Photoreduction of IrCl₆^{2–} Complex in Alcohol Solutions and Its Reaction with Hydroxyalkyl Radicals

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ABSTRACT: The photochemistry of $IrCl_6^{2-}$ complex in simple alcohols have been studied using laser-flash photolysis. Single electron transfer from the solvent molecule to the light-excited complex has been shown to be the primary photochemical process. Quantum yields of the photoreduction of $IrCl_6^{2-}$ complex and the rate constants of its reaction with hydroxyalkyl radicals were determined at 200–330 K. Deviations of the rate constants from Debye–Smoluchowski equation for diffusion-controlled reactions are discussed. © 1998 John Wiley & Sons, Inc. Int J Chem Kinet: 30: 711–719, 1998

INTRODUCTION

Catalytic and photocatalytic reactions, involving complex ions of transient metals, such as generation of molecular hydrogen from water [1] and oxidation of organic compounds [2], have been intensively studied for the last years. To develop the quantitative models of these processes, one should know the rate constants of fast (close to diffusion-controlled) reactions of organic radicals with complex ions in various solvents and in wide temperature range.

There is a lack of reference data on the reactions between transient metal complexes and alcohol radicals. As a rule, the data available is concerned to water solutions at a room temperature. So, the rate constants of radical reactions with Cu_{aq}^{2+} [3–6], Fe_{aq}^{3+} [5], $\text{Fe}(\text{CN})_{6}^{3+}$ [7], and IrCl_{6}^{2-} [8] complexes are measured by the method of pulse radiolysis. For halide complexes, the reaction rate constants of alcohol radicals with CuCl_2 [9] and FeCl_4^{-} [10] in alcohol solutions were determined.

In this article, laser-flash photolysis was used to determine the rate constants of $IrCl_6^{2-}$ complex reduction by hydroxyalkyl radicals in alcohol solutions at 200–330 K. These reactions are important for studying the photochemical and radiation-chemical processes, involving iridium complexes. Particular interest to halide iridium complexes is inspired by both their application as oxidizers of organic compounds [11] and the generation of hydrogen by radiation-chemical decomposition of alcohols in aqueous solutions (actually, colloid iridium is a catalyst of this process [12,13]).

Recently, we have demonstrated [14,15] the formation of hydroxyalkyl radicals upon the photolysis of IrCl_6^{2-} in methanol and ethanol due to singleelectron transfer from solvent molecule to the excited complex

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$$\operatorname{IrCl}_{6}^{2-} \xrightarrow{h\nu} (\operatorname{IrCl}_{6}^{2-})^{*} \xrightarrow[\mathrm{RH}]{}$$
$$\operatorname{IrCl}_{6}^{3-} + \mathrm{R}^{\bullet} + \mathrm{H}^{+} \quad (1)$$

where R[•] is the hydroxyalkyl radical ($^{\circ}CH_2OH$ and $CH_3 ^{\circ}CHOH$ for methanol and ethanol solutions, respectively). In deoxygenated solutions, the radicals react with the initial complex to form $IrCl_6^{3-}$ and a corresponding aldehyde (A) [8]

$$\mathbf{R}^{\bullet} + \mathrm{IrCl}_{6}^{2-} \longrightarrow \mathrm{IrCl}_{6}^{3-} + \mathbf{A} + \mathbf{H}^{+} \qquad (2)$$

In the presence of oxygen R^{\bullet} is rapidly trapped to form the peroxide radical

$$\mathbf{R}^{\bullet} + \mathbf{O}_2 \longrightarrow \mathbf{RO}_2^{\bullet} \tag{3}$$

Due to its inactivity RO_2^{\bullet} does not participate in a subsequent transformations of iridium complexes. This mechanism is typical of the photoreduction of halide complexes of transient metals in polar organic solvents [9,10,16]. The present article reports on the quantum yields of $IrCl_6^{2-}$ photoreduction and shows that the photolysis mechanism (1–3) is also characteristic for other simple alcohols.

