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Environmental effect on photoquenching reaction of hexamolybdenum(II) clusters capped by chloride with hexachloroiridate(IV) in solution

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Abstract

Luminescence quenching of $[(Mo_6Cl_8)Cl_6]^{2-}$ by $[IrCl_6]^{2-}$ in acetonitrile and aqueous hydrochloric acid has been studied. Flash photolysis in acetonitrile suggested participation of both electron and energy transfer processes. The second-order rate constant, k_0, in acetonitrile under atmospheric pressure differs significantly depending on the kind of cation ($(9\pm2)\times10^7$ M^{-1} s^{-1} in 0.10 M $LiClO_4$ and $(2.1\pm0.2)\times10^9$ M^{-1} s^{-1} in 0.1 M $Mg(ClO_4)_2$). The importance of the precursor ion-triplet formation between the two anionic reactants and the cation is suggested. The k_0 in aqueous solution ($(5.0\pm0.3)\times10^9$ M^{-1} s^{-1}) is virtually independent of the HCl concentration (0.60–2.0 M) and added salts (1.4 M NaCl or NH_4Cl in 0.6 M HCl). The volume of activation takes different values under various conditions in acetonitrile, whilst it is virtually zero in aqueous HCl solution. The results were interpreted with reference to the rearrangement of the solvation sphere on the precursor formation in ion-triplet form.

Introduction

The hexamolybdenum(II) cluster, $[(Mo_6Cl_8)Cl_6]^{2-}$, gives strong red emission both in solution and solid state on irradiation of UV light [1–9][†]. The cluster undergoes thermal electron transfer reaction with difficulty ($E_{1/2}=+1.56$ V versus SCE in acetonitrile at 25 °C) [10], but its luminescence is quenched by various redox reagents in water and organic solvents [1]. We have communicated briefly that the quenching rate constant with $[IrCl_6]^{2-}$ in acetonitrile and its activation volume ($\Delta V^{\ddagger}$) show significant dependence on the variety and concentration of cationic cosolutes [11, 12]. An important participation of the cation on the encounter complex between the two negatively charged species has been indicated [11, 12]. Subsequently, one of the authors has examined the effect of coexisting cations on the photoquenching of $[Pt_2(pop)_4]^{4-}$ (pop^{2-} = pyrophosphite(2−)) with $[Mo(CN)_8]^{4-}$ in aqueous media, and reinforced the importance of the ion-triplet as a precursor for the photoquenching reactions between two negatively charged reactants [13]. The hexamolybdenum cluster ion, $[(Mo_6Cl_8)Cl_6]^{2-}$, gives alkali metal and tetraalkylammonium salts, which are soluble in water and organic solvents, respectively [1], and provides an opportunity to carry out comparative studies in both solvents. This paper deals with details of kinetic studies on the photoquenching reactions of $[(Mo_6Cl_8)Cl_6]^{2-}$ with $[IrCl_6]^{2-}$ with reference to the effect of cationic species as well as applied pressure.

Experimental

Materials

The cluster

Potassium and tetraethylammonium salts of the hexamolybdenum(II) cluster, $K_2[(Mo_6Cl_8)Cl_6]$ and $[(C_2H_5)_4N]_2[(Mo_6Cl_8)Cl_6]$, were prepared as described

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[†] Electrochemically generated luminescence was also observed for $[(Mo_6Cl_8)Cl_6]^{2-}$ [10].

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previously [3]. The purity was confirmed by visible and UV spectroscopy and the emission lifetime: potassium salt, λ_{max} at 308 nm ($\epsilon = 2970$ M^{-1} cm^{-1}) in 6.0 HCl [1, 14] and $\tau \doteq 22.7$ μs in 6.0 M HCl–6.0 M $LiClO_4$; tetraethylammonium salt, λ_{max} at 330 nm ($\epsilon = 2920$ M^{-1} cm^{-1}) and τ (at 780 nm) $= 180 \pm 10$ μs in acetonitrile [1].

The quencher

Commercial $Na_2[IrCl_6] \cdot 6H_2O$ (Johnson-Matthey) was recrystallized from 6 M HCl. The tetraethylammonium salt was precipitated in HCl solution by adding $(C_2H_5)_4NCl$ and recrystallized from acetonitrile as dark red crystals. The concentration of the solution of efflorescent sodium salt was determined by absorption spectroscopy before use. The standard ϵ value was determined to be 4130 M^{-1} cm^{-1} at 488 nm in water by the use of the tetraethylammonium salt which is stable in air and soluble both in water and acetonitrile [15]*. The λ_{max} (nm) (ϵ_{max} (M^{-1} cm^{-1})) values in acetonitrile were 492 (4960) and 435 (4530).

