{16}$$

where $\gamma=k_{13}/k_{11}$ is the ratio of the rate constants of the reactions of $CH_3O^{\cdot}$ radical with Br^- ion and methanol, respectively. If the reacting particle is the $CH_3OH^{+\cdot}$ radical cation, the value of $\gamma=k_{12}/(k_9+k_{10})$ would be the function of the ionic strength: $\gamma=\gamma_0\times10^f$, similar to Eqs. (14) and (15).

If the Br^- ion reacts with the metoxy radical, the relative yield of $Br_2^{\cdot-}$ radical ion obeys the equation

$$\frac{\Delta[Br_2^{\cdot-}]}{\Delta[IrCl_6^{2-}]}=\frac{\gamma x}{1+\gamma x}\times\frac{\beta x}{1+\beta x}. \tag{17a}$$

In the case of Br^- reaction with $CH_3OH^{+\cdot}$, the relative yield of $Br_2^{\cdot-}$ is equal to

$$\frac{\Delta[Br_2^{\cdot-}]}{\Delta[IrCl_6^{2-}]}=\frac{10^f\gamma_0x}{1+10^f\gamma_0x}\times\frac{\beta x}{1+\beta x}. \tag{17b}$$

We consider the probability of the oxidation of bromide ion by the metoxy radical. In Refs. [44–46] using the method of spin traps, it has been shown that upon radiolysis of liquid methanol $CH_3O^{\cdot}$ radical is the primary product after radical-cation, i.e. compared to the gas phase, only reaction (9) is realized. The $^{\cdot}CH_2OH$ radical results from the reaction of methoxy radical with methanol (reaction (11)). The rate constant of this reaction is not large ($k_{11}=2.6\times10^5$ dm^3 mol^{-1} s^{-1} [26]) and the characteristic lifetime of methoxy radical in this case is about 160 ns, which allows the effective competition of bromide ions with alcohol molecules for $CH_3O^{\cdot}$ radical (reaction (13)).

Eq. (17a) with $\gamma=35$ adequately describes the experimental data when $[Br^-]>0.12$ M. In this case, if $k_{15}=2.6\times10^5$ dm^3 mol^{-1} s^{-1}, the rate constant of the reaction between $CH_3O^{\cdot}$ and Br^- (k_{13}) would be equal to

9.1×10^6 dm^3 mol^{-1} s^{-1}. But the initial S-type character of the experimental curve in principal could not be described in the framework of this model. This is evident from the fact that the rate constant of the reaction between bromide ion and electrically neutral CH$_3$O$^\bullet$ radical occurring in the bulk solution, practically must not depend on the ionic strength.

Additional argument against the hypothesis for the oxidation of bromide ion by metoxy radical is evident from work [26], in which the reactions between CH$_3$O$^\bullet$ and halide ions have been studied by the method of pulse radiolysis. According to this paper, the reaction of Br$^-$ ion (0.1–0.3 M solutions of LiBr have been used) with CH$_3$O$^\bullet$ occurs only with the addition of a fairly large amount of acid (0.01 M HClO$_4$). This is explained by the proposal that the precursor of bromine atom is CH$_3$OBr$^{\bullet-}$ species which is in the equilibrium with either separate Br$^-$ and CH$_3$O$^\bullet$ or separate bromine atom and CH$_3$O$^-$ anion (reaction 18). In the presence of acid this equilibrium shifts towards bromine atom formation.

$$CH_3O^\bullet + Br^- \rightleftarrows CH_3OBr^{\bullet-} \rightleftarrows CH_3O^- + Br^\bullet \qquad (18)$$

A similar effect is observed for the reactions of halide ions with $^\bullet$OH radical in aqueous solutions [47]. In our case, the effective oxidation of bromide ion in neutral medium would not be consistent with mechanism (18) put forward in Ref. [26].