EXPERIMENTAL

Solutions of the $IrCl_6^{2-}$ complex were prepared using Na₂IrCl₆•6H₂O (Aldrich) and optically pure alcohols (Merck). Oxygen was removed by bubbling the solutions with nitrogen for 20 min. Tetraethylthiuramdisulfide was prepared as described in [17]. Optical absorption spectra were recorded on UNICAM 8735/50 or Specord UV-Vis (Carl Zeiss) spectrophotometers. For stationary photolysis of $IrCl_6^{2-}$ an eximer XeCl laser (308 nm) was used.

Laser-flash photolysis setup [18] consisted of an eximer laser for excitation (wavelength 308 nm, pulse duration 20 ns), a xenon arch lamp with a monochromator as a source of probing light and a monochromator with a photomultiplier in the measuring channel. The photomultiplier signal was supplied to a digital Tektronix 7912AD oscilloscope connected with an IBM type computer. In some experiments the laser-flash photolysis setup described in ref. [16] was used. While measuring the temperature dependence of the reaction rate constants, we have taken into account a change in the concentration of the initial complex due to the heat expansion of a solvent. The parameters of volumetric alcohol expansion were taken from ref. [19]. In these experiments the samples were placed into a quartz cryostat with optical windows blown out with cold nitrogen or air flow. The temperature was automatically maintained with accuracy of 0.5 C.

Quantum yield of $IrCl_6^{2-}$ photolysis was measured by two methods: in stationary and flash experiments. At 295 K the quantum yield of stationary photolysis in ethanol, 1- and 2-propanol, and 1-butanol was determined from the known value for methanol (0.1 [14]). In flash-photolysis experiments the energy of each laser pulse was measured. The quantum yield was determined from the decrease in optical density of the absorption band of the initial complex with its maximum at 495 nm.

RESULTS AND DISCUSSION

Mechanism of $IrCl_6^{2-}$ Photolysis in Alcohols at 295 K

Optical absorption spectrum of $IrCl_6^{2-}$ complex consists of the electron transfer bands in both visible and UV regions, as well as of the d-d bands in the region of 300–380 nm [20]. Figure 1 shows the temperature dependence of the absorption spectrum of $IrCl_6^{2-}$ in methanol solution. With the temperature decreasing, the charge transfer bands in the region from 400 to 500 nm narrow down, and their extinction coefficients increase. This effect was taken into account when



Figure 1 Optical absorption spectrum of $IrCl_6^{2-}$ complex in methanol at different temperatures. Curves 1–4 denote T = 300, 225, 175, and 77 K, respectively.



Figure 2 Laser-flash photolysis of $IrCl_6^{2-}$ in alcohols at 295 K. (a) Kinetic curves in 2-propanol (recording at 490 nm; $[IrCl_6^{2-}] = 3.5 \times 10^{-4}$ M; and 1 cm cuvettee): curve 1, natural content of oxygen, and curve 2, without oxygen. (b) Dependence of the observed rate constant of $IrCl_6^{2-}$ decay in 1-propanol (curve 1), 2-propanol (curve 2), and 1-butanol (curve 3) on the concentration of the complex.

measuring the temperature dependence of the quantum yield. Charge transfer bands in the visible region of $IrCl_6^{2-}$ spectrum display no photoactivity in both aqueous [21] and methanol [14] solutions. The irradiation of methanol and ethanol solutions of $IrCl_6^{2-}$ in the region of charge transfer bands overlap with the d-d band (308 nm) results in the photoreduction with a subsequent formation of $IrCl_6^{3-}$ complex [14].

Stationary and laser-flash photolysis experiments

Table IQuantum Yields (ϕ) at 295 K, PreexponentialFactors (ϕ_0), and Activation Energies ($E_a(\phi)$) of theQuantum Yield of IrCl₆²⁻ Photoreduction

Alcohol	ϕ	ϕ^0	$E_{\rm a}(\phi), {\rm kJ/mole}$
methanol	0.10 ^a	0.43 ± 0.05	3.4 ± 0.3
ethanol	0.13	1.00 ± 0.20	5.3 ± 0.5
1-propanol	0.07		
2-propanol	0.08	0.53 ± 0.07	4.4 ± 0.3
1-butanol	0.06	0.42 ± 0.05	4.7 ± 0.3

