Stereoselective Photosensitized Decomposition of Tris(oxalato)cobaltate(III) and Tris(acetylacetonato)-cobalt(III) by Tris(2,2′-bipyridine)ruthenium(II)

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The photosensitized decomposition of $[Co(ox)_3]^{3-}$ (H_2ox = oxalic acid) and $[Co(acac)_3]$ (Hacac = acetylacetone) proceeded stereoselectively in the presence of optically active $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine). Homochiral (Δ-Δ or Λ-Λ) preference for $[Co(ox)_3]^{3-}$ contrary to heterochiral (Δ-Λ) preference for $[Co(acac)_3]$ was found in aqueous solution according to the circular dichroism appearing upon decomposition of the racemic complex, and by the decomposition rate of each optical isomer. For the $[Co(ox)_3]^{3-}$ complex the selectivity varied with the addition of an organic solvent such as methanol and acetonitrile following a decrease in the decomposition rate. The factors resulting in the different stereoselectivity between the similar tris-chelate complexes containing planar bidentate ligands have been investigated. Quenching rate constants for Δ-$^*[Ru(bipy)_3]^{2+}$ obtained from emission lifetimes demonstrated the homochiral preference in the quenching process with both $[Co(ox)_3]^{3-}$ and $[Co(acac)_3]$ in aqueous solution. Chromatographic experiments using a SP-sephadex C-25 column exchanged with Δ-$[Ru(bipy)_3]^{2+}$ demonstrated the higher stability of the Δ-Δ compared with the Δ-Λ pair. It is concluded that overall selectivity is controlled by the relative and competitive rates between the back electron transfer and decomposition processes.

Chiral discrimination in association and electron transfer between optically active metal complexes has been widely studied.[1] Since Porter and Sparks[2] reported a photoinduced stereoselective decomposition of $[Co(acac)_3]$ (Hacac = acetylacetone) in the presence of Δ-$[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine), chiral discrimination has been found to be one of the most interesting but difficult problems also in photochemical processes involving excited metal complexes. Recently, the occurrence of stereoselectivity in many photochemical reaction systems has been demonstrated using steady-state and time-resolved experiments,[3-6] but the details of the mechanism remain to be elucidated.

In the photoinduced decomposition of $[Co(acac)_3]$ mentioned above, Λ-$[Co(acac)_3]$ is decomposed preferentially by electron transfer from the excited state of Δ-$[Ru(bipy)_3]^{2+}$, so that the stereoselectivity of the reaction is Δ-Λ. On the contrary, it has been generally accepted on the basis of the many investigations such as chromatographic experiments,[7,8] extraction equilibria,[9] and theoretical approaches[10] that the associated pair with the same chirality (Δ-Δ or Λ-Λ) is more stable than that with differing chiralities (Δ-Λ) for tris-chelate complexes having planar bidentate ligands such as β-diketone and α-diimine providing interaction along C_3 axis is prevented. Thus the apparent stereoselectivity in the photoinduced decomposition of $[Co(acac)_3]$ reported by Porter and Sparks is not in accord with such homochiral preference. More investigations on individual steps of the photochemical reaction are required to explain this discrepancy. For this purpose, we report herein the stereoselectivity in the photosensitized decomposition of $[Co(ox)_3]^{3-}$ (H_2ox = oxalic acid) as well as $[Co(acac)_3]$ in the presence of optically active $[Ru(bipy)_3]^{2+}$. It is known that the decomposition reactions of cobalt(III) complexes is greatly accelerated or induced by electron transfer from the excited $[Ru(bipy)_3]^{2+}$ complex which acts as a photocatalyst.[11-13] In these two systems, complicated problems such as hydrogen bonds between the associated complexes are excluded, so that the same stereoselectivity could be expected from the stereochemical viewpoint. Surprisingly, we found that the overall stereoselectivity in the reaction of $[Co(ox)_3]^{3-}$ was opposite to that of $[Co(acac)_3]$ in aqueous solution (*i.e.* homochiral preference) and varied with the solvent composition. The quenching and ion-pairing behaviours were also investigated in order to account for the selectivity in each process.

