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Contribution from the Department of Chemistry,
University of California at San Diego,
La Jolla, California 92093, and Chemistry Department,
Royal Veterinary and Agricultural University,
DK-1871 Frederiksberg C., Denmark

# Photochemistry Originating in the Ligand Field Triplet State of Rhodium(III) Amines: A Thermally Activated Process

D. Magde,*[1] G. E. Rojas,[1] and L. H. Skibsted*[2]

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Ligand field excitation of rhodium(III) amines in aqueous solution results in rather efficient photoaquation that is independent of wavelength. Early characterization[3-6] was accomplished about the same time that spectroscopic and photophysical measurements[7] at low temperatures revealed excited-state properties.

Photosubstitution occurs mostly, if not entirely, from a metastable, but very short-lived, triplet state.[8] Almost 10 years ago[9] it became possible to determine triplet-state lifetimes by measuring phosphorescence decay times, despite the fact that phosphorescence quantum yields are only $10^{-6}$. By combining photolysis quantum yields with state lifetimes, one may deduce actual photoreaction rates, which is much superior to trying to interpret only reaction yields. Given the availability of relatively precise measurements of photochemical rates, a detailed characterization of the photochemical mechanism emerged from careful studies of isomerization yields in photoaquation[10] and the effects of pressure upon reaction rates.[11] Reviews have appeared.[12-16] Evidence for a limiting dissociative pathway is persuasive, and theoretical models based on that assumption have enjoyed considerable success.[17-19]

Our work has always assumed that the photochemical reaction is a thermally activated process originating from the thermalized triplet ligand field state and that there is a competitive, nonradiative pathway that also originates from the triplet, is quite distinct, and is also thermally activated. This model leads to the simple conclusion that the chemistry of the excited state is much like the ligand substitution thermal reactivity of the ground state, except that it is speeded up by 14 orders of magnitude and has different stereoselectivity because the symmetry of the electronic wave functions is significantly different. One reason for thinking that photosubstitution is thermally activated is simply that the photochemistry, although fast, is far from instantaneous. By the standards of today's ultrafast laser kinetic studies, these triplet states, whose lifetimes typically range from 1 to 40 ns at room temperature, are truly metastable; they are 3-4 orders of magnitude longer than both the time resolution of the measuring apparatus and the time scale for thermal equilibration in a molecule of this size in aqueous solution. However, quantitative measurements of the activation energy near room temperature for photosubstitution and for nonradiative decay have been quite limited, and the significance of any attempt at a transition-state analysis of excited-state reactivity is not well established.

From measurements at 298 and 282 K, Frink and Ford[20] conclude that $Rh(NH_3)_6^{3+}$ and $Rh(ND_3)_6^{3+}$ each exhibit activation energies near 30 kJ $mol^{-1}$ for both nonradiative decay and photochemistry, with the photosubstitution activation energy being about 15% larger. This difference is comparable to the uncertainity. Furthermore, the symmetric hexaammine has the longest lived triplet (20-90 ns) among the acido ammine Rb(III) complexes and might not be typical of the entire series of complexes.

For the monohalides $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5Br^{2+}$, Bergkamp and co-workers[21] deduced activation energies that were similar in magnitude to those observed for the hexaammine but showed larger differences: For the chloride species, the photosubstitution activation energy was about double that for nonradiative decay; for the bromide species the ratio was even larger. These complexes have somewhat shorter, but still fairly long, triplet lifetimes (12-50 ns). Even so, the precision at that time, almost a decade ago, was not great. There is one totally independent measurment[8] of the apparent activation energy for the triplet lifetime of $Rh(NH_3)_5Cl^{2+}$, which was deduced to be $22.6 \pm 1.3$ kJ $mol^{-1}$. This analysis did not distinguish the photochemical process from the nonradiative process, both of which contribute to the decay of the triplet state. The numerical value is different from (approximately at the error limit of) the corresponding number in the Bergkamp paper.[21] Reviewing these analyses of activation energies, Endicott and co-workers[16] express reservations and caution "that no strong mechanistic inference is justified".

