Structural and Mechanistic Studies of Co-ordination Compounds. Part 32.[1] Different Photochemical Pathways of Some *trans*-Dihalogenobis(ethylenediamine)ruthenium(III) Cations: Ligand-field *versus* Ligand-to-metal Charge-transfer Excited States

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It has been demonstrated that the ligand-field (l.f.) excitation of *trans*-$[Ru(en)_2I_2]^+$ (en = ethylenediamine) leads to iodide aquation with extensive stereochemical change (>85%), whereas ligand-to-metal charge-transfer (l.m.c.t.) excitation leads to iodide aquation with complete retention of configuration. For *trans*-$[Ru(en)_2X_2]^+$ (X = Cl or Br), where l.f. and l.m.c.t. bands accidentally overlap with each other, the observed photochemical behaviour of halide aquation with extensive stereochemical change is taken to occur from the l.f. excited states, whether these states are populated by direct absorption into the l.f. bands or by internal conversion from the l.m.c.t. states. The gradual decrease in the isomerization quantum yields from X = Cl through Br to I (6.2×10^{-3}, 3.2×10^{-3}, and 2.3×10^{-3} respectively) is discussed.

As part of our programme to investigate the chemistries of octahedral ruthenium(III)–amine complexes, we have reported [2–6] the syntheses of complexes of the types *trans*-$[RuLAX]^{n+}$ and *cis*-$[RuLX_2]^+$, where L represents either one quadridentate or two bidentate amines, A a monodentate ligand, and X a halide. We have also reported the kinetics of the acid [7] and base [8] hydrolysis and chromium(II) reduction [1] of some of these complexes and also the acid hydrolysis of some ruthenium(II) complexes by the method of cyclic voltammetry.[9] Ruthenium(II) complexes are, in general, much more labile than the corresponding ruthenium(III) complexes by a factor of *ca.* 10^5. The aim of the present investigation is to examine the photochemical behaviour of *trans*-$[Ru(en)_2X_2]^+$ (en = ethylenediamine; X = Cl, Br, or I).

Although the photochemistry of d^3 and d^6 systems has been extensively studied,[10,11] relatively little is known about d^5 systems. Among the ruthenium(III)–amine complexes, the photochemistry of $[Ru(NH_3)_6]^{3+}$ (ref. 12), $[Ru(NH_3)_5Cl]^{2+}$ (ref. 12), and *cis*-$[Ru(NH_3)_4X_2]^+$ (ref. 13) (X = Cl, Br, or I) has been reported. Recently, Rerek and Sheridan [14] reported the photochemistry of *cis*- and *trans*-$[Ru(en)_2Cl_2]^+$ and $[Ru(en)_2Cl(H_2O)]^{2+}$ but their conclusion as to the nature of the reaction precursors, whether ligand-field (l.f.) or ligand-to-metal charge-transfer (l.m.c.t.) states, are uncertain because l.f. and l.m.c.t. bands accidentally overlap with each other. The purpose of the present investigation is to clear this mechanistic ambiguity. Although both l.f. and l.m.c.t. bands of *trans*-$[Ru(en)_2Cl_2]^+$ occur in much the same wavelength region, the l.m.c.t. bands of *trans*-$[Ru(en)_2I_2]^+$ are well separated from the l.f. bands because of the much greater polarizability of iodide relative to that of chloride (Figure 1). It becomes, therefore, possible to investigate the photochemical behaviour of these two different excited states.

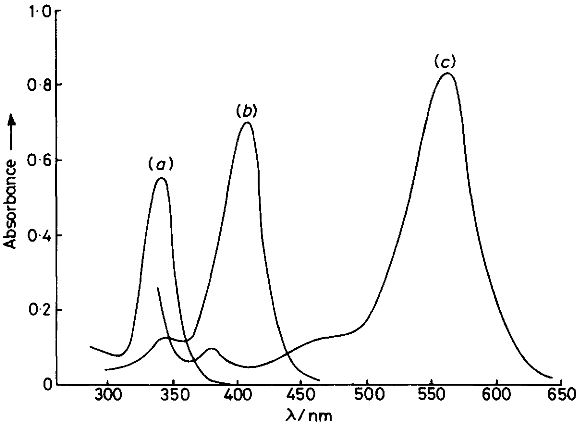


FIGURE 1 U.v. and visible absorption spectra of *trans*-$[Ru(en)_2X_2]^+$ (1.5×10^{-4} mol dm^{-3}) in toluene-*p*-sulphonic acid (1.0×10^{-2} mol dm^{-3}), optical pathlength = 1 cm: (*a*) X = Cl, (*b*) X = Br, (*c*) X = I