Experimental

Materials.—The complex $[Ru(bipy)_3]^{2+}$ was prepared by the general procedure[14] and its optical resolution achieved using sodium antimonyl tartrate, $Na_2[Sb_2(C_4H_2O_6)_2]\cdot 5H_2O$, by a method similar to that in the literature.[15] The Δ and Λ forms were obtained from the diastereomeric salts with lower and higher solubility, respectively. Both optical active isomers were crystallized as chlorides after anion exchange with Dowex 1-X8 (Cl^- form): α_m(298 K, 589 nm) = −901° [α_n(298 K, 589 nm) = −6745°] for Δ-$[Ru(bipy)_3]Cl_2\cdot 6H_2O$, +847° (+6341°) for Λ-$[Ru(bipy)_3]Cl_2\cdot 6H_2O$. The absolute value for the Δ isomer is slightly larger than that reported.[15] The complexes $K_3[Co(ox)_3]\cdot 3H_2O$ and $[Co(acac)_3]$ were prepared by the well established methods and optically resolved completely according to the literature.[16,17] The other chemicals used were of guaranteed reagent grade.

Measurements.—The photosensitized decomposition experiments were carried out using the same apparatus as before.[12] As light sources, two 100 W tungsten lamps or a 250 W halogen lamp were used with a lens and UV cut-off filters (Toshiba L-39, U-42) placed in front of the reaction vessel depending on the reaction efficiency. For example, an experiment for comparison of the decomposition rates between the $[Co(ox)_3]^{3-}$ and $[Co(acac)_3]$ systems was performed as follows. The sample solution (200 cm^3, pH 6–7) containing 5×10^{-5} mol dm^{-3} $[Ru(bipy)_3]^{2+}$ and 2×10^{-3} mol dm^{-3} of the cobalt complex was irradiated continuously with visible light (> 400 nm) from the halogen lamp located at the distance of 30 cm. During the reaction the temperature was kept at 25 °C and nitrogen gas was bubbled through the solution. Aliquot samples were withdrawn at appropriate times and the absorbance measured at 602 nm for the $[Co(ox)_3]^{3-}$ system and at 594 nm for the $[Co(acac)_3]$ system before and after treating with cation-exchange resin (Dowex 50W-X8, Na^+ form) to remove $[Ru(bipy)_3]^{2+}$. In order to investigate the stereoselectivity, the CD spectrum or angle of optical rotation at 589 nm of the samples was measured together with the absorbance on JASCO J-20, UNION PM-101, and Shimadzu UV-240 spectrometers, respectively.

Quenching experiments were performed at 25 °C using solutions deoxygenated with solvent-saturated argon. The emission decays were measured on a Horiba NAES-500 fluorescence lifetime measuring system equipped with a temperature-controlled circulating bath. The lifetime of Δ-$^*[Ru(bipy)_3]^{2+}$ in the absence of a quencher such as $[Co(ox)_3]^{3-}$ and $[Co(acac)_3]$ is 602 ns in water, in good agreement with the reported value.[18]

Column chromatography was carried out using a glass column (15 mm internal diameter × 250 mm) packed with SP-Sephadex C-25 cation-exchange resin which was saturated with Δ-$[Ru(bipy)_3]^{2+}$. A small amount of the Na^+-form resin was placed at the end of the column to avoid elution of Δ-$[Ru(bipy)_3]^{2+}$. A solution (1 cm³, 5×10^{-2}–5×10^{-3} mol dm^{-3}) of the racemic cobalt complexes was located on the top of the column and eluted with water or 50% methanol. The eluate was collected and the absolute configuration determined by CD measurement. As the separation was incomplete for $[Co(acac)_3]$, the eluate was collected fractionally.