Other reagents

$(n\text{-}C_4H_9)_4NClO_4$ and $(C_2H_5)_4NCl$ were recrystallized from acetonitrile; LiCl, $Mg(ClO_4)_2$, $LiClO_4$, $NaClO_4$ and $(C_2H_5)_4NClO_4$ from water. $LiClO_4$ and $Mg(ClO_4)_2$ were dehydrated at 200 °C *in vacuo*, and $NaClO_4$ was dried at 110 °C. Acetonitrile for fluorometry (Kanto Chemical Co.), and NaCl and NH_4Cl were used without further purification.

Measurements and analysis

Quenching rate constants

Quenching rate constants were obtained for degassed and air-saturated solutions. For the measurements under air-free conditions, the sample solution was degassed in a vacuum line by repeating the freezing and melting cycle four times and then introduced into the cell. The cell was placed in the cell holder which was thermostated by circulating water from a Haake D3 Thermostat. The excitation light source was a nitrogen laser JS-1000L of NDC, and the pulse energy was *c.* 2 mJ with a half width of 5 ns. The luminescent light was passed through a Jobin-Yvon H 20V monochromator and incident on a Hamamatsu-Photonix R-955 photomultiplier. The decay of the emission intensity at 690 to 700 nm was monitored. Linear regression analysis of $\ln(I/I_0)$ versus time (512 data points within 3 to 4 half lives) gave a reasonably good fit. The emission lifetime was calculated from the reciprocal of the gradient of such diagrams. Errors were given at 0.7 confident level.

The Stern–Volmer equation was applied for the evaluation of the quenching rate constant, k_q (second-order rate constant in M^{-1} s^{-1}).

$$1/\tau_q - 1/\tau_0 = k_q[Q] \qquad (1)$$

Here τ_0 and τ_q are the emission lifetime in the absence and presence of the quencher, respectively, and [Q] is the concentration of the quencher. In solutions containing $[IrCl_6]^{2-}$ and $[(Mo_6Cl_8)Cl_6]^{2-}$ in equal concentrations (*c.* 10^{-5} M), only less than 10% of the molybdenum complex was excited, so that a pseudo first-order condition is established.

For the measurements under elevated pressure, the sample solution in a cylindrical quartz cell was placed in a thermostated cell holder with four sapphire windows. Since it was difficult to carry out the experiments under strictly air-free conditions, the air-saturated solutions or those with arbitrary oxygen concentration were used for the measurements of k_q under high pressures, and the results were analyzed as described later. The pressure was applied by a hand pump up to 250 MPa, and measured by a Bourdon gauge calibrated with a Heise pressure meter CM-30053. The activation volume, $\Delta V^{\ddagger}$, is related to the rate constants by eqn. (2), where T and R are absolute temperature and the gas constant, respectively.

$$(\sigma \ln k_q/\sigma p)_T = -(\Delta V^{\ddagger}/RT) \qquad (2)$$

If $\Delta V^{\ddagger}$ is independent of p, the rate constants (k_q) at atmospheric pressure (k_0) and elevated pressure p (k_p) are related to $\Delta V^{\dagger}$ by eqn. (3) [16].

$$\ln(k_p/k_0) = -(\Delta V^{\ddagger}p/RT) \qquad (3)$$

In fact, the plots of $\ln(k_p/k_0)$ versus p were linear in the studied systems, and compressibility of activation was reckoned virtually zero.

In order to evaluate activation volumes of the quenching rate constants, additivity law was assumed for the quenching by dissolved oxygen and $[IrCl_6]^{2-}$. Such an assumption is reasonable, since the quenching rate by $[IrCl_6]^{2-}$ is not affected by dissolved oxygen under atmospheric pressure (see Table 1). In air-saturated HCl solutions, k_q at each pressure was obtained directly from the Stern–Volmer plot, since the contribution of the oxygen quenching is negligible. In acetonitrile solutions, $\Delta V^{\ddagger}$ values of oxygen quenching were evaluated to be -5.8 ± 1.0 and -6.8 ± 1.0 cm^3 mol^{-1} for 0.1 M $(C_2H_5)_4NClO_4$ and 0.1 M $NaClO_4$ solutions, respectively. The k_q values at individual pressures were estimated from the reasonably linear Stern–Volmer plots at each pressure using the quenching rate after correcting the observed overall quenching rates for the contribution of dioxygen quenching. While such correction is straightforward in air-saturated solutions (applied in 0.1 M $(C_2H_5)_4NClO_4$ solutions), more complicated procedures

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*The ϵ value of 4070 M^{-1} cm^{-1} at 487 nm in aqueous solution was reported [15].

were required for the partially degassed solutions (applied in 0.1 M $NaClO_4$ solutions)*.