EXPERIMENTAL

The complexes *trans*-$[Ru(en)_2X_2][ClO_4]$ (X = Cl or Br) and *trans*-$[Ru(en)_2I_2]I$ were prepared according to published methods.[3]

Photolysis.—Photolyses were performed using a 350-W high-pressure mercury short-arc lamp (Illumination Industries, Inc.). The desired wavelength was selected using a high-intensity monochromator (Bausch and Lomb). Incident light intensities were taken from the average values measured just before and after each photolysis experiment using either a ferrioxalate actinometry [15,16] (below 450 nm) or Reinecke's actinometry [17] (above 450 nm). Electronic absorption spectra were measured with a Beckman Acta CIII spectrophotometer. To minimize any effects arising from secondary photolysis, quantum yields were determined within the first 10% of the photolysis reactions. They were found to be independent of acid concentration (0.01—0.1 mol dm^{-3}), complex concentration [(1.0—8.0) × 10^{-4} mol dm^{-3}], reaction temperature (15—30 °C), and the presence or absence of oxygen in the reaction solutions.

RESULTS

When an acidic solution of *trans*-$[Ru(en)_2I_2]^+$ was irradiated at 545 nm the intensity of the l.m.c.t. band at 563 nm gradually decreased with isosbestic points maintained at 473 and 521 nm for about 3 h of the reaction. The spectral change was identical with that of the stereoretentive thermal aquation of the complex.[18] Addition of excess NaI to the partially photolysed solution, which was then warmed to 40 °C for about $\frac{1}{2}$ h, gave back the starting *trans*-$[Ru(en)_2I_2]^+$. The pH of the solution remained unchanged during photolysis indicating that the amine ligands remained co-ordinated. Ruthenium(II) could not be detected. All these observations suggest that excitation with 545 nm light leads to the production of *trans*-$[Ru(en)_2I(H_2O)]^{2+}$. Quantum yield was calculated spectrophotometrically (ε_{I_2} = 5 420 and $\varepsilon_{I(H_2O)}$ = 720 dm^3 mol^{-1} cm^{-1} at 563 nm). Excitation at 563 nm also gave the same complex, *trans*-$[Ru(en)_2I(H_2O)]^{2+}$, with identical quantum yields.

Irradiation at 390 nm, however, leads to a different kind of spectral change with isosbestic points maintained at 473 and 514 nm for the first 3 h of the reaction. Addition of excess NaI to the partially photolysed solution gave a mixture of *cis*- and *trans*-$[Ru(en)_2I_2]^+$. Since we have not been able to obtain a reliable spectrum of *cis*-$[Ru(en)_2I(H_2O)]^{2+}$ we could not determine accurately the total aquation quantum yield and the isomeric composition of the aquoiodo products. However, it could be estimated that the product was mainly *cis* (>85%). The quantum yield for the production of *cis*-$[Ru(en)_2I(H_2O)]^{2+}$ was determined by treating the photolysed solution with excess NaI, thus regenerating the di-iodo complexes *via* the stereoretentive thermal anation reactions and then measuring the amount of *cis*-$[Ru(en)_2I_2]^+$ produced {ε values for *trans*- and *cis*-$[Ru(en)_2I_2]^+$ are 5 420 and 790 dm^3 mol^{-1} cm^{-1} respectively at 563 nm}.