^a Measured in [14]; the measurement accuracy of the quantum yield is 10%.

for IrCl_6^{2-} in 1-propanol, 2-propanol, and 1-butanol have shown the primary photochemical act to be similar to that observed for methanol and ethanol. In the experiments with the solutions containing oxygen, an instant decrease in the optical density of the absorption bands of the initial complex is observed (Fig. 2(a), curve 1). The spectrum of this bleaching coincides with that of IrCl_6^{2-} . The values of quantum yields at room temperature are shown in Table I.

For deoxygenated solutions, after a laser pulse, we observe not only the instant bleaching in $IrCl_6^{2-}$ absorption bands but also the kinetics of additional decrease in the optical density. The value of the final bleaching is by a factor of two larger than that of the initial one (just after the laser pulse). The reaction kinetics is exponential (Fig. 2(a), curve 2). This process, however, is of a pseudo-first-order because the effective rate constant depends linearly on $IrCl_6^{2-}$ concentration (Fig. 2(b)). Thus, in deoxygenated solutions the hydroxyalkyl radicals react with $IrCl_6^{2-}$ complex. Table II lists the values of the rate constant for this reaction at room temperature.

In analyzing the kinetic data we have neglected radical-radical reactions (dimerization and disproportionation [22]) which occur with rate constants of $1.4 \times$

Table II Rate Constants at 295 K (k_2), Preexponential Factors (k_2^{0}), and Activation Energies ($E_a(k_2)$) of $IrCl_6^{2-}$ Reaction with Hydroxyalkyl Radicals, Diffusion Rate Constants (k_{diff}) at 295 K and Activation Energies (E_{diff}) of Diffusion Motion

		$L \times 10^{-9}$	$L 0 \times 10^{-11}$	E(h)	$L \times 10^{-9}$ h	E c
Alcohol	Radical	$\mathbf{M}^{-1}\mathbf{s}^{-1}$	$K_2^{\circ} \times 10^{-1} \text{s}^{-1}$	$L_{\rm a}(k_2)$, kJ/mole	$\kappa_{\rm diff} \times 10^{-1} { m s}^{-1}$	L _{diff} kJ/mole
methanol	•CH ₂ OH	3.2 ± 0.1^{a}	0.46 ± 0.11	6.3 ± 0.5	12.1	12.9
ethanol	CH ₃ • CHOH	2.3 ± 0.1^{a}	0.65 ± 0.22	8.2 ± 0.6	6.8	15.1
1-propanol	CH ₃ CH ₂ CHOH	1.4 ± 0.1			3.4	19.9
2-propanol	(CH ₃) ₂ •COH	2.0 ± 0.1	1.2 ± 0.5	9.6 ± 0.7	3.8	23.8
1-butanol	$CH_3(CH_2)_2$ • CHOH	1.3 ± 0.1	0.22 ± 0.05	7.2 ± 0.4	2.5	21.7

^a Measured in [14].

^b Calculated according to eq. (4).

^c Determined from the temperature dependence of k_{diff} using temperature-dependent viscosities [19].

10° M⁻¹s⁻¹ for •CH₂OH [23] and 3.0 × 10⁸ M⁻¹s⁻¹ for CH₃ •CHOH radicals [24]. Similar values are typical of the radicals of the other alcohols. When radical concentration is about 10⁻⁵ M (the maximum value in our experiments), the characteristic time of •CH₂OH recombination amounts to 35 μ s which is by an order of magnitude higher than the time of radical decay in the reaction with IrCl₆²⁻. The doubling of the initial bleaching in the absorption band of the IrCl₆²⁻ complex also testifies to a negligible contribution of the recombination reaction.

Temperature Dependence of Quantum Yields of IrCl₆²⁻ Photolysis and Rate Constants of its Reaction with Hydroxyalkyl Radicals

Laser-flash photolysis measurements performed within a wide temperature range (200-320 K) allowed one to determine the temperature dependence of the initial quantum yield of IrCl_6^{2-} photoreduction in various alcohols and of the rate constants of its reaction with hydroxyalkyl radicals (Fig. 3). Activation energy values and preexponential factors for the quantum yield are shown in Table I and those for the rate constants are given in Table II.