Now we consider an alternative possibility of Br$^-$ oxidation by the primary CH$_3$OH$^{+\bullet}$ radical cation (reaction 12). In this case, the radical cation does not escape into the bulk from the second coordination sphere of IrCl$_6^{3-}$ ion due to Coulomb attraction. So, the oxidation of bromide ion is hampered by the necessary approach of the negatively charged Br$^-$ to [IrCl$_6^{3-}$...CH$_3$OH$^{+\bullet}$]$^{2-}$ complex which also has a common negative charge. The reaction is possible only due to the screening of Coulomb repulsion by counter-ions with increasing ionic strength of solution up to 0.1.
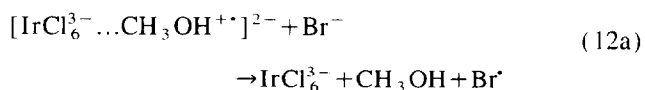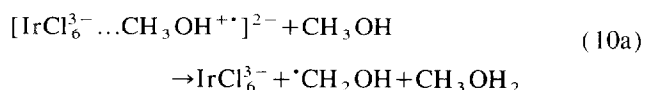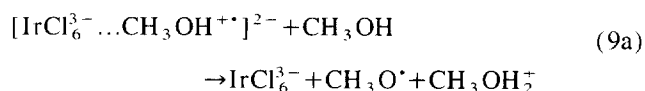
The experimental data on the yield of bromine atom and Br$_2^{\bullet-}$ anion radical in the reaction between the [IrCl$_6^{3-}$...CH$_3$OH$^{+\bullet}$]$^{2-}$ complex and bromide ion were treated using Eqs. (17b) and (6) with the diameters of reacting species $d_a = d(IrCl_6^{3-}) + d(CH_3OH) = 12.7$ A and $d_b = d(Br^-) = 3.9$ A [43]. Two parameters were varied. These were γ_0 (the relation of rate constants of the reactions of [IrCl$_6^{3-}$...CH$_3$OH$^{+\bullet}$]$^{2-}$ with bromide ion and methanol at zero ionic strength) and d_{act} (diameter of the activated complex). In a framework of the least squares method, the best agreement of calculated and experimental curves (Fig. 6b,c) were achieved when $\gamma_0 = 42.4 \pm 28.4$ and $d_{act} = 15.1 \pm 3.3$ A. The optimal value of d_{act} practically coincides with the sum of diameters of the reacting particles. The inclusion of ionic strength according to Eq. (6) in the range of $\mu \sim 0.1$–0.25 gives a practically constant correction factor of about 2 (Curve 2 in Fig. 5). Correspondingly, in our experimental conditions the relation of rate constants $\gamma = k_{12}/(k_9 + k_{10})$ is equal to 21 ± 14.

So, the mechanism based on the oxidation of Br$^-$ by the solvent radical cation agrees with the experiment better than the reaction of methoxy radical. To estimate the probability of the proposed mechanism, it is necessary to discuss the value of rate constant of the reaction between primary radical cation with methanol.

The rate constants of proton transfer from the primary radical cation to methanol molecule (reactions (9) and (10)) have been measured in the gas phase. Their values significantly exceed the gaseous kinetic rate constant: the total rate constant of CH$_3$OH$^{+\bullet}$ radical cation disappearance $(k_9 + k_{10})$ is equal to 6.7×10^{12} dm^3 mol^{-1} s^{-1} according to Ref. [27] and 7.2×10^{11} dm^3 mol^{-1} s^{-1} according to Ref. [48]. The yields of CH$_3$O$^\bullet$ and $^\bullet$CH$_2$OH radicals in the gas phase are almost equal [26]. In the liquid phase these constants were not measured. In Ref. [27] their values have been assumed to be comparable with the gas-phase data. This viewpoint is supported by the authors of most papers on the radiolysis of liquid methanol (see Ref. [42]). In this case, the lifetime of CH$_3$OH$^{+\bullet}$ radical cation is shorter than 100 fs. But the electronic migration of the hole in the solvent, which leads to the reactions of type (12) in presence of free halide ions, can occur still faster than the proton transfer (9, 10). So, the relation of rate constants of similar reactions in concentrated solutions of NaCl in H$_2$O and D$_2$O is equal to 21 and 25, correspondingly [49].