Results

Stereoselective Decomposition of Racemic and Optically Active $[Co(ox)_3]^{3-}$.—When an aqueous solution containing Δ-$[Ru(bipy)_3]^{2+}$ and racemic $[Co(ox)_3]^{3-}$ was irradiated with visible light at 5 °C a CD spectrum with positive sign in the 550–700 nm region appeared. The intensity increased with decomposition of $[Co(ox)_3]^{3-}$ [Fig. 1(*a*)] and then decreased a little at the end of the reaction. The spectra, which are assigned to Λ-$[Co(ox)_3]^{3-}$,[19] demonstrate that Δ-$[Co(ox)_3]^{3-}$ was decomposed preferentially by electron transfer from excited Δ-$[Ru(bipy)_3]^{2+}$, so that Λ-$[Co(ox)_3]^{3-}$ was in excess in the solution. The optical purity of Λ-$[Co(ox)_3]^{3-}$ was estimated to *ca.* 5% e.e. (enantiomeric excess) after 180 min at which time about 70% of the initial complex had decomposed. However, the photosensitized decomposition in 20% (v/v) methanol generated no circular dichroism [Fig. 1(*b*)], and interestingly a negative CD band due to the Δ isomer arose as the decomposition proceeded in the presence of a higher methanol concentration [Fig. 1(*c*) and (*d*)]. A similar effect of the solvent composition on stereoselectivity was observed in the water–acetonitrile system. We also confirmed that the reaction in the presence of Λ-$[Ru(bipy)_3]^{2+}$ instead of the Δ isomer generated the CD spectrum of Δ-$[Co(ox)_3]^{3-}$ in water and that of Λ-$[Co(ox)_3]^{3-}$ in a 50% (v/v) methanol solution. In other words, the overall reaction shows homochiral (Δ-Δ or Λ-Λ) preference in water, but heterochiral (Δ-Λ) preference in the mixed solvents. The concentration of $[Ru(bipy)_3]^{2+}$ was kept constant during the reaction though a decrease in the optical purity was observed in proportion to the decomposition (3–25% e.e.). Fig. 2 shows the decrease in the concentration of each optical isomer of $[Co(ox)_3]^{3-}$ obtained from the absorbance and the CD intensity at the various solvent compositions. Another important feature is that the decomposition rate decreased remarkably with increasing amount of methanol. First-order rate constants are listed in the caption of Fig. 2.

Similar experiments were carried out using the optically active forms of $[Co(ox)_3]^{3-}$ in the presence of Δ-$[Ru(bipy)_3]^{2+}$. The total concentration of the cobalt complexes obtained from the absorbance and optical purity obtained from the rotatory power gave the change in the concentration of the individual Δ and Λ isomers, respectively. The results for Δ-$[Co(ox)_3]^{3-}$ are shown in Fig. 3. It clearly shows that the Δ-$[Co(ox)_3]^{3-}$ isomer

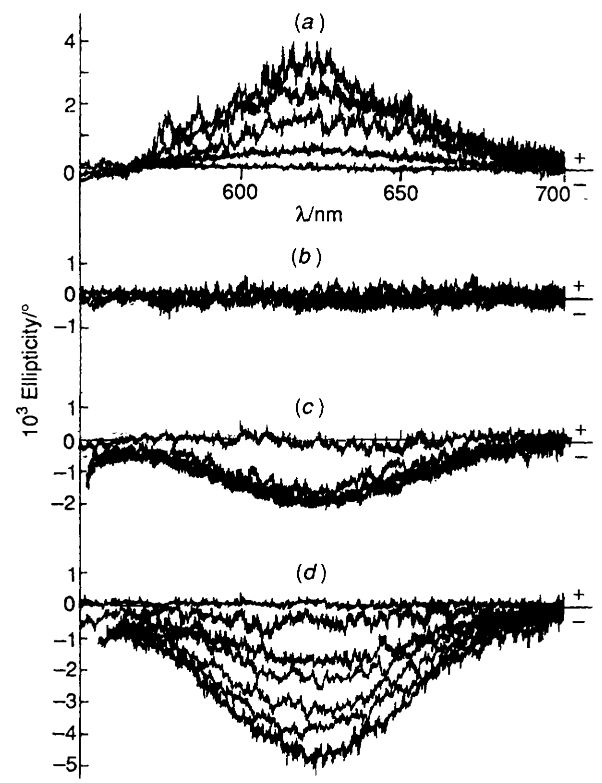


Fig. 1 The CD spectra of $[Co(ox)_3]^{3-}$ appearing upon photosensitized decomposition in the presence of 5×10^{-5} mol dm^{-3} Δ-$[Ru(bipy)_3]^{2+}$ at 5 °C in: (*a*) water, (*b*) 20% (v/v) MeOH, (*c*) 30% (v/v) MeOH and (*d*) 50% (v/v) MeOH. Spectra were obtained at 30 min intervals. The negative sign at wavelengths shorter than *ca.* 565 nm is due to the Δ-$[Ru(bipy)_3]^{2+}$ complex