Two latter columns in Table II summarize the dif-



Figure 3 Arrhenius plot of the rate constant k_2 for the reaction of the $^{\circ}CH_2OH$ radical with $IrCl_6^{2-}$ (a) and the quantum yield of $IrCl_6^{2-}$ photoreduction in methanol (b).

fusion rate constants at 295 K and the activation energy of diffusion in alcohols, calculated using the Smoluchowski–Debye eq. (4) and the viscosity/temperature ratio [19]

$$k_{\rm diff} = 8 RT/3000\eta \tag{4}$$

The values of the rate constants of the reactions between radicals and $IrCl_6^{-2}$ at room temperature are 2–4 fold smaller than calculated value of the diffusion-controlled rate constant.

When the reaction is limited by diffusion, a decrease in the experimental rate constants, compared to the diffusion rate constants, could be assigned to the existence of a spin-statistic factor. The $IrCl_6^{-2}$ ion is a low-spin complex with electron configuration 5d⁵ and electron spin 1/2. The radical also has spin 1/2. Therefore, the total spin of the system may be either 1 or 0. The reaction gives rise to the $IrCl_6^{3-}$ complex with $5d^6$ electron configuration and zero electron spin. The radical transforms into the molecule with zero spin, i.e., the total system spin may be only zero. Thus, the spinstatistic factor f is 1/4. In this case, the reaction rate constant is $k_{\text{diff}} \times f$ and the activation energy must approach the activation energy of diffusion motion. Table II shows that the activation energy of the reaction between radicals and IrCl₆²⁻ is from 2 to 3 times smaller than that of diffusion. So, the experimental data can not be explained by the value of spin-statistic factor.

Figure 4 demonstrates the dependencies of logarithms $k_{obs} = k_2$ and k_{diff} on the inverse temperature for methanol and 1-butanol solutions of $IrCl_6^{2-}$. It is seen that for butanol at low temperature (200 K) k_{obs} exceeds k_{diff} , calculated using the Smoluchowski–Debye eq. (4) by more than an order of magnitude. The same holds for the isopropanol solutions.

Superdiffusion values of k_{obs} in isopropanol and 1butanol may arise due to the peculiarities of both the diffusion motion of reagents and the chemical reaction itself. First, the question arises of the applicability of the Stokes–Einstein eq. (5) [25] for the diffusion coefficient at low temperatures

$$D = kT/\alpha \pi r \eta \tag{5}$$

where r is the hydrodynamic radius of a diffusing molecule, $\alpha = 6$ for the most frequent case of stick boundary conditions.

Equation (5) refers to the case of large spherical particles which diffuse in homogeneous solvent. In practice, however, this equation is often used to describe the diffusion of molecules of arbitrary size and shape. Direct measurements of the self-diffusion co-



Figure 4 Temperature dependencies of the reaction rate constants in methanol (a) and 1-butanol (b). (1) Rate constant of the diffusion-controlled reaction calculated according to Smoluchowsky–Debye eq. (4); (2) Rate constant of the reaction between IrCl_6^{2-} and hydroxyalkyl radical; (3) Rate constant of the recombination of dithiocarbamate radicals (k_{rec}); and (4) (Dot line) Kinetic rate constant of the reaction between IrCl_6^{2-} and hydroxyalkyl radical calculated according to eq. 7 with $k_{\text{diff}} = k_{\text{rec}}$.

efficients of alcohol molecules were performed only at temperatures above 0°C [26], where they depend linearly on the T/η ratio. In this case, if the $(3V_0/4\pi)^{1/3}$ value is considered to represent the molecular radius r (V_0 is the molecular volume calculated using the available empirical rules of Edward [27]), the value of coefficient α in (5) tends to 4. In detail, α is equal to 4.7, 4.2, 4.3, and 4.0 for methanol, ethanol, isopropanol, and butanol, respectively. The value of $\alpha = 4$ corresponds to the case of slip boundary conditions. This is preferable for the diffusion of particles, comparable in size with the solvent molecules [25]. However, it is insufficient just to change the α value in eq. (5) from 6 to 4 in order to explain the experimental data on the reaction of radicals with IrCl₆²⁻ in isopropanol and butanol.