Recently our experimental capabilities progressed to the point that we could undertake a detailed study of a tetraammine complex for comparison with the hexaammine and halo pentaammines. The dibromo complex was selected as a favorable instance: It shows somewhat stronger emission than most rhodium(III) amines, presumably because a heavy-atom effect due to the two bromide ligands enhances the radiative rate constant, and it has a relatively small photochemical quantum yield $\phi_p = k_p/(k_p + k_n)$, so that variations in the photochemical rate $k_p$ are sharply distinguished from variations in the nonradiative rate $k_n$, allowing more precision.

Quantitative data on the temperature dependence of the triplet-state rate constants not only support the model of distinct, activated photochemical and nonradiative processes but also distinguish that model from an alternative. Endicott and Ferraudi[22] suggested that both the photochemical substitution pathway and the nonradiative return to the ground state might proceed through a common intermediate. If a single barrier crossing leads from the triplet to such an intermediate (a "hot ground state" of very short lifetime), which then decays with some branching ratio either to the photosubstitution product or to the ground state, one would expect a single activation energy for both processes. It is inconceivable that a hot ground state can have more than fleeting existence, and it seems very unlikely that it could have a temperature-dependent branching ratio.

## Experimental Section

**Materials.** *trans*-$[Rh(en)_2Br_2]ClO_4$ was prepared as described previously.[10]

**Photolysis Experiments.** Continuous-wave photolyses were carried out in aqueous solutions by the same methods described previously.[23] Temperature control was better than ±1 K. Light intensities were measured by ferrioxalate actinometry.[24] The photochemical quantum yields were determined from spectral and pH changes as described previously.[10,23]

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(2) Royal Verterinary and Agricultural University.
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**Table I.** Measured Quantum Yields for Bromide Ligand Aquation of *trans*-$[Rh(en)_2Br_2]^+$ in Aqueous $10^{-3}$ M $HClO_4$[a]

| $T$/°C | $\phi_c$/mol einstein$^{-1}$ | no. of expts | $T$/°C | $\phi_c$/mol einstein$^{-1}$ | no. of expts |
|---|---|---|---|---|---|
| 6.6 | 0.0294 (12) | 2 | 25.0 | 0.047 (1) | *b* |
| 12.7 | 0.0364 (12) | 2 | 28.9 | 0.0467 (20) | 3 |
| 18.9 | 0.0407 (26) | 3 | | | |

[a] $\lambda_{irr}$ = 436 nm. [b] From ref 10; $\lambda_{irr}$ = 366, 405, and 436 nm.

**Table II.** Measured Lifetimes for Phosphorescent Emission from *trans*-$[Rh(en)_2Br_2]^+$ in Aqueous $10^{-3}$ M $HClO_4$[a]

| $T$/°C | $\tau$/ns | $T$/°C | $\tau$/ns | $T$/°C | $\tau$/ns |
|---|---|---|---|---|---|
| 8 | 2.9 | 17 | 2.4 | 29 | 1.95 |
| 11 | 2.7 | 24 | 2.25 | 36 | 1.85 |

[a] $\lambda_{exc}$ = 458 nm; estimated standard deviation 5%.

**Emission Lifetime Measurements.** The phosphorescence lifetimes were measured by using single-photon time correlation, as described previously.[10] Excitation was with a mode-locked argon ion laser operating at 458 nm. The detection monochromator had a 5-nm band-pass; phosphorescence lifetimes were measured at 750 nm. The instrument response function was determined by measuring the Raman scattering of water at 550 nm. Sample solutions were circulated continuously by a small peristaltic pump from a reservior of 20 mL through a fused silica sample cell of 1 cm optical path. Both the reservoir and the optical cell were thermostated to better than ±1 K.