The photochemistry of *trans*-$[Ru(en)_2X_2]^+$ (X = Cl or Br) is much more complicated than that of *trans*-$[Ru(en)_2I_2]^+$ since the l.f. and l.m.c.t. bands of these two complexes overlap with each other. Electronic excitation would probably populate both l.f. and l.m.c.t. excited states, at least initially, and it is not immediately clear which state is actually responsible for any observed chemical reactions. When *trans*-$[Ru(en)_2X_2]^+$ was irradiated at 363 (X = Cl) or 404 nm (X = Br), the intensity of the l.m.c.t. bands gradually decreased with isosbestic points maintained for about 3 h at 301, 326, and 372 nm (X = Cl) or at 342 and 479 nm (X = Br). Ruthenium(II) and amine aquation could not be detected. These spectral changes were quite different from those of the corresponding stereoretentive thermal aquation of the complexes.[7,18] Unfortunately, we could not obtain a reliable spectrum of *cis*-$[Ru(en)_2X(H_2O)]^{2+}$, since the aquo-complexes are rather unstable due to their ease of polymerization to oxo-bridged complexes, and accordingly, we could not determine accurately the total aquation quantum yields and the associated isomeric composition of the aquo-products. However, it could be estimated that the products were mainly *cis* (>85%) in both cases. To simplify the investigation, all complex solutions were treated with a large excess of X^- (LiX, 5—10 mol dm^{-3}), which effectively suppressed the formation of aquo-complexes and the only observed reactions were the isomerization of *trans*-$[Ru(en)_2X_2]^+$ (isosbestic points at 325 and 360 nm for X = Cl and at 383 and 437 nm for X = Br). The isomerization yields, which effectively give the quantum yields for the production of *cis*-$[Ru(en)_2X(H_2O)]^{2+}$ without being affected by any secondary photolysis effects, were determined spectrophotometrically at 343 nm (ε_{trans} = 3 930 and ε_{cis} = 1 930 dm^3 mol^{-1} cm^{-1} for X = Cl) or at 414 nm (ε_{trans} = 4 370 and ε_{cis} = 1 160 dm^3 mol^{-1} cm^{-1} for X = Br). This technique of studying photoisomerization in the presence of a large excess of X^- cannot be applied to *trans*-$[Ru(en)_2I_2]^+$ since the presence of excess I^- would complicate the reaction. All the quantum yield data are collected in the Table.

Quantum yields for the photolysis of *trans*-$[Ru(en)_2X_2]^+$ in dilute toluene-*p*-sulphonic acid (0.01 mol dm^{-3})

X	Medium (concentration)	$\lambda_{irr.}$/nm	Primary product	Quantum yield
Cl	LiCl (10 mol dm^{-3})	330	*cis*-$[Ru(en)_2Cl_2]^+$	5.9×10^{-3}
		363	*cis*-$[Ru(en)_2Cl_2]^+$	6.4×10^{-3}
Br	LiBr (5 mol dm^{-3})	363	*cis*-$[Ru(en)_2Br_2]^+$	3.3×10^{-3}
		403	*cis*-$[Ru(en)_2Br_2]^+$	3.0×10^{-3}
		430	*cis*-$[Ru(en)_2Br_2]^+$	3.2×10^{-3}
I		390	*cis*-$[Ru(en)_2I(H_2O)]^{2+}$	2.3×10^{-3}
		545	*trans*-$[Ru(en)_2I(H_2O)]^{2+}$	7.2×10^{-4}
		563	*trans*-$[Ru(en)_2I(H_2O)]^{2+}$	7.4×10^{-4}

DISCUSSION

In general, irradiation of *trans*-$[Ru(en)_2X_2]^+$ (X = Cl, Br, or I) near 400 nm leads to halide aquation with extensive stereochemical change (>85%). In the presence of a large excess of X^- (Cl^- or Br^-), the photochemistry is one of photoisomerization to *cis*-$[Ru(en)_2X_2]^+$. The isomerization yield (6.2×10^{-3}) for *trans*-$[Ru(en)_2Cl_2]^+$ agrees quite well with Sheridan's photoaquation yield [14] (5×10^{-3}) for the same complex. This seems to suggest that the photoaquation gives nearly 100% *cis*-$[Ru(en)_2Cl(H_2O)]^{2+}$. Since the photoisomerization of *cis*- and *trans*-$[Ru(en)_2Cl(H_2O)]^{2+}$ is much more efficient than the photoaquation of the dichloro-complexes [14] it is possible that the observed isomeric distribution [14] of the chloroaquo-products during the photolysis of *trans*-$[Ru(en)_2Cl_2]^+$ arises from secondary photolysis. The same is probably true for the other two complexes.