The realization of anomalous k_{obs} values may be related to the fact that at low temperature the applicability of the Stokes–Einstein equation is violated and the microviscosity may be substantially lower than the macroviscosity. However, the absence of direct measurements of the diffusion coefficients at $t < 0^{\circ}$ C does not allow one to estimate the reliability of this hypothesis.

Another reason for the superdiffusion values of k_{obs} may be connected with the peculiarities of electron

tunneling from the radical to the complex observed when decreasing temperature. In particular, as the diffusion rate decreases, the effective reaction radius may increase. This may be verified by measuring the rate constant of another diffusion-controlled reaction which has no relation to the electron transfer. For this purpose, we have used the reaction of the dithiocarbamate radicals recombination.

Determination of Diffusion Rate Constant Using Reaction of Dithiocarbamate Radicals Recombination

Dithiocarbamate radicals $(R_2NCS_2^{\bullet} = dtc^{\bullet})$ arise upon flash photolysis of the solutions of thiuramdisulfide $(R_2NC(S)S - S(S)CNR_2 = tds, in our case$ $R = C_2H_5)$

$$tds \xleftarrow{h\nu}{k_{rec}} 2 dtc^{\bullet}$$
 (6)

These radicals display the optical absorption band with a maximum at 600 nm ($\epsilon = 3100 \text{ M}^{-1}\text{cm}^{-1}$ [17]) and in majority of solvents they recombine with a diffusion rate constant [17].

Figure 4 shows the dependence of the logarithm of the recombination rate constant (k_{rec}) of dtc[•] radicals in methanol and butanol on the inverse temperature. At room temperature in methanol $k_{\rm rec} = (7.9 \pm$ $0.7) \times 10^9 \,\mathrm{M^{-1}s^{-1}}$. This value actually coincides with the rate constant of the redox quenching of the excited $[Ru(bpy)_3^{2+}]$ complexes by N, N, N', N'-tetramethylparaphenylendimanine $k_{\text{quen}} = 6.9 \times 10^9 \,\mathrm{M}^{-1}\mathrm{s}^{-1}$ taken in ref. [28] as the reference diffusion-controlled reaction (a large negative value of Gibbs' free energy $\Delta G^0 = -58.8$ kJ/mole and the equality of spin-statistic factor to unity have stimulated the choice). This holds that for the recombination reaction (6) the spinstatistic factor is close to unity (due to hyperfine interaction in radicals and due to spin-orbital interaction in the complex it may increase from 1/4 to 1 [29]).

The value of $k_{\rm rec}$ in methanol at room temperature is smaller than the diffusion limit (Table II). However, when the temperature is lower than 260 K, $k_{\rm rec}$ begins to exceed $k_{\rm diff}$. In butanol and isopropanol over the entire temperature range (190–320 K), $k_{\rm rec}$ exceeds the diffusion rate constant, calculated using the Smoluchowski–Debye eq. (4). The preexponential factors and the activation energies for $k_{\rm rec}$ are listed in Table III. Note that at room temperature $k_{\rm rec}$ is almost the same for all alcohols although the viscosity changes substantially (for butanol it is by a factor of five higher than for methanol).