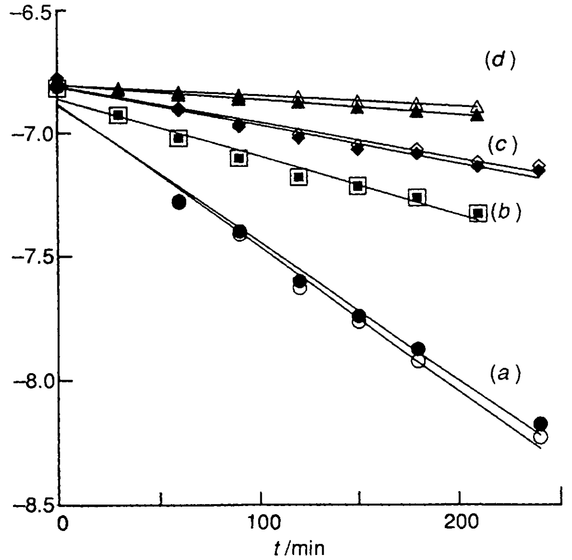


Fig. 2 First-order rate plots for the Δ and Λ isomers in the photosensitized decomposition of *rac*-$[Co(ox)_3]^{3-}$ in the presence of Δ-$[Ru(bipy)_3]^{2+}$ at various solvent compositions: (*a*) water, Δ form (○), Λ form (●), (*b*) 20% (v/v) MeOH, Δ form (□), Λ-form (■), (*c*) 30% (v/v) MeOH, Δ form (◇), Λ form (◆) and (*d*) 50% (v/v) MeOH, Δ form (△), Λ form (▲), where *c* denotes the concentration of Δ- or Λ-$[Co(ox)_3]^{3-}$. The corresponding rate constants for each isomer are as follows: 9.70×10^{-5}, 9.29×10^{-5}, 3.95×10^{-5}, 3.95×10^{-5}, 2.50×10^{-5}, 2.64×10^{-5}, 7.33×10^{-6}, 1.01×10^{-5} s^{-1}

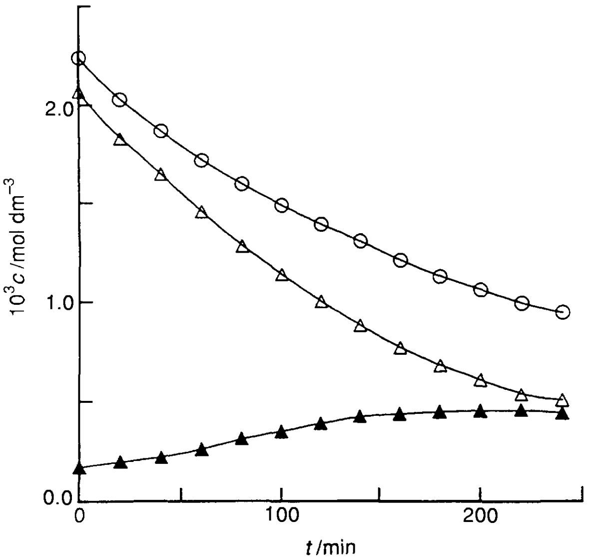


Fig. 3 Concentration changes of the Δ (△) and Λ isomer (▲) during the photosensitized decomposition of Δ-$[Co(ox)_3]^{3-}$ (85% e.e. at t = 0) in the presence of Δ-$[Ru(bipy)_3]^{2+}$: (○) total concentration of $[Co(ox)_3]^{3-}$

decreased not only because of the decomposition but also by the inversion to the Λ form during the reaction. In the absence of Δ-$[Ru(bipy)_3]^{2+}$, the inversion of the cobalt complex was negligible, whereas only slight decomposition was observed under the experimental conditions. This suggests that the inversion of the cobalt complex occurs in its divalent state generated by electron transfer from the excited ruthenium complex until it is returned to the trivalent state by back electron transfer. The variation in the concentrations of the Δ and Λ isomers as main components exhibited first-order behaviour and the rates are summarized in Table 1. The results also indicate that the reaction between the Δ-Δ pair is faster than that for the Δ-Λ pair in water, while the Δ-Λ reaction is faster in the mixed solvents. However, it was impossible to determine the decomposition and inversion rate constants of each optical isomer accurately.