The difference in the photochemical behaviour upon irradiation of *trans*-$[Ru(en)_2I_2]^+$ at 545 and 390 nm clearly indicates that these photochemical reactions occurred from two different reaction precursors. Upon irradiating the l.m.c.t. band at 545 nm (or 563 nm), the complex would most probably terminate in the lowest doublet l.m.c.t. state. The geometry of this excited state (t_{2g}^6) would be rather similar to that of the ground state (t_{2g}^5). Therefore, the observed photoaquation with complete stereoretention is fully consistent with the known thermal aquation stereochemistry of this class of complexes, *trans*-$[Ru(en)_2X_2]^{n+}$ (n = 0 or 1, X = Cl, Br, or I).[7,18] This l.m.c.t. excited-state reaction would probably follow the same dissociative mechanism involving a square-pyramidal five-co-ordinate intermediate with the remaining halide in the apical position (apical isomer). The absence of any photoreduction of the metal centre and the overall photoinertness of this l.m.c.t. excited state (ϕ in the order of 10^{-3}) are also consistent with those of the ' well behaved ' $[Ru(NH_3)_5X]^{2+}$ (ref. 12) and *cis*-$[Ru(NH_3)_4X_2]^+$ (ref. 13) (X = Cl, Br, or I) systems.

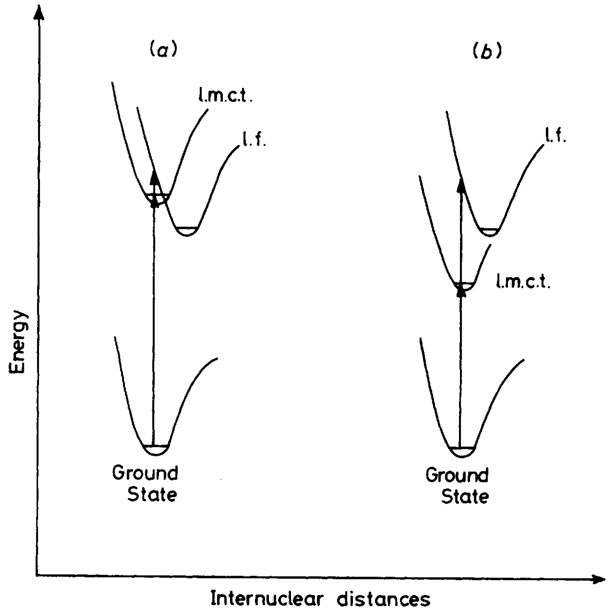
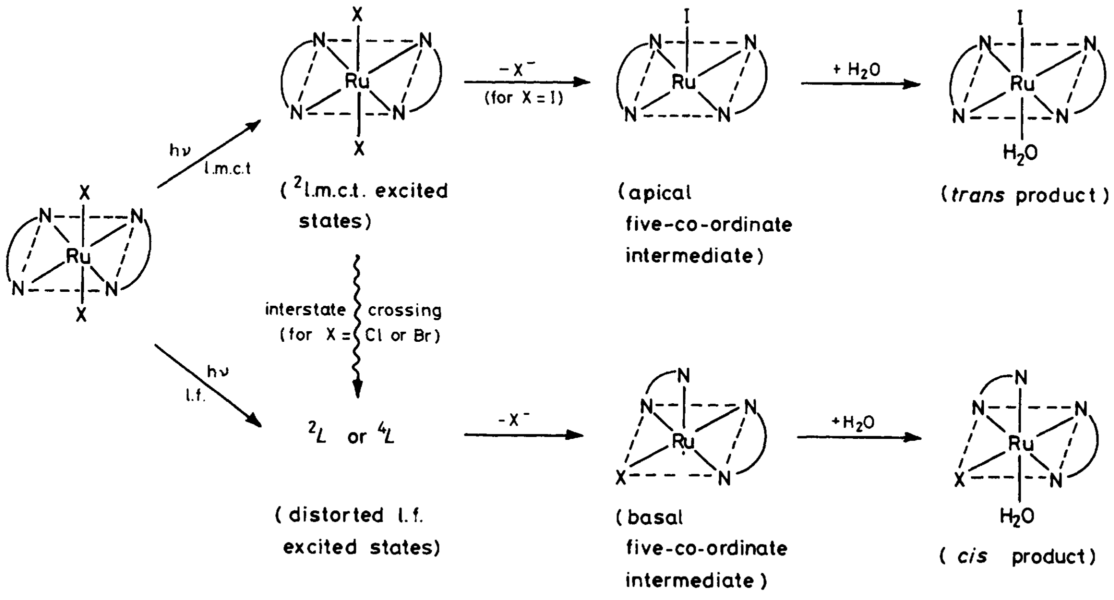