Table III The Rate Constants at 295 K (k_{rec}), Preexponential Factor (k_{rec}^{0}), and Activation Energy ($E_a(k_{rec})$) of the Reaction of Dithiocarbamate Radical Recombination and the Exponent n in the Experimental Dependence k_{rec} ca. T/ η^n

Alcohol	$k_{ m rec} imes 10^{-9}$ ${ m M}^{-1}{ m s}^{-1}$	$k_{ m rec}^{0} imes 10^{-11} { m M}^{-1} { m s}^{-1}$	E(k) kI/mole	n
	141 5	141 5	$L_{\rm a}(\kappa_{\rm rec}),{\rm K}$	11
methanol	7.9 ± 0.7	8.8 ± 0.9	6.0 ± 0.2	0.37 ± 0.02
ethanol	3.3 ± 0.6	1.1 ± 0.3	8.6 ± 0.4	0.50 ± 0.03
2-propanol	6.2 ± 0.6	11 ± 5	12.5 ± 0.9	0.48 ± 0.04
1-butanol	7.8 ± 0.8	4.6 ± 1.5	10.0 ± 0.6	0.41 ± 0.03

Moreover, in all studied alcohols the recombination constant of dtc[•] radicals over the entire temperature range does not obey the Smoluchowski–Debye dependence $k_{\rm rec}$ ca. (T/η) . The slope of straight lines in linear equations $\ln(k_{\rm rec}) - \ln(\eta/T)$ (Fig. 5) for various alcohols is within the range (-0.38)-(-0.50) (the last column in Table III) and within the experimental accuracy it differs from the theoretical value of -1.

Known are the cases [30–38] where the Smoluchowski–Debye equation fails for the rate constants of diffusion-controlled reactions and, accordingly, the Stokes–Einstein equation fails for the diffusion coefficient. As a rule, this holds for the reactions, occurring in highly viscous liquids (η ca. 1–1000 P). The observed experimental k ca. $\eta^{-1/2}$ dependence [30– 33], as well as the D ca. $\eta^{-1/2}$ dependence of the dif-



Figure 5 Dependence of $\ln(k_{rec}/T)$ on $\ln(\eta)$ for the recombination of dithiocarbamate radicals in methanol.

fusion coefficient [37,38] usually attribute to the influence of a microheterogeneous structure of viscous liquid, leading to non-Fick's diffusion [38]. As it has been mentioned, these effects are stronger for binary mixtures and for solute molecules diffusion compared to the self-diffusion of solvent molecules [34].

In our experiments the deviations from the Smoluchowski–Debye equation are observed for the liquids with low viscosity (alcohols, η ca. 0.2–10 cP). As a rule, this equation is reported to hold for the diffusion-controlled reactions in low-viscous nonpolar solvents [39,40]. The anomalous character of diffusion constants is typical of the solvents with hydrogen bonds, such as alcohols [36,41–43].

Direct measurements of diffusion coefficients in usual (low-viscous) solvents also exemplify the anomalous dependencies on viscosity [44]. As in the case of strongly viscous liquids, the anomalies arise upon diffusion of small admixtures [45,46]. The diffusion of various admixtures in 2-methylpentane-2,4-diol has been studied in [47]. It has been shown that the planar molecules (benzene, naphthalene, phenantrene, and pyrene) diffuse much faster than a rather spherical-shape CBr₄ molecule. In this case, the parameter α in the Stokes-Einstein eq. (5) is temperature-dependent and its value for the benzene molecule is smaller than unity already at 295 K. Note that the dtc[•] radical is also planar and its diffusion may display similar peculiarities.

There are also cases of a "normal" behavior of the diffusion-controlled rate constants in alcohols. Thus, Gilles and Boyd [48] have established that the recombination of $(CH_3)_2$ COH radicals, arising upon pulse radiolysis of isopropanol within the temperature range of 147–300 K, obey the $k_{\rm rec}$ ca. $T \times \eta^{-1}$ dependence. Probably, for the radicals with the structure resembling that of the solvent molecules, the anomalies of diffusion motion are of minor importance.

Note that the articles on diffusion, mentioned in this section, are purely empirical and have no theoretical concepts in common [44]. Thus, the question of the

reasons of superdiffusion values of the reaction rate constants, including dithiocarbamate radicals recombination in alcohols needs further studying. However, these results indicate that the increase of the reaction radii at low temperature in the reactions of the electron transfer from radicals to the $IrCl_6^{2-}$ complex is hardly probable. This is evident from the fact that the rate constants, exceeding calculated by eq. (4), are also observed for the recombination of radicals, which is a reaction of another type.