Flash photolysis

The mixture containing 3.6×10^{-4} M of the cluster and 1.8×10^{-5} M $[IrCl_6]^{2-}$ in 0.1 M $(C_2H_5)_4NClO_4$ or $NaClO_4$ solution, was placed in a cylindrical quartz cell with a diameter 10 cm (optical path length) and irradiated from the side window by pulsed light from a Xenon lamp (150 J per pulse, half width 7 μs) through a filter UVP (transparent in 300–400 nm region), and the change in transmission intensity at 492 nm (in $(C_2H_5)_4NClO_4$ solution) or 487 nm (in $NaClO_4$ solution) was recorded.

Other measurements

Electronic absorption spectra were recorded on Hitachi 330 and Shimadzu UV-200S spectrophotometers. Water content in organic solvents was determined by Karl Fisher titration with a Metrohm Herisau Multi-Dosimat E 415.

Results

Mechanism of quenching

Figure 1 exemplifies the result of flash photolysis**, The transmission at 487 nm (corresponds to the absorption peak of $[IrCl_6]^{2-}$) first increases within *c.* 100 μs and then decreases to reach the original value within *c.* 500 μs. The time scale of the increase in transmission is of equal order of magnitude to that of the quenching reaction. The slow second step proceeds as a bimolecular process. These observations are consistent with the participation of the electron transfer pathway for the present quenching reaction. The reduced product, $[Ir^{III}Cl_6]^{3-}$, has no significant absorption at 487 nm [17]. Reported values of redox potential of $*[(Mo_6Cl_8)Cl_6]^{2-}$ (−0.3 V versus SCE in acetonitrile [10]) (* indicates photochemically generated excited state) and $[IrCl_6]^{2-}$ (+0.65 V versus SCE in aqueous 0.1 M $NaClO_4$ solution [18]) are also consistent with the participation of electron transfer mechanism†.

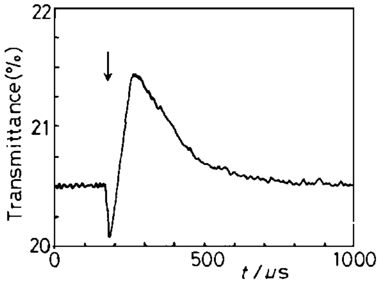

Fig. 1. The change in transmittance at 487 nm on flash photolysis of the acetonitrile solution of $[(C_2H_5)_4N]_2[(Mo_6Cl_8)Cl_6]$ (3.6×10^{-4} M) and $[(C_2H_5)_4N]_2[IrCl_6]$ (1.8×10^{-5} M) ($[NaClO_4] = 0.1$ M). The arrow indicates the irradiation.

The first increase in transmission corresponds to the decrease of $[IrCl_6]^{2-}$ due to eqn. (4).

$$*[Mo_6Cl_{14}]^{2-} + [IrCl_6]^{2-} \longrightarrow [Mo_6Cl_{14}]^{-} + [IrCl_6]^{3-} \qquad (4)$$

Cyclic voltammetry clearly shows that the product $[Mo_6Cl_{14}]^{-}$ has a very strong oxidizing power [1, 10] and oxidizes the iridium(III) complex so that the reaction of eqn. (5) proceeds thermally in the second step of Fig. 1.

$$[Mo_6Cl_{14}]^{-} + [IrCl_6]^{3-} \longrightarrow [Mo_6Cl_{14}]^{2-} + [IrCl_6]^{2-} \qquad (5)$$

Although the electron-transfer mechanism certainly participates in the present quenching reaction, extent of the transmittance change corresponds to at most *c.* 10% of $[IrCl_6]^{2-}$. Since excessive amount of the excited state $[(Mo_6Cl_8]Cl_6]^{2-}$ to $[IrCl_6]^{2-}$ should be generated under the experimental conditions, there must also be an energy transfer pathway for the quenching reaction. The product of the energy transfer reaction, $*[IrCl_6]^{2-}$ must return to the ground state rapidly, so that the transmission at 487 nm is practically unaffected. The following discussion on k_q is for the competitive electron and energy transfer pathway.