Stereoselective Decomposition of $[Co(acac)_3]$.—The complex $[Co(acac)_3]$ was also decomposed stereoselectively in the presence of Δ-$[Ru(bipy)_3]^{2+}$. The CD spectrum of Δ-$[Co(acac)_3]$ appeared upon decomposition in water as reported previously.[2] In this case the Δ-Λ selectivity was always observed independent of the solvent composition as shown in Fig. 4. The experiments using optically active forms showed the same tendency in stereoselectivity, *i.e.* Δ-Λ selectivity, at all solvent compositions. As well as the $[Co(ox)_3]^{3-}$ complex, the decomposition of $[Co(acac)_3]$ was suppressed remarkably with increasing amount of methanol. In this system, however, considerable racemization and the low efficiency of Δ-$[Ru(bipy)_3]^{2+}$ as a photocatalyst prevented a quantitative treatment, as also reported by Porter and Sparks.[15]

Stereoselective Quenching.—In order to investigate the stereoselectivity in the quenching process, the luminescence decay of Δ-$[Ru(bipy)_3]^{2+}$ was measured in the presence of optically active $[Co(ox)_3]^{3-}$ and $[Co(acac)_3]$. Effective luminescence quenching by these cobalt complexes was observed similar to that by their racemic forms reported previously.[20] The decay curve of Δ-$[Ru(bipy)_3]^{2+}$ showed a single exponential behaviour at all concentrations of the quenchers $[(0\text{-}2.5) \times 10^{-4}$ mol dm$^{-3}]$. Fig. 5 shows the Stern–Volmer plots for quenching of Δ-*$[Ru(bipy)_3]^{2+}$ by Δ- and Λ-$[Co(ox)_3]^{3-}$ in water and Table 2 lists the corresponding rate constants at 25 °C at various solvent compositions: $k_q^{\Delta\text{-}\Delta}$ is a

Table 1 First-order rate constants for the photosensitized decomposition of Δ- and Λ-$[Co(ox)_3]^{3-}$ in the presence of Δ-$[Ru(bipy)_3]^{2+}$ *

Solvent	$k^{\Delta\text{-}\Delta}$/s^{-1}	$k^{\Delta\text{-}\Lambda}$/s^{-1}
Water	1.01×10^{-4}	7.97×10^{-5}
50% MeOH	1.25×10^{-5}	1.64×10^{-5}

* At 5 °C, 5×10^{-5} mol dm^{-3} Δ-$[Ru(bipy)_3]^{2+}$.

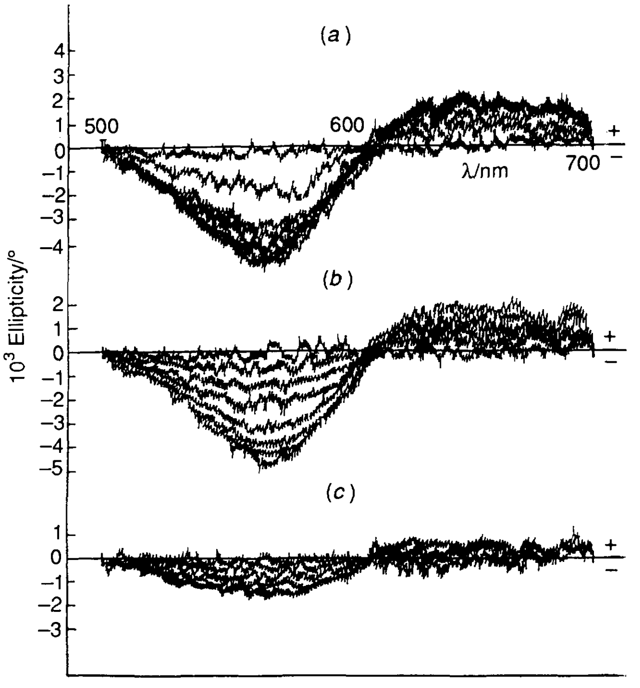


Fig. 4 The CD spectra of $[Co(acac)_3]$ appearing upon photosensitized decomposition in the presence of Δ-$[Ru(bipy)_3]^{2+}$ at 25 °C in: (*a*) water, (*b*) 20% MeOH and (*c*) 40% MeOH. The spectra were obtained at 30 min intervals; Δ-$[Ru(bipy)_3]^{2+}$ was removed just before the measurements