Determination of Kinetic Rate Constants of $IrCl_6^{2-} + R^{\circ}$ Reaction

The contradiction caused by the superdiffusion rate constant of reaction (2) vanishes if the reaction of dithiocarbamate radicals recombination is assumed to be diffusion-controlled (over the entire temperature range k_2 being smaller than k_{rec}). For methanol (Fig. 4(a)) the activation energies of these two reactions almost coincide (Tables II and III) and the values of their rate constants differ by a factor of two.

For the reaction of $IrCl_6^{2-}$ with isopropanol and butanol radicals the activation energies are also close to that of dtc[•] radicals recombination (smaller by ca. 3kJ/mole) and at room temperature the rate constant k_2 is smaller than k_{rec} by a factor of three and six, respectively. A parallel decrease in the rate constant and in the reaction activation energies compared to k_{rec} , assumed as k_{diff} ($k_{diff} = k_{rec}$), may be explained by the fact that the rate of electron transfer in the encounter pair $IrCl_6^{2-}$. . . R[•], i.e., the rate constant of the kinetic stage, k_{kin} , is smaller than the rate constant of diffusion motion, k_{diff} . In this case, the observed rate constant k_{obs} can be written as [49]

$$k_{\rm obs} = \frac{k_{\rm kin} k_{\rm diff}}{k_{\rm kin} + k_{\rm diff}}$$
(7)

Figure 4 shows the temperature dependence of k_{kin} , determined using eq. (7). Table IV summarizes the activation energies and preexponential factors for this constants. The activation energy of the kinetic stage is

observed to be low and almost the same for all alcohols within the experimental accuracy. The monomolecular rate constant of electron transfer in the $IrCl_6^{2-}$... R[•] encounter pair may be estimated using the relationship [50]

$$k_{\rm kin} = k_{\rm mono} \times V \tag{8}$$

where $V = 4\pi R^2 \Delta$ is the volume of the reaction zone; R is the total radius of partners; and Δ is the thickness of the reaction zone (a distance over which an electron is transferred). The total radius for both the complex and radical is $R \approx 5.6 \text{ A}$ ($R_{Ir} \approx 4.3 \text{ A}$ [51], $R_{rad} \approx$ 1.4 A). Taking Δ ca. 1 A, one may calculate $V \approx$ 0.25 M⁻¹ and $k_{mono} \approx 2 \times 10^{10} \text{ s}^{-1}$. Thus, the electron tunneling from radical to complex at room temperature may occur during about 50 ps. For Δ ca. 0.1 A this time decreases to 5 ps.

Comparison of Rate Constants of the Reactions of Hydroxyalkyl Radicals with IrCl₆²⁻ and Other Coordination Compounds

Table V gives the literature data on some known reactions of transient metal complexes of with hydroxyalkyl radicals at 295 K. There are two points to be discussed.

Firstly, the rate constants of the reactions between $IrCl_6^{2-}$ and hydroxyalkyl radicals (*CH₂OH, CH_3 °CHOH, and $(CH_3)_2$ °COH) in water solutions at 295 K, measured in [8] are twice as obtained in alcohol solutions (see Table II). This difference is not rather comprehensible. It should be noted that he work [8] doesn't contain primary kinetic information. So, one is inclined to think that the values of rate constants measured in [8] may become over-estimated because of the influence of competing channels of radicals decay. These channels may be the recombination of radicals or its reaction with the impurities of oxygen.

Secondly, the rate constants of the reaction between radicals and $IrCl_6^{2-}$ exceed substantially the similar values for chloride and aquated complexes of Fe(III)

Table IV Parameters of Rate Constant k_{kin} for $\mathbb{R}^{\bullet} + \operatorname{IrCl}_{6}^{2-}$ Reaction: Rate Constants at 295 K (k_{kin}), Preexponential Factor (k_{kin}^{0}) and Activation Energy ($E_a(k_{kin})$)