FIGURE 2 Schematic representation of the possible relative positions of lowest energy l.m.c.t. and l.f. excited states of *trans*-$[Ru(en)_2X_2]^+$: (*a*) X = Cl or Br, (*b*) X = I

However, upon irradiating the l.f. bands at 390 nm, *trans*-$[Ru(en)_2I_2]^+$ would terminate at a l.f. state, whether the lowest doublet ^2L or quartet ^4L state. The possibility of interstate crossing to a l.m.c.t. state of lower energy is unlikely, otherwise the same photochemistry of stereoretentive aquation would have been observed. The geometry of the l.f. states, with an electron in the strongly σ-antibonding (σ*) level, should be seriously distorted from that of the ground state. Therefore, it would be relatively easier for the l.f. states than the l.m.c.t. states to provide a suitable pathway for isomerization of the complex.

For *trans*-$[Ru(en)_2X_2]^+$ (X = Cl or Br), since l.f. and l.m.c.t. bands overlap with each other, both states would probably be populated initially. With reference to the photochemical behaviour of *trans*-$[Ru(en)_2I_2]^+$ discussed above, the observed photoisomerization of these two complexes would most probably come from the l.f. states. Although both l.f. and l.m.c.t. bands apparently occur at much the same place, the distorted nature of the l.f. states means that the thermally equilibrated l.f. states would be lower in energy than the relatively undistorted l.m.c.t. states (Figure 2). The fact that the quantum yields are independent of wavelengths of irradiation means that the l.m.c.t. to l.f. interstate crossing is highly efficient.

The l.f. product stereochemistry of *trans*-$[Ru(en)_2X_2]^+$ (X = Cl, Br, or I) is very similar to that of *trans*-$[Cr(en)_2Cl_2]^+$ (ref. 19) but is distinctly different from that of *trans*-$[M(en)_2Cl_2]^+$ (M = Rh[20] or Ir[11]). An associative mechanism involving a *trans* attack was suggested by Kutal and Adamson[21] to explain the specific *trans*→*cis* isomerization during the photoaquation of *trans*-$[Cr(en)_2Cl_2]^+$. Here, the observed decreasing trend of quantum yields with X (Cl > Br > I) is consistent with this mechanism since associative reactions should become less favourable with increasing bulkiness of X^-. On the other hand, the same stereochemical consequence can also be explained by a dissociative mechanism involving a square-pyramidal intermediate with the remaining halide in the basal plane (basal isomer). Although it is not possible to deduce the exact geometry of the l.f. excited states, the presence of a σ* electron along the weak-field, X–Ru–X, axis probably means that the halide ligands are bent away from this axis. This may be accompanied by the movement of some of the Ru–N bonds in order to achieve a distorted geometry with the lowest energy. The ultimate removal of a halide,



SCHEME Representation of the photochemistry of *trans*-$[Ru(en)_2X_2]^+$ (X = Cl, Br, or I) accompanied by a further but concomitant re-adjustment of the Ru–N bonds, may possibly lead to the desired basal five-co-ordinate intermediate. The observed decreasing trend of quantum yields with X^- is also consistent with this dissociative mechanism since the basal five-co-ordinate intermediate is relatively more stabilized than the apical isomer[11] by a stronger σ-donor Cl^- than the weaker Br^- and I^-.

Although it is not possible, based on the limited amount of experimental data available, to draw any firm conclusion as regards to the most probable mechanism for these l.f. excited-state reactions, a dissociative mechanism is relatively preferred. First, all ruthenium(II) and ruthenium(III) amine complexes are known to react by dissociative mechanism under thermal condition. Secondly, the l.f. states do not possess any vacant t_{2g} orbital, which is the case for the chromium(III) system, to promote associative mechanisms. Thirdly, the instability of the l.f. states with a σ* electron is best stabilized by the removal of a halide from the destabilized X–Ru–X axis.

As a conclusion, the photochemistry of *trans*-[Ru(en)$_2$X$_2$]$^+$ can be summarized by the Scheme.

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