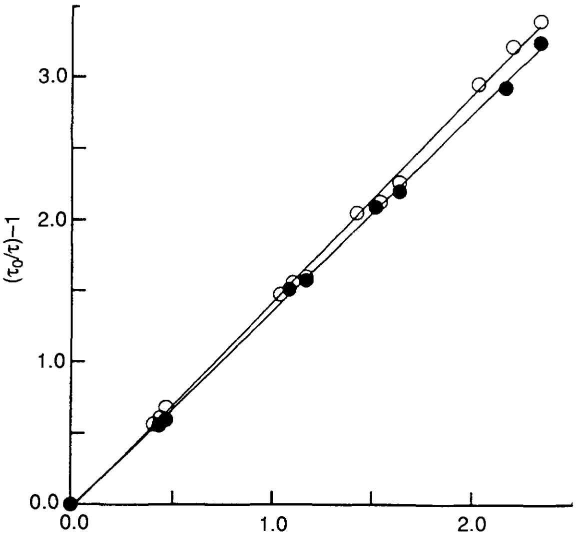
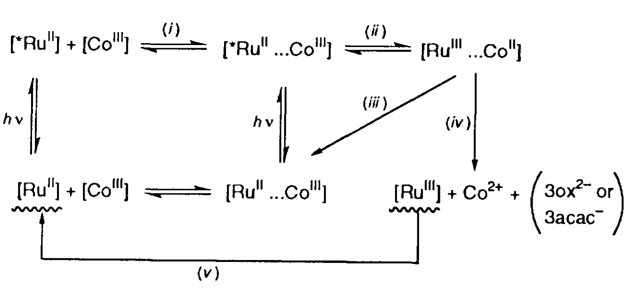


Fig. 5 Stern–Volmer plots for quenching of Δ-*$[Ru(bipy)_3]^{2+}$ by Δ-$[Co(ox)_3]^{3-}$ (○) and Λ-$[Co(ox)_3]^{3-}$ (●) in water at 25 °C

Table 2 Quenching rate constants of Δ-*$[Ru(bipy)_3]^{2+}$ by Δ and Λ forms of $[Co(ox)_3]^{3-}$ and $[Co(acac)_3]$

	$[Co(ox)_3]^{3-}$		$[Co(acac)_3]$	
Solvent	$10^{-10}k_q^{\Delta\text{-}\Delta}$/dm^3 mol^{-1} s^{-1}	$10^{-10}k_q^{\Delta\text{-}\Lambda}$/dm^3 mol^{-1} s^{-1}	$10^{-9}k_q^{\Delta\text{-}\Delta}$/dm^3 mol^{-1} s^{-1}	$10^{-9}k_q^{\Delta\text{-}\Lambda}$/dm^3 mol^{-1} s^{-1}
Water	2.42 ± 0.04	2.30 ± 0.03	1.35 ± 0.02	1.27 ± 0.02
20% (v/v) MeOH	2.00 ± 0.03	1.92 ± 0.03	—	—
50% (v/v) MeOH	1.81 ± 0.02	1.79 ± 0.02	—	—
80% (v/v) MeOH	2.69 ± 0.02	2.68 ± 0.02	—	—
EtOH	—	—	0.50 ± 0.02	0.51 ± 0.01



Scheme 1 $[Ru^{II}] = [Ru(bipy)_3]^{2+}$, $[Co^{III}] = [Co(ox)_3]^{3-}$ or $[Co(acac)_3]$. (*i*) Encounter; (*ii*) electron transfer; (*iii*) back electron transfer; (*iv*) decomposition; (*v*) reduction

little greater than $k_q^{\Delta\text{-}\Lambda}$ for both quenchers in water, though the difference is not positive in alcoholic solvents.

Stereoselectivity in Association.—Chromatographic experiments using a SP-Sephadex C-25 column exchanged with Δ-$[Ru(bipy)_3]^{2+}$ demonstrated the stability of the associated pair. When racemic $[Co(ox)_3]^{3-}$ was eluted with water, the band of $[Co(ox)_3]^{3-}$ soon separated into two. The first band eluted was confirmed to be Λ-$[Co(ox)_3]^{3-}$ and the residual component to be the Δ form by CD measurement. When 50% methanol was used as an eluent the separation was further improved. It is reasonable that the interaction between the ion pair is stronger in the solvent with lower polarity. In the case of the neutral complex, $[Co(acac)_3]$, similar stereoselective interaction was observed though the separation of the band was incomplete: Λ-$[Co(acac)_3]$ was eluted first, followed by the Δ form. Thus, the homochiral preference in association between these complexes is independent of solvent.

Discussion

Scheme 1 presents the reaction processes relating to the photosensitized decomposition. It is known that both $[Co(ox)_3]^{3-}$ and $[Co(acac)_3]$ are reduced by electron transfer from the photoexcited $[Ru(bipy)_3]^{2+}$ complex leading to decomposition in aqueous solution.[11–13,15] The oxidized $[Ru(bipy)_3]^{3+}$ complex rapidly returns to the divalent state on being reduced by the decomposition products such as oxalate and acetylacetonate ions, so that $[Ru(bipy)_3]^{2+}$ acts as a photocatalyst in the reaction.