Ref. [24] reports the capture of primary holes by bromide ions studied by pulse radiolysis of liquid methanol with addition of 0.5–2 M NaBr. However, the authors of Ref. [24] can not cite evidence that a bromine atom is formed just in the ionic reaction (12), other than in the ion-molecular reaction (13). The last interpretation would not contradict the results of Ref. [26], because the concentration of Br$^-$ in Ref. [24] was sufficiently higher.

In the model under discussion, contrastingly to pulse radiolysis studies, the oxidation of bromide ion takes place in the vicinity of negatively charged complex, other than in the bulk solution. In order for the oxidation to happen, the bromide ion must effectively compete with methanol molecules for the CH$_3$OH$^{+\bullet}$ radical cation, stabilized in the Coulomb field of IrCl$_6^{3-}$ ion. I.e., instead of Eqs. (9), (10) and (12) one needs to consider the reactions of ion pairs Eqs. (9a), (10a) and (12a).

$$[IrCl_6^{3-}...CH_3OH^{+\bullet}]^{2-} + CH_3OH \qquad (9a)$$
$$\rightarrow IrCl_6^{3-} + CH_3O^\bullet + CH_3OH_2^+$$

$$[IrCl_6^{3-}...CH_3OH^{+\bullet}]^{2-} + CH_3OH \qquad (10a)$$
$$\rightarrow IrCl_6^{3-} + {}^\bullet CH_2OH + CH_3OH_2$$

$$[IrCl_6^{3-}...CH_3OH^{+\bullet}]^{2-} + Br^- \qquad (12a)$$
$$\rightarrow IrCl_6^{3-} + CH_3OH + Br^\bullet$$

The rate constant of reaction (12a) can be estimated using the formula for rate constants of diffusion-controlled ionic reactions [50] having regard to the ionic strength effect:

$$k_{12a} = k_{diff} \times \frac{R_0}{R \, \exp\left(\frac{R_0}{R}\right) - 1} \times 10^J \tag{19}$$

where $R_0 = 34$ A is the Onzager radius of interacting ions, $R = R_1 + R_2$ is the sum of its Van-der-Vaals radii (in our case, $R \approx 8.2$ A), and k_{diff} is the rate constant of diffusion-controlled reaction of neutral species in methanol. Taking $k_{diff} = 7 \times 10^9$ dm^3 mol^{-1} s^{-1} [51] and $10^J \approx 2$ (Curve 2 in Fig. 5), one can calculate $k_{12a} \approx 1 \times 10^9$ dm^3 mol^{-1} s^{-1}. Then, using the experimentally found value of parameter $\gamma \approx 20$, we conclude that the total rate constant of the ionic pair $[IrCl_6^{3-}...CH_3OH^{+\cdot}]^{2-}$ with methanol $(k_{9a} + k_{10a})$ does not exceed 5×10^7 dm^3 mol^{-1} s^{-1}. This is by four orders of magnitude smaller than the minor value of the gas-phase constant $(k_9 + k_{10}) = 7.2 \times 10^{11}$ M^{-1} s^{-1} [48], used for the estimation of the lifetime of a hole in pure methanol. Correspondingly, it turns out that the characteristic lifetime of the discussed ionic pair $[IrCl_6^{3-}...CH_3OH^{+\cdot}]^{2-}$ $(\tau \approx 1/((k_{9a} + k_{10a}) \times [CH_3OH])$ is slightly less than 1 ns.

It should be noted that the occurrence of transient ionic pairs in the pulsed photochemical and radiochemical experiments is well known in literature. E.g. both in pulse radiolysis and flash photolysis of CCl_4, there occurs a transient optical absorption band in the region of 470–500 nm [52]. This band is usually considered to belong to the solvated ionic pair $[CCl_3^+...Cl^-]_{solv}$ [52]. The lifetime of such a pair in CCl_4 is about 14 ns [52], decreasing with the addition of the polar solvent.