Quenching in acetonitrile solution

Tetrabutylammonium salts of $[(Mo_6Cl_8)Cl_6]^{2-}$ and $[IrCl_6]^{2-}$ were used for the measurements in acetonitrile. The mixture of the two reactants gives the same absorption pattern as with the sum of both compounds††. In the presence of added salt the absorption pattern of $[IrCl_6]^{2-}$ differs slightly, which is due to ion-pair formation between the complex anion and the added cation. The formation constant of $\{Na[IrCl_6]\}^{-}$ was calculated to be 12 ± 2 M^{-1} at 25 °C and ionic strength 0.1 M ($(C_2H_5)_4NClO_4$).

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*An example of the correction: a solution containing 3.25×10^{-4} M $[IrCl_6]^{2-}$ in the high-pressure cell gave $\tau_q = 13.8$ μs ($1/\tau_q = 72\,600$ s^{-1}). Since the $1/\tau_q$ value for the solution under completely deoxygenated condition is calculated to be 57 500 s^{-1} (using $\tau_0 = 146$ μs and $k_q = 1.56 \times 10^8$ $M^{-1}\,s^{-1}$), the quenching rate by O_2 in the solution in the high pressure-cell is estimated to be 15 100 s^{-1}. From the $\Delta V^{\ddagger}$ value (−5.8 cm^3 mol^{-1}), the quenching rate by O_2 of the solution at 197 MPa is calculated to be 23 700 s^{-1}. The observed τ_p of the solution at 197 MPa is 7.91 μs ($1/\tau_p = 119\,600$ s^{-1}). Thus the quenching rate by $[IrCl_6]^{2-}$ is calculated to be 95 900 s^{-1}.

**The initial rapid decrease in transmission (*c.* 10^{-8} s) may be related to the change in absorption brought about by the photoexcitation of $[Ir^{IV}Cl_6]^{2-}$. This part was not included in the analysis.

†Although the redox potentials of the two reactants are reported in different media, the difference between the two values is sufficiently large to assume that the electron transfer mechanism can operate in both acetonitrile and aqueous HCl solution.

††The pattern remains unchanged for 5 h and we concluded that there was no dark reaction between them.

The emission lifetime, τ_0, is 180 μs in degassed acetonitrile without added electrolyte. It is *c.* 15% smaller in the presence of various electrolytes at 0.1 M [7]. The τ_0 value is *c.* 11.5 μs in air-saturated solution regardless of the kind of added electrolytes.

The Stern–Volmer plot gives a convex curve in $>5\times10^{-4}$ M $[IrCl_6]^{2-}$ in the absence of added electrolyte (Fig. 2). This is due to the variation in ionic strength, and more specifically to the concentration of counter cation (*vide infra*). The plot becomes linear on addition of excessive amounts of electrolytes. The k_q values listed in Table 1 increase with the increase in the concentration of $(C_2H_5)_4NClO_4$ and vary significantly with the kind of electrolytes at constant concentration (0.1 M). Figure 3 shows the Stern–Volmer plots at various $NaClO_4$ concentrations at constant ionic strength 0.1 M ($[NaClO_4]+[(C_2H_5)_4NClO_4]$). The plot of k_q against $[NaClO_4]$ (Fig. 4) is concave and becomes almost horizontal as $[NaClO_4]$ increases.

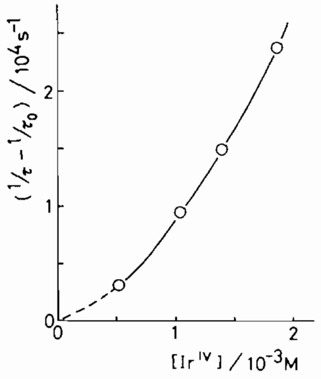

Fig. 2. Stern–Volmer plot for the photoquenching reaction of $[(C_2H_5)_4N]_2[(Mo_6Cl_8)Cl_6]$ (*c.* 1×10^{-4} M) with $[(C_2H_5)_4N]_2[IrCl_6]$ in acetonitrile at 25.0 °C (no electrolyte added).