## Results and Discussion

The lowest excited state of rhodium(III) complexes lives a few nanoseconds. Three processes contribute to its decay

$$\tau^{-1} = k_c + k_n + k_r \tag{1}$$

where $\tau$ is the actual lifetime of the state, $k_c$ is the rate constant for photoaquation, $k_n$ is the rate constant for nonradiative decay to re-form the ground state of the molecule by intersystem crossing, and $k_r$ is the radiative rate for phosphorescence. The rate constants and the state lifetime determine the quantum yields $\phi_x$:

$$\phi_c = k_c\tau \tag{2a}$$

$$\phi_n = k_n\tau \tag{2b}$$

$$\phi_r = k_r\tau \tag{2c}$$

We assume that the radiative rate is constant near room temperature but the other processes exhibit Arrhenius behavior:

$$k_c(T) = k^0{}_c \exp[-E_c/RT] \tag{3a}$$

$$k_n(\mathrm{T}) = k^0{}_n \exp[-E_n/RT] \tag{3b}$$

$$k_r = k^0{}_r \tag{3c}$$

Both $k_c$ and $k_n$ are on the order of $10^9$ s$^{-1}$, while the radiative rate is on the order of $10^3$ s$^{-1}$. Consequently, to an excellent approximation

$$\phi_n = 1 - \phi_c \tag{4}$$

The experimental values of $\phi_c$ and $\tau$ are collected in Tables I and II. Since the photochemical and phosphorescence measurements were not carried out at the same temperatures, we use an iterative procedure to find a self-consistent solution of (1)–(4) that optimizes simultaneously the fit to (3a) and (3b). The final best-fit Arrhenius plots for the temperature dependence of the experimental measurements are displayed in Figure 1. The Arrhenius activation energies are $E_c$ = 26.6 ± 4.0 kJ mol$^{-1}$ and $E_n$ = 11.0 ± 2.0 kJ mol$^{-1}$. The preexponential factors are $k^0{}_c$ = (9.46 ± 5.90) × $10^{11}$ s$^{-1}$ and $k^0{}_n$ = (3.81 ± 1.50) × $10^{10}$ s$^{-1}$.

Using the results of the simultaneous regression analysis of (3a) and (3b), we calculate the rate constants and quantum yields for photoaquation and nonradiative decay of *trans*-$[Rh(en)_2Br_2]^+$ at the standard temperature, 25 °C. These are $k_c$ = (2.11 ± 0.22) × $10^7$ s$^{-1}$, $k_n$ = (4.43 ± 0.33) × $10^8$ s$^{-1}$, $\phi_c$ = 0.0455 ± 0.0010, $\phi_n = 1 - \phi_c$, and $\tau = (k_c + k_n)^{-1}$ = (2.15 ± 0.15) × $10^{-9}$ s. Uncertainties are much less than for the activation energies and preexponential factors because the latter are correlated; lower activation energies are permitted only if the preexponential factors are reduced simultaneously. Finally, the kinetic parameters can be expressed in the terminology of transition-state theory,[25] giving the results displayed in Table III. Also included in Table III are the transition-state parameters for $Rh(NH_3)_5Br^{2+}$, which is the sole instance among those measured previously for which the reported precision seems adequate to support the claim that $E_c$ differs from $E_n$.

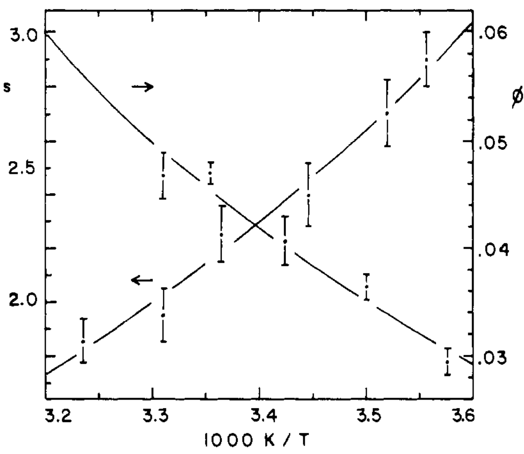

**Figure 1.** Temperature dependence of photoaquation quantum yields, $\phi_c$, and triplet lifetimes, $\tau$, versus reciprocal temperature. The lines are the best fit to (3a) and (3b) satisfying all the constraints (1–4) simultaneously.