So, the mechanism involving the formation of the ionic pair $[IrCl_6^{3-}...CH_3OH^{+\cdot}]^{2-}$ explains all the experimental results.

3.3.3. Oxidation of bromide ion by the secondary excited state of $IrCl_6^{2-}$ complex

There is another formal possibility of explaining all experimental results on the formation of $Br_2^{\cdot-}$ radical ions. Actually, it is an alternative mechanism of direct electron transfer from bromide ion to the light-excited complex considered in Section 3.3.1. Assume that the primary stage of $IrCl_6^{2-}$ complex photoreduction is as follows. Let the excited $(IrCl_6^{2-})^*$ complex, arising from the absorption of light quantum, be either deactivated to the ground state or transformed into another excited state due to monomolecular reaction

$$IrCl_6^{2-} \xleftarrow{k_0} (IrCl_6^{2-})^* \xrightarrow{k_{20}} (IrCl_6^{2-})^{*\#} \tag{20}$$
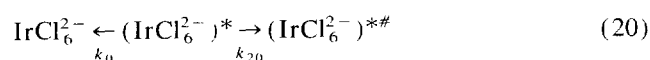
Assume further that the complex in the $(IrCl_6^{2-})^{*\#}$ state reacts, with a probability close to unity, with either a solvent molecule or bromine ion, which leads to photoreduction by electron transfer via reactions (7) or (8). The quantum yield of photoreduction in this case is

$$\varphi = \frac{k_{20}}{k_0 + k_{20}} \tag{21}$$

and is independent of bromine ion concentration which is confirmed experimentally. The relative yield of dihaloid radical ion is defined by Eq. (17b). The effect of ionic strength, corresponding to the considered model of an active center, is shown in Fig. 5 (Curve 3).

The similar schemes of the photolysis of transient metal complexes which develop further the Adamson models of radical pairs [53,54], were repeatedly proposed in the literature. Thus, in Ref. [55], the mechanism of the photolysis of vanadium (V) chloride complexes is represented as the reaction of radical pair, following the absorption of light quantum (reaction 22), with chlorine atom, located in the nearest environment of the complex

$$[V^{5+}Cl^-] \underset{h\nu}{\rightleftarrows} [V^{5+}Cl^-]^* \rightarrow [V^{4+},Cl^0] \tag{22}$$
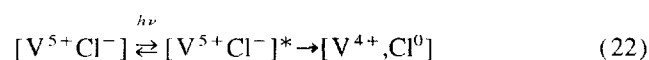
According to Ref. [55], the radical pair is actually the chlorine atom, stabilized in the coordination sphere of vanadium ion.

A similar model may be found in the literature on the photochemistry of $IrCl_6^{2-}$ complex. In Ref. [56], the authors explain the peculiarities of $IrCl_6^{2-}$ photolysis in aqueous solutions with addition of free chloride ions, assuming the existence of two intermediates. The primary intermediate complex $[Ir^{3+}(Cl^-)_5,Cl^0]^{2-}$ is the chlorine atom, stabilized in the coordination sphere of iridium ion. The solvation of this particle gives rise to the secondary intermediate $[Ir^{3+}(Cl^-)_5(H_2O),Cl^0]^{2-}$ which transforms completely into the end product of photoreaction.

The model discussed is used in the literature to explain the experimental results on stationary photolysis. The data on the actual recording of these intermediates are unavailable. In our work, the time resolution of the method does not allow to extract direct information about the process of bromine atom formation. Therefore, we only mention the possibility of the alternative explanation of experimental data without specifying a possible structure of $(IrCl_6^{2-})^{*\#}$ intermediate.

Thus, our results on the formation of $Br_2^{\cdot-}$ radical ions may be explained in terms of the reaction between Br^- ion and either $CH_3OH^{\cdot+}$ radical cation (12) or secondary intermediate complex $(IrCl_6^{2-})^{*\#}$. To choose between these possibilities, it is necessary to perform experiments on picosecond time resolution.