The stereoselectivity in the decomposition in the presence of optically active $[Ru(bipy)_3]^{2+}$ was demonstrated by two methods: (*i*) the appearance of a CD spectrum in the decomposition of the racemic cobalt complexes; (*ii*) comparison of the decomposition rates for the Δ- and Λ-cobalt complexes. Both methods gave consistent results: for $[Co(ox)_3]^{3-}$, homochiral preference in water and a change in selectivity to heterochiral preference with increase in the amount of the organic solvent; on the other hand, for $[Co(acac)_3]$, heterochiral preference at all solvent compositions. Such selectivity should arise by interaction of $[Ru(bipy)_3]^{2+}$ with the cobalt complexes, so that the selectivity in the quenching process must be considered first. As shown in Fig. 5 and Table 2, for both $[Co(ox)_3]^{3-}$ and $[Co(acac)_3]$, a slight but meaningful difference between $k_q^{\Delta\text{-}\Delta}$ and $k_q^{\Delta\text{-}\Lambda}$ was obtained in aqueous solution. The tendency of the homochiral pair to be more favoured is consistent with the stability of the association between the ground-state complexes. However, the obvious difference between $k_q^{\Delta\text{-}\Delta}$ and $k_q^{\Delta\text{-}\Lambda}$ cannot be observed in alcoholic solvents.

Rexwinkel *et al.*[6a] reported a solvent dependence of stereoselectivity in the luminescence quenching of *$[Tb(pydca)_3]^{3-}$ (pydca = pyridine-2,6-dicarboxylate) by the optically active $[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline), *i.e.* Λ-Δ selectivity in water but Δ-Δ selectivity in methanol. Their results seem to correspond to ours and thus suggest that a solvent effect on the stereoselective quenching exists in our systems. On the other hand, the effect of the stereoselective ion pairing in the ground state must be taken into consideration for the stereoselective quenching. Especially in the case of $[Co(ox)_3]^{3-}$ as a quencher, the effect would not be negligible as the chromatographic experiments have demonstrated. The real rate constants k_q^0 of dynamic quenching are expressed by equation (1) where τ_0 and τ are the emission lifetimes of $[Ru(bipy)_3]^{2+}$

$$k_q\tau_0 = [(\tau_0/\tau) - 1]/[Q]_0 = k_q^0\tau_0\,[Q]/[Q]_0 \qquad (1)$$

in the absence and the presence of quencher, respectively and $[Q]_0$ and $[Q]$ are the added concentration of quencher and the concentration of free (non-associated) quencher, respectively. Equation (1) shows that k_q^0 has a larger value compared with k_q in the system where the association occurs and thus $[Q]$ is lower than $[Q]_0$. Demas and Addington[20] obtained an association constant (or ion-pairing constant), K_{eq}, of 1900 dm^3 mol^{-1} for $[Co(ox)_3]^{3-}$ in water at 21 °C from data on both the emission intensity and lifetime quenching. As we could not obtain ion-pairing constants between the optical isomers, we tried to calculate k_q at various K_{eq} values and the results are shown in Fig. 6. This shows that the corrected value of the quenching rate constant, k_q^{corr}, increases with k_{eq}. The difference between the real quenching rate constant of Δ-*$[Ru(bipy)_3]^{2+}$ by Δ- and Λ-$[Co(ox)_3]^{3-}$, $k_q^{0(\Delta\text{-}\Delta)}$ and $k_q^{0(\Delta\text{-}\Lambda)}$, respectively, is expected to be greater compared with that between apparent quenching rate constants, $k_q^{\Delta\text{-}\Delta}$ and $k_q^{\Delta\text{-}\Lambda}$, listed because the association constant for the Δ-Δ pair should be larger than that for the Δ-Λ pair. In alcoholic solution the K_{eq} value and homochiral preference for the ion-pairing in the ground state further increases. Thus the relation $k_q^{0(\Delta\text{-}\Delta)} > k_q^{0(\Delta\text{-}\Lambda)}$ could be expected also in alcoholic solution, though no obvious difference between the observed $k_q^{\Delta\text{-}\Delta}$ and $k_q^{\Delta\text{-}\Lambda}$ values is seen because of any solvent effect on the stereoselective quenching. As a result, the homochiral preference in the quenching process directly corresponds to the overall selectivity in the case of $[Co(ox)_3]^{3-}$ in water, but not in the other cases.