TABLE 1. Rate constants for the quenching reaction of $*[(Mo_6Cl_8)Cl_6]^{2-}$ with $[IrCl_6]^{2-}$ in acetonitrile at 25 °C

Added salt	Conc. (M)	k_q (10^8 M^{-1} s^{-1})[a]
None		0.03 ± 0.01*[b]
$(C_2H_5)_4NClO_4$	0.025	0.74 ± 0.06
	0.050	1.04 ± 0.12
	0.10	1.54 ± 0.05
	0.10	1.56 ± 0.04*
	0.20	2.11 ± 0.08
$(C_2H_5)_4Cl$	0.10	1.4 ± 0.1*
$(n\text{-}C_4H_9)_4NClO_4$	0.10	0.27 ± 0.01*
$NaClO_4$	0.10	10.3 ± 0.5*
	0.10	10.0 ± 0.1
HCl	0.10	1.3 ± 0.2 ($k_{q(0)}$)[c]
	0.10	2.3 ± 0.3 ($k_{q(\infty)}$)[c]
$LiClO_4$	0.10	0.9 ± 0.2 ($k_{q(0)}$)[c]
	0.10	3.0 ± 0.3 ($k_{q(\infty)}$)[c]
$Mg(ClO_4)_2$	0.10	<4 ($k_{q(0)}$)[c]
	0.10	21 ± 2 ($k_{q(\infty)}$)[c]

[a] Measured in air-saturated solution except the values which are marked by * where measurements were carried out under deaerated condition. [b] Extrapolated to zero concentration of electrolyte. [c] In these systems the k_q values depend on the water concentration in acetonitrile. The $k_{q(0)}$ and $k_{q(\infty)}$ values are those extrapolated to zero and infinite water concentration, respectively.

The k_q values were sensitive to the water concentration when HCl, $LiClO_4$ or $Mg(ClO_4)_2$ is present in the reaction mixture. In the solutions containing $(C_2H_5)_4N^+$, $(n\text{-}C_4H_9)_4N^+$ or Na^+ as a counter cation, there was no influence of water concentration upon k_q in the range 0.02–0.3 M H_2O. The relationship between k_q and water concentration for the water sensitive systems is shown in Fig. 5. There is a trend that the gradient of curves approaches zero as the water concentration overwhelms that of the electrolytes. The k_q values at zero ($k_{q(0)}$) and infinite concentrations of water ($k_{q(\infty)}$) were roughly estimated by extrapolating the curves and are listed in Table 1.

The pressure dependence of k_q values are listed in Table 2. The $\ln(k_p/k_0)$ versus p diagrams are linear up to 250 MPa in 0.1 M $(C_2H_5)_4NClO_4$ and $NaClO_4$ solution, respectively. The $\Delta V^\ddagger$ values thus obtained are listed in Table 3.

Quenching in hydrochloric acid solution

The potassium salt of the cluster and the sodium salt of the quencher were used for the measurements.

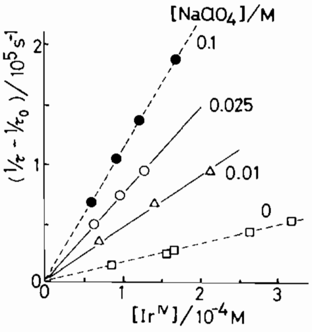

Fig. 3. Stern–Volmer plots for the photoquenching reaction of $[(C_2H_5)_4N]_2[(Mo_6Cl_8)Cl_6]$ (*c.* 7×10^{-5} M) with $[(C_2H_5)_4N]_2[IrCl_6]$ at $[[(C_2H_5)_4N]ClO_4]+[NaClO_4]=0.1$ M in acetonitrile at 25.0 °C.

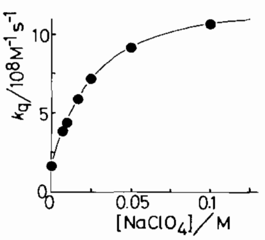

Fig. 4. Dependence of k_q on $[NaClO_4]$ for the photoquenching reaction of $[(C_2H_5)_4N]_2[(Mo_6Cl_8)Cl_6]$ (*c.* 7×10^{-5} M) with $[(C_2H_5)_4N]_2[IrCl_6]$ ($(7-22)\times10^{-5}$ M) at $[[(C_2H_5)_4N]ClO_4]+[NaClO_4]=0.1$ M in acetonitrile at 25.0 °C.

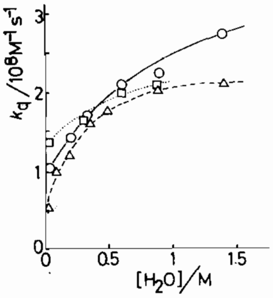

Fig. 5. Dependence of k_q on water concentration for the photoquenching reaction of $[(C_2H_5)_4N]_2[(Mo_6Cl_8)Cl_6]$ (*c.* 8×10^{-5} M) with $[(C_2H_5)_4N]_2[IrCl_6]$ ($(7-37)\times10^{-5}$ M) in acetonitrile at 25 °C at $[LiClO_4]=0.1$ M (——), $[HCl]=0.1$ M (·····), or $[Mg(ClO_4)_2]=0.1$ M (– – –).