3.4. Flash photolysis of $IrCl_6^{2-}$ methanol solutions in the presence of free Cl^- ions

Laser pulse in methanol solutions of $IrCl_6^{2-}$ complex with a concentration of free Cl^- ions of more than 2 M is followed by formation of intermediate absorption in the form of a band with a maximum at 350 nm (Fig. 7) which belongs to the $Cl_2^{\cdot-}$ radical ion ($\varepsilon = 9600$ dm^3 mol^{-1} cm^{-1} [57]). A relative yield of $Cl_2^{\cdot-}$ even with LiCl concentration of about 7 M does not exceed 10% which is substantially lower than
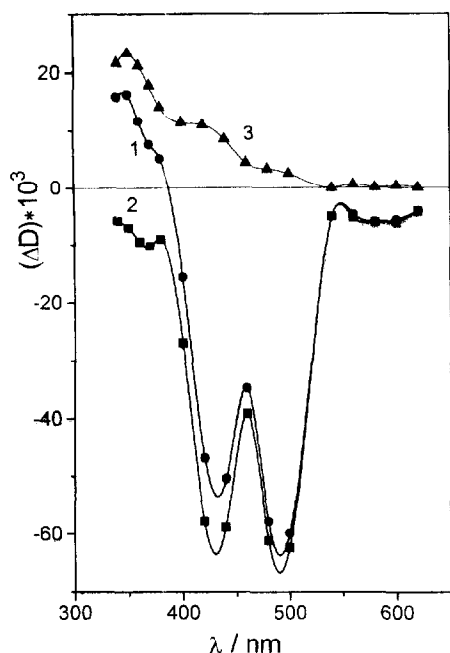
Fig. 7. Laser flash photolysis of $IrCl_6^{2-}$ in methanol with 7 M of LiCl (cuvettee thickness, 1 cm; $|IrCl_6^{2-}| = 6 \times 10^{-4}$ M). Changes in the optical density: just after a laser pulse (curve 1); 90 μs after laser pulse (curve 2); difference between (1) and (2) (curve 3)—$Cl_2^{\cdot-}$ spectrum.

the yield of $Br_2^{\cdot-}$. The quantum yield of photolysis, in this case, within experimental accuracy remains unchanged.

A decrease in the $Cl_2^{\cdot-}$ yield, compared to that of $Br_2^{\cdot-}$, is likely to be related to an increase in the rate constant of chlorine atom with methanol (2.7×10^9 dm^3 mol^{-1} s^{-1} [58]) by more than three orders of magnitude, compared to the reaction for bromine atom. The rate constant of the reaction between a chlorine atom and chlorine ion is diffusion-controlled (1.2×10^{10} dm^3 mol^{-1} s^{-1} [10]). For the appearance of chlorine atom, there are the same possibilities as in the case of the system with free bromide ions. Besides, since $Cl_2^{\cdot-}$ formation is recorded only at large ionic strength of the solution, one cannot exclude the possibility of the reaction of chloride ion with methoxy radical $CH_3O^{\cdot}$. When the latter possibility is realized, one may estimate the rate constant of reaction between $CH_3O^{\cdot}$ radical and Cl^- ion using Eq. (17a). This estimation gives the upper limit of this value is 1.8×10^5 dm^3 mol^{-1} s^{-1}, which is by four orders of magnitude smaller than for iodide ion [26].

4. Conclusions

The formation of dihaloid radical ions $Br_2^{\cdot-}$ and $Cl_2^{\cdot-}$ has been recorded upon photolysis of methanol solutions of $IrCl_6^{2-}$ complex in the presence of free halide ions Br^- and Cl^-. The precursor of $X_2^{\cdot-}$ radical ion is a halogen atom. The main channel of its appearance is the X^- ion oxidation by a species which arises in the early stage after electron transfer from alcohol molecule to the excited complex. This intermediate may be represented by either the solvent radical

cation $CH_3OH^{\cdot+}$ or the secondary excited state of the initial complex.