For $[Co(ox)_3]^{3-}$ the quenching rates are of the order of diffusion-controlled ones and the slight variation with solvent composition corresponds to the differences in viscosities of the media as was pointed out for the complex $[Co(edta)]^-$ (H_4edta = ethylenediaminetetraacetic acid) by Kaizu *et al.*[3] In spite of such efficient quenching independent of solvent, the

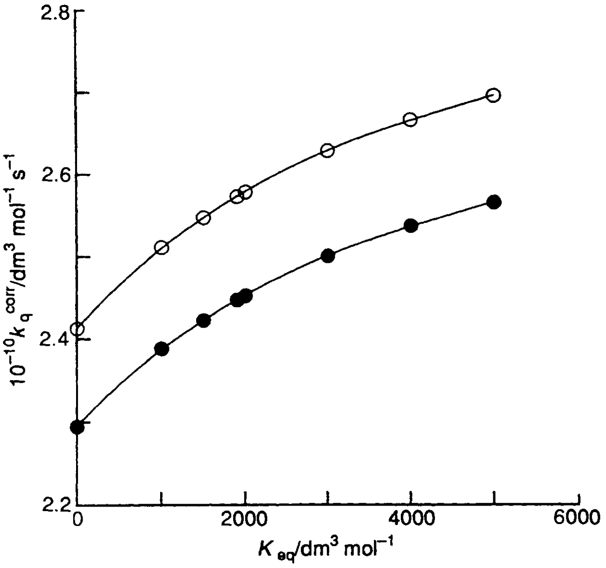


Fig. 6 Effect of ion pairing in the ground state on the quenching rate constants for Δ-*[Ru(bipy)$_3$]$^{2+}$. Quenchers: Δ-[Co(ox)$_3$]$^{3-}$ (○), Λ-[Co(ox)$_3$]$^{3-}$ (●)

decomposition rate decreased remarkably with increasing amount of methanol as shown in Fig. 2. This suggests that in the alcoholic solution the back electron transfer in Scheme 1 becomes relatively important compared with the decomposition process. It can be explained in terms of the lowering of the relative permittivity of the solvent and thus the stabilization of a transient pair after the electron transfer, {[Ru^{III}(bipy)$_3$]$^{3+}$ ··· [Co^{II}(ox)$_3$]$^{4-}$}, with increasing amount of methanol. In this situation the back electron transfer would occur easily. The solvent dependence of the overall stereoselectivity for [Co(ox)$_3$]$^{3-}$ seems to be related to the rate of the back electron transfer. In aqueous solution the Δ-Δ preference in the quenching process reflects the overall stereoselectivity because the transient ion pair dissociates rapidly. In the mixed solvent, however, the more stable pair (Δ-Δ) has a higher possibility of back electron transfer than does the corresponding Δ-Λ pair. This could explain the solvent dependence of the overall stereoselectivity for the [Co(ox)$_3$]$^{3-}$ system.

On the other hand, for [Co(acac)$_3$], a relatively large ratio of the back electron transfer to the decomposition is assumed even in aqueous solution. In fact, the photosensitized decomposition rate of [Co(acac)$_3$] is quite low compared with that of [Co(ox)$_3$]$^{3-}$ and the observed decomposition rate of [Co(acac)$_3$] is almost 1/100 of that of [Co(ox)$_3$]$^{3-}$ under the same conditions (see Experimental section). Therefore, the back electron transfer would be relatively important considering that the quenching rate constant of [Co(acac)$_3$] is about 1/10 of that of [Co(ox)$_3$]$^{3-}$.

In conclusion, the stereoselectivity in the bimolecular quenching and association is essentially homochiral for these complexes, and it reflects directly the overall selectivity in the case of [Co(ox)$_3$]$^{3-}$ in water where the decomposition of the homochiral pair [Ru^{III} ··· Co^{II}] in Scheme 1 proceeds efficiently. On the other hand, heterochiral stereoselectivity in the overall reaction is realized when the back electron transfer is more favourable compared with the decomposition process, because the more stable homochiral pair [Ru^{III} ··· Co^{II}] would be more difficult to dissociate and decompose. Thus the overall selectivity in the photochemical reactions is mainly controlled by kinetic factors, *i.e.* the relative and competitive rates between the back electron transfer and decomposition processes.

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