TABLE 2. Pressure dependence of k_q for the photoquenching reaction of $[(Mo_6Cl_8)Cl_6]^{2-}$ by $[IrCl_6]^{2-}$ in acetonitrile in the presence of $(C_2H_5)_4NClO_4$ or $NaClO_4$ at 25 °C

Electrolyte (0.13 mol kg^{-1})	p (MPa)	k_q (10^8 mol^{-1} kg s^{-1})
$(C_2H_5)_4NClO_4$ [a]	0.1	1.22 ± 0.04
	51	1.4 ± 0.3
	100	1.6 ± 0.4
	149	2.0 ± 0.4
	196	2.3 ± 0.5
	246	2.7 ± 0.6
$NaClO_4$ [b]	0.1	7.9 ± 0.3
	51	7.5 ± 0.4
	100	7.1 ± 0.7
	149	6.8 ± 0.5
	198	6.4 ± 0.6
	247	5.9 ± 0.3

[a] $[Mo_6Cl_{14}^{2-}]=c.\ 1.3\times10^{-4}$ mol kg^{-1}, $[IrCl_6^{2-}]=(2.6-7.8)\times10^{-4}$ mol kg^{-1}. [b] $[Mo_6Cl_{14}^{2-}]=c.\ 1\times10^{-4}$ mol kg^{-1}, $[IrCl_6^{2-}]=(1.2-3.5)\times10^{-4}$ mol kg^{-1}.

TABLE 3. Activation volume for the photoquenching reaction of $[(Mo_6Cl_8)Cl_6]^{2-}$ in solution

Solvent	Quencher	Electrolyte (conc./mol kg^{-1})	$\Delta V^\ddagger$ (cm^3 mol^{-1})
CH_3CN	O_2	none	-8.2 ± 0.5[a]
		$(C_2H_5)_4NClO_4$ (0.13)	-5.8 ± 1.0[a]
		$NaClO_4$ (0.13)	-6.8 ± 1.0[a]
	$[IrCl_6]^{2-}$	$(C_2H_5)_4NClO_4$ (0.13)	-8 ± 2
		$NaClO_4$ (0.13)	$+2.5\pm0.5$
H_2O	$[IrCl_6]^{2-}$	HCl (0.59)	0 ± 1
		HCl (1.94)	0 ± 1

[a] These values were obtained from the pressure dependence of the emission lifetime in oxygen saturated solution.

TABLE 4. Rate constants for the quenching reaction of $*[(Mo_6Cl_8)Cl_6]^{2-}$ with $[IrCl_6]^{2-}$ in hydrochloric acid at 25 °C[a]

[HCl] (M)	Added salt	p (MPa)	k_q (10^9 mol^{-1} kg s^{-1})
0.60	none	0.1	4.5 ± 0.2
	none	51	4.9 ± 0.2
	none	100	4.7 ± 0.4
	none	149	4.7 ± 0.3
	none	198	4.4 ± 0.5
	none	247	4.5 ± 0.4
	1.4 M NaCl	0.1	4.9 ± 0.4
	1.4 M NH_4Cl	0.1	5.3 ± 0.3
2.0	none	0.1	4.9 ± 0.2
	none	100	5.0
	none	198	4.8
	none	247	5.1

[a] $[(Mo_6Cl_8)Cl_6^{2-}]=(5-8)\times10^{-5}$ M, $[IrCl_6^{2-}]=(6-14)\times10^{-5}$ M.

The emission lifetime τ_0 of the cluster in hydrochloric acid (3.7 μs in 0.6 M HCl, 5.0 μs in 2.0 M HCl, 13.5 μs in 6 M HCl) is significantly shorter than that in acetonitrile (180 μs) [7]. It is not significantly affected in the presence of air [7].

Hydrochloric acid solutions containing $K_2[(Mo_6Cl_8)Cl_6]$ and $Na_2[IrCl_6]$ give visible absorption spectra corresponding to the sum of those of both solutes, and the pattern remains unchanged for more than 5 h in the dark. Table 4 gives the k_0 value obtained in the range $(0.6–1.4)\times10^{-4}$ M in $[IrCl_6]^{2-}$ (Mo complex, 5×10^{-5} M). The k_0 ($(5.0\pm0.3)\times10^9$ M^{-1} s^{-1}) is virtually independent of the concentration of HCl and other salts.