References

[1] G. Caspari, R.G. Huges, J.F. Endicott, M.Z. Hoffman, J. Am. Chem. Soc. 92 (1970) 6801.
[2] J. Lilie, J. Am. Chem. Soc. 101 (1979) 4419.
[3] P. Natarajan, J.F. Endicott, J. Phys. Chem. 77 (1973) 971.
[4] P. Natarajan, J.F. Endicott, J. Phys. Chem. 77 (1973) 1823.
[5] T.L. Kelly, J.F. Endicott, J. Am. Chem. Soc. 94 (1972) 1797.
[6] A.T. Thornton, G.S. Laurence, J. Chem. Soc. Dalton Trans. 8 (1973) 804.
[7] J. Sykora, I. Giannini, C.F. Diomedi, J. Chem. Soc. Chem. Commun. 5 (1978) 207.
[8] M.E. Langmuir, E. Hayon, J. Phys. Chem. 71 (1967) 3808.
[9] O. Horvath, J. Photochem. Photobiol. A: Chem. 48 (1989) 243.
[10] M. Anbar, J.K. Thomas, J. Phys. Chem. 68 (1964) 3829.
[11] V. Nagarajan, R.W. Fessenden, J. Phys. Chem. 89 (1985) 2330.
[12] J.C. Scaiano, M. Barra, M. Krzywinski, R. Sinta, G. Calabrese, J. Am. Chem. Soc. 115 (1993) 8340.
[13] I.V. Khmelinski, V.F. Plyusnin, V.P. Grivin, Zh. Fiz. Khim. 53 (1989) 2722.
[14] I.V. Khmelinski, V.F. Plyusnin, V.P. Grivin, Izv. AN SSSR, ser. khim., 1988, 1247.
[15] V.F. Plyusnin, N.M. Bazhin, O.B. Kiseleva, Khim. Vys. Energ. 12 (1978) 87.
[16] N.P. Gritsan, V.F. Plyusnin, N.M. Bazhin, Teor. Eksper. Khim. 21 (1986) 39.
[17] I.V. Khmelinski, V.F. Plyusnin, V.P. Grivin, Khim. Vys. Energ. 22 (1988) 239.
[18] I.V. Khmelinski, K.A. Amosov, V.F. Plyusnin, V.P. Grivin, Koord. Khim. 16 (1990) 1373.
[19] V.P. Grivin, I.V. Khmelinski, V.F. Plyusnin, J. Photochem. Photobiol. A: Chem. 51 (1990) 379.
[20] V.P. Grivin, I.V. Khmelinski, V.F. Plyusnin, I.I. Blinov, K.P. Balashev, J. Photochem. Photobiol. A: Chem. 51 (1990) 167.
[21] V.F. Plyusnin, N.M. Bazhin, Khim. Vys. Energ. 15 (1981) 142.
[22] P.K. Eidem, A.W. Mawerick, H.B. Gray, Inorg. Chim. Acta 50 (1981) 59.
[23] T. Sawai, W.H. Hamill, J. Phys. Chem. 74 (1970) 3914.
[24] V.I. Feldman, V.I. Popov, V.N. Belevski, L.T. Bugaenko, V.M. Moralev, Khim. Vys. Energ. 20 (1986) 131.
[25] S.I. Belopushkin, V.N. Belevski, L.T. Bugaenko, Khim. Vys. Energ. 14 (1980) 121.
[26] F. Dainton, I. Janovsky, G.A. Salmon, Proc. R. Soc. Lond. A 327 (1972) 305.
[27] D.H. Ellison, G.A. Salmon, F. Wilkinson, Proc. R. Soc. Lond. A 328 (1972) 23.
[28] C.K. Jorgensen, Mol. Phys. 2 (1959).
[29] G.L. Hug, Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution, National Bureau of Standards, Washington, DC, 1981, Vol. NSRDS-NBS 69, p. 160.
[30] E.M. Glebov, V.F. Plyusnin, N.I. Sorokin, V.P. Grivin, A.B. Venediktov, H. Lemmetyinen, J. Photochem. Photobiol. A: Chem. 90 (1995) 31.