Radical R [•]	$k_{ m kin} imes 10^{-9}, { m M}^{-1} { m s}^{-1}$	$k_{ m kin}{}^0 imes 10^{-10},{ m M}^{-1}{ m s}^{-1}$	$E_{\rm a}$ ($k_{\rm kin}$), kJ/mole
•CH ₂ OH	6.6	9.9 ± 6.5	6.6 ± 0.9
CH ₃ • CHOH	7.7	12.9 ± 12	6.9 ± 2.3
$(CH_3)_2$ COH	3.4	6.4 ± 4.3	7.2 ± 2.2
CH ₃ CH ₂ CH ₂ CHOH	1.4	2.0 ± 0.5	6.6 ± 1.0

Complex	Radical	Solvent	$k_2, \mathrm{M}^{-1}\mathrm{s}^{-1}$	Refs.
CuCl ₂	(CH ₃) ₂ •COH	2-propanol	$(2-3) \times 10^{8}$	[9]
FeCl ₄ ⁻	CH ₃ • CHOH	Ethanol	$(6 \pm 1) \times 10^8$	[10]
IrCl ₆ ²⁻	•CH ₂ OH	H_2O	$6.0 imes 10^{9}$	[8]
IrCl ₆ ²⁻	CH ₃ •CHOH	H ₂ O	4.5×10^{9}	[8]
IrCl ₆ ²⁻	•CH ₂ CH ₂ OH	H ₂ O	ca. 2×10^{9}	[8]
IrCl ₆ ²⁻	$(CH_3)_2$ COH	H_2O	4.7×10^{9}	[8]
IrCl ₆ ²⁻	$^{\circ}CH_{2}C(CH_{3})_{2}OH$	H_2O	1.2×10^{9}	[8]
$Fe(CN)_6^{3+}$	•CH ₂ OH	H ₂ O	4×10^9	[7]
$Fe(CN)_6^{3+}$	CH ₃ • CHOH	H ₂ O	5.3×10^{9}	[7]
$\operatorname{Fe}(\operatorname{CN})_{6}^{3+}$	CH ₃ CH ₂ CHOH	H_2O	3.7×10^{9}	[7]
$Fe(CN)_6^{3+}$	$(CH_3)_2$ COH	H_2O	4.7×10^{9}	[7]
Fe _{a0} ³⁺	CH ₃ •CHOH	H ₂ O	3.8×10^{8}	[5]
Cu_{aq}^{2+}	•CH ₂ OH	H ₂ O	$(1.1-1.9) \times 10^8$	[3-6]
Cu_{aq}^{2+}	CH ₃ [•] CHOH	H_2O	$(9 \pm 2) \times 10^{7}$	[5,6]
Cu_{aq}^{2+}	$(CH_3)_2$ COH	H_2O	$(4.5-5.2) \times 10^{7}$	[3,5,6]
Cu _{aq} ²⁺	•CH ₂ (CH ₃)COH	H_2O	3.2×10^{6}	[5]

Table V Rate Constants of the Reaction between Complexes and Hydroxyalkyl Radicals

and Cu(II) which may be due to the different reaction mechanisms. The research into pulse radiolysis of water-alcohol solutions, containing Cu_{aq}^{2+} complex, report the appearance of intermediate absorption, related to the formation of the Cu^{2+} . . . R^{\bullet} radical complex [5], i.e., the reaction occurs via the inner-sphere mechanism. The rate constants for $IrCl_6^{2-}$ are close to the typical values for the Fe(CN)₆³⁺ complex. Both complexes display stable coordination sphere and the reaction with radicals occurs via the mechanism of outersphere electron transfer.

CONCLUSION

Thus, for five simple alcohols the $IrCl_6^{2-}$ photoreduction is shown to be due to electron transfer from a solvent molecule to the excited complex. The quantum yield and its temperature characteristics are measured. The hydroxyalkyl radicals, arising from photoreduction, disappear in the reaction with the initial $IrCl_6^{2-}$ complex. Rate constants and activation energies of these reactions are slightly smaller than those for the reaction of dithiocarbamate radical recombination taken as the diffusion-controlled reaction. This makes it possible to determine the parameters of electron transfer stage in a contact radical-complex pair. According to estimations, the electron transfer occurs during the time which is shorter than 100 ps.

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