Table 4 also includes the influence of pressure upon the rate constants, which remain constant in the given range of pressure. The $\Delta V^\ddagger$ value was estimated to be 0 ± 1 cm^3 mol^{-1}.

Discussion

Regardless of whether it proceeds through electron or energy transfer, the quenching should be preceded by the approach of the sensitizer and the quencher to each other, i.e. the formation of the precursor. The overall quenching process is analyzed by the following reaction scheme

$$*S+Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \{*SQ\} \xrightarrow{k_a} \text{products} \quad (K_d=k_d/k_{-d})$$

where $*S$ and Q stand for the excited sensitizer ($*[(Mo_6Cl_8)Cl_6]^{2-}$) and the quencher ($[IrCl_6]^{2-}$), respectively, and the braces indicate the precursor. The observed k_q values in acetonitrile are considered to be smaller than the expected value of diffusion-controlled rate constants at room temperature ($>10^9$ M^{-1} s^{-1}). Also, the significant dependence of k_q on the different media indicates that k_q is not diffusion controlled. It is thus concluded that the pre-equilibrium is established much faster than the quenching process. Since K_d is expected to be much smaller than unity,* the rate (R_a) is expressed by eqn. (6).

$$R_a = k_a K_d[*S][Q] = k_q[*S][Q] \qquad (6)$$

Namely, the observed second-order rate constant k_q is equal to the product of K_d and k_a.

Table 1 shows that the quenching rate constant (k_q) of the photoexcited $[(Mo_6Cl_8)Cl_6]^{2-}$ with $[IrCl_6]^{2-}$ in acetonitrile depends significantly on the variety and concentration of the electrolytes. A change in anionic species gives no difference in the rate constant. The difference in k_q values should be primarily related to the ability of the cations to give an 'effective precursor', namely an ion-triplet between the two reactants and the cation, for the electron (or energy) transfer reaction**.

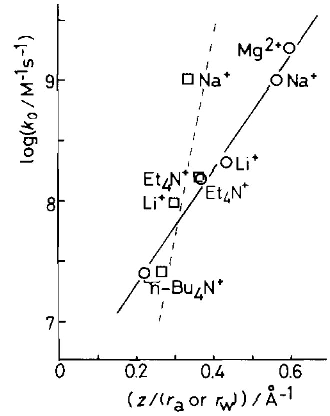

Fig. 6. Dependence of k_0 for the photoquenching reaction of $[(C_2H_5)_4N]_2[(Mo_6Cl_8)Cl_6]$ with $[(C_2H_5)_4N]_2[IrCl_6]$ in acetonitrile on $1/r_a$ (□) (r_a, Stoke's radius of the added cation in acetonitrile), and on z/r_w (○) (z and r_w are the electronic charge number and the Stoke's radius in water, respectively). All the electrolytes are added as perchlorate at 0.1 M (see text).

The significant effect of cations on the thermal electron transfer reactions between two negatively charged reactants has been discussed in several systems [22–26]. There has been a great deal of discussion as to whether the influence is seen in the precursor formation or the electron transfer stage. For thermal electron transfer reactions between two negatively charged reactants in water, the rate constant often shows a linear relationship with the reciprocal of Stokes radius of the cation. A linear relationship was also found for the photoquenching reaction of $[Pt^{II}_2(pop)_4]^{4-}$ with $[Mo(CN)_8]^{4-}$ in aqueous solution, and it was concluded that the quenching reaction takes place through precursor ion-triplet formation between the added foreign cation and the two reactant anions [13]. We have applied such an analysis to our results in acetonitrile. Figure 6 shows the plots of k_0 (second-order rate constant k_q under atmospheric pressure) against $z/r_{(a)}$ (z, charge number of the cation; r_a, Stokes radii in acetonitrile [27, 28]). For the solution containing $LiClO_4$, k_q values extrapolated to zero water concentration ($k_{q(0)}$) were used as k_0. The data are available only for the four univalent cations. Since the abscissa is spread only in a limited region, precise discussion cannot be substantiated. A similar plot of k_0 (or $k_{q(\infty)}$ (Table 1)) against z/r_w (r_w, Stokes radius in water [29]) is also given in Fig. 6. Reasonably linear correlation seems to indicate that cations with greater charge density facilitate the precursor ion-triplet formation between the two anionic reactants and the cation. The correlation between k_q and z/r_w seems to indicate the preferential solvation of water molecules in acetonitrile.