[31] E.M. Glebov, V.F. Plyusnin, V.L. Vyazovkin, A.B. Venediktov, J. Photochem. Photobiol. A: Chem. 107 (1997) 93.

[32] H.M. Daggett, J. Am. Chem. Soc. 73 (1951) 4977.

[33] B.P. Nikolskii (Ed.), Spravochnik Khimika (Handbook of Chemist), Vol. 1, Khimiya, Moskow–Leningrad, 1966, pp. 609, 674.

[34] D. Dobos, Electrochemical Data, Academiai Kiado, Budapest, 1975, p. 61.

[35] A.M. Shkoldin, L.P. Sadovnichaya, V.A. Podolyanko, Elektrokhim. 4 (1968) 718.

[36] H. Lemmetyinen, R. Ovaskanien, K. Nieminen, K. Vaskonen, I. Sychtchikova, J. Chem. Soc. Perkin Trans. 2 (1992) 113.

[37] B. Cercek, M. Ebert, J.P. Keene, A.J. Swallow, Science 145 (1964) 919.

[38] V.F. Plyusnin, Khim. Vys. Energ. 20 (1986) 333.

[39] P. Neta, R.E. Huie, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 1027.

[40] G.V. Buxton, F.S. Dainton, M. Hammerli, Trans. Faraday Soc. 63 (1967) 1191.

[41] W.B. Person, J. Chem. Phys. 38 (1963) 109.

[42] C. Ferradini, J.P. Jay-Gerin, Radiat. Phys. Chem. 48 (1996) 473.

[43] R.A. Lidin, L.L. Andreev, V.A. Molochko, Sprovochnik po Neorganicheskoi Khimii (Handbook on Inorganic Chemistry), Khimiya, Moskow, 1987, p. 151.

[44] J.A. Wargon, F. Williams, J. Am. Chem. Soc. 94 (1972) 7917.

[45] M. Shiotani, S. Murabayashi, J. Sohma, Int. J. Radiat. Phys. Chem. 8 (1976) 483.

[46] N. Getoff, A. Ritter, F. Schworer, P. Bayer, Radiat. Phys. Chem. 41 (1993) 797.

[47] M. Anbar, P. Neta, Int. J. Appl. Radiat. Isotopes 16 (1965) 227.

[48] J.C.J. Thynne, F.K. Amenu-Kpodo, A.G. Harrison, Can. J. Chem. 44 (1966) 1655.

[49] H. Ogura, W.H. Hamill, J. Phys. Chem. 77 (1973) 2952.

[50] S.G. Entelis, R.P. Tiger, Kinetika Reaktsii v Rastvorah. Kolichestvennyi Uchet Vliyaniya Sredy (Kinetics of Reactions in Solutions. Qualitative Inclusion of the Influence of Media), Khimiya, Moskow, 1973, p. 34.

[51] J.E. Baggott, J. Phys. Chem. 87 (1983) 5223.

[52] R.E. Buhler, Rad. Phys. Chem. 21 (1983) 139.

[53] A.W. Adamson, A.H. Spoter, J. Am. Chem. Soc. 80 (1958) 3865.

[54] A.W. Adamson, Discuss. Faraday Soc. 29 (1960) 163.

[55] S.Ya. Kuchmii, A.V. Korzhak, A.I. Kryukov, Ukr. Khim. Zh. 50 (1984) 1050.

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

[57] D.J. Adams, S. Barlow, G.V. Buxton, T.M. Malone, G.A. Salmon, J. Chem. Soc. Faraday Trans. 91 (1995) 3303.

[58] T. Sumiyohi, K. Miura, H. Hagiwara, M. Katayama, Chem. Lett., 1987, 1429.