Spiccia and Swaddle gave a sophisticated discussion on the influence of alkali metal ions on the electron self-exchange rate between MnO_4^- and MnO_4^{2-} [26]. They observed lower enthalpy and more positive volume of activation for the cation assisted pathway as compared with those for the cation independent pathway, and ascribed the reason, at least partly, to the easing of solvational constraint on the formation of an ion-triplet precursor. Since the precursor formation stage would involve more significant coulombic barrier than the electron (or energy) transfer stage, extensive desolvation from the cation is expected by the interaction of solvated cations and the anionic reactants. In the present study, the $\Delta V^{\ddagger}$ value in 0.1 M $(C_2H_5)_4NClO_4$ media is negative (-8 cm^3 mol^{-1}), while that in 0.1 M $NaClO_4$ is positive ($+2.5$ cm^3 mol^{-1}). This is explained primarily by considering desolvation on precursor ion-triplet formation. The positive $\Delta V^{\ddagger}$ in $NaClO_4$ solution may result from significant desolvation of Na^+ ions. The resulting increase in volume overcompensates the volume decrease brought about by the approach of the negatively charged sensitizer and the quencher. In the case of the $(C_2H_5)_4ClO_4$ solution, the much smaller charge density of the cation results in less significant desolvation from it to give an overall negative $\Delta V^{\ddagger}$ value.

It is necessary to discuss other factors influencing the observed $\Delta V^{\ddagger}$ at this stage. The observed $\Delta V^{\ddagger}$

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*Calculation of K_d using the Fuoss equation [19] gives an approximate value of 0.2 M^{-1} at $I = 0.1$ M. The distance between the two reactants was assumed to be 10.2 Å on the basis of the X-ray structural analysis of these ions [20, 21].

**Excited state $[(Mo_6Cl_8)Cl_6]^{2-}$ may have some attractive force towards the exciplex formation with $[IrCl_6]^{2-}$ mediated by a counter cation. Such a possibility cannot be excluded. The salt effect and the pressure dependence observed in this study are similar in magnitude to those found in some thermal electron transfer reactions (*vide infra*), however, and are interpreted without considering any special excited state interaction.

should be the sum of reaction volume ΔV^0 accompanied by the precursor formation, and the activation volume $\Delta V^\ddagger$ for the electron (or energy) transfer quenching process. In each stage, pressure effect upon the volume of reacting species themselves (with suffix 'int') and that upon the solvational sphere (with suffix 'out') are considered [30].

$$\Delta V^\ddagger = \Delta V^0_{\text{int}} + \Delta V^0_{\text{out}} + \Delta V^\ddagger_{\text{in}} + \Delta V^\ddagger_{\text{out}} \qquad (7)$$

We conclude that factors other than ΔV^0_{out} give only a small contribution to the observed $\Delta V^\ddagger$ for the following reasons. It is expected in the present system that the difference in bond distance of the sensitizer and quencher before and after the electron transfer is very small. The difference in the Ir–Cl distance between $[Ir^{IV}Cl_6]^{2-}$ and $[Ir^{III}Cl_6]^{3-}$ is claimed to be 0.03 Å [21]. There is no available data as to the difference in the distances Mo–Mo, Mo–capping Cl^- and Mo–terminal Cl^- of the sensitizer before and after the electron transfer. Our crystallographic data of related mixed capping ligand complexes, $Cs_4[(Mo_6Cl_6Se_2)Cl_6]\cdot H_2O$ (Mo_6 in 12+ state) and $[(Mo_6Cl_6Se_2)Cl_6]\cdot H_2O$ (Mo_6 in 13+ state) show, however, that the difference in these distances is less than 0.03 Å [31]. By considering the very big motive force of the electron transfer [10, 18] in addition to these structural data, it is concluded that the structural change on going from the original to the transition state should be very small. The structural change should be also small when the energy transfer mechanism operates. Hence we can presume that the third and fourth terms in eqn. (7) ($\Delta V^\ddagger_{\text{in}} + \Delta V^\ddagger_{\text{out}}$) are very small. The change in the intrinsic volume of reacting species on precursor formation (ΔV^0_{int}) should be very small [30]. Participation of counter ions and solvent molecules to the activation volume of some thermal electron transfer reactions was further demonstrated recently [32–35].

In hydrochloric acid, the k_q values seem to be comparable to the diffusion controlled second-order rate constants. Activation volume is virtually zero in this medium. When the quenching rates are controlled by the rate of diffusion to give the precursor, there would be no time for the solvated molecules to rearrange to cope with the ion-triplet formation [36, 37].

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