**Table III.** Thermodynamic Parameters for Transition-State Analysis of Triplet-State Processes in Two Rh(III) Complex Ions[a]

| | *trans*-$[Rh(en)_2Br_2]^+$ | $Rh(NH_3)_5Br^{2+}$ | units |
|---|---|---|---|
| $\Delta G_c{}^{\ominus *} = -RT \ln [k_c h/k_B T]$ | 31.3 ± 0.3 | 31.9 ± 0.5 | kJ mol$^{-1}$ |
| $\Delta H_c{}^{\ominus *} = E_c - RT$ | 24 ± 4 | 40 ± 14 | kJ mol$^{-1}$ |
| $\Delta S_c{}^{\ominus *} = (\Delta H_c{}^{\ominus *} - \Delta G_c{}^{\ominus *})/T$ | −24 ± 14 | 28 ± 46 | J mol$^{-1}$ K$^{-1}$ |
| $\Delta G_n{}^{\ominus *} = -RT \ln (k_n h/k_B T)$ | 23.7 ± 0.3 | 28.4 ± 0.3 | kJ mol$^{-1}$ |
| $\Delta H_n{}^{\ominus *} = E_n - RT$ | 8.6 ± 2.0 | 16 ± 5 | kJ mol$^{-1}$ |
| $\Delta S_n{}^{\ominus *} = (\Delta H_n{}^{\ominus *} - \Delta G_n{}^{\ominus *})/T$ | −51 ± 11 | −40 ± 17 | J mol$^{-1}$ K$^{-1}$ |

[a] Data for $Rh(NH_3)_5Br^{2+}$ calculated from $k_c$, $k_n$, $E_c$, and $E_n$ in ref 21.

From this kinetic analysis, we draw the following conclusions:

1. The photoaquation that takes place from the triplet state of this compound and, no doubt, similar halo amine rhodium complexes is an activated process.

2. The nonradiative intersystem crossing that accounts for most of the decay of the triplet state is also an activated process.

3. Even for states with lifetimes near 2 ns, a factor of 10 shorter than the lifetimes of the Rh(III) complexes treated previously, experimental techniques are now adequate to distinguish the various rate constants that together determine lifetimes and quantum yields and give enough information about their variations with temperature so that transition-state analysis is possible. Of course, the precision possible for such weak emitters ($k_r$ = $10^3$ s$^{-1}$; $k_n$ = $10^9$ s$^{-1}$; $\phi_r$ = $10^{-6}$) is still limited.

4. The photoaquation process and the nonradiative decay are characterized by distinctly different kinetic parameters. The activation energies and the preexponential factors are quite different. The two processes must be passing through different transition states out of the triplet; they cannot be passing over a common barrier out of the triplet state to form some sort of hot-ground-state intermediate and then branching onto alternative

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pathways that lead either to photoproducts or back to the starting material, as suggested by one model discussed in the beginning of the paper. Of course, it remains possible to invent even more complicated schemes that postulate two distinct transition states, one of which leads to such an intermediate (hot ground state), and thus preserve all features of both models, but it would be a formidable experimental task to obtain experimental evidence for such a complicated scheme in these compounds.

5. Even if one rightly emphasizes that the precision of transition-state thermodynamic parameters measured for short-lived excited states is not as good as one would expect for stable ground states, it is difficult to ignore the fact that a consistent pattern is emerging for Rh(III) complexes. In every case $E_c$ exceeds $E_n$, and this result really only depends on the observation that the photochemistry is "more temperature sensitive" than is the phosphorescence lifetime, so that photochemical yield increases at higher temperatures despite the fact that the lifetime is reduced.

Table III invites further speculation. We caution against overinterpretation of the numerical quantities. However, the qualitative conclusions seem plausible: For both compounds, photosubstitution processes exhibit larger activation energies but smaller entropy changes in the activated state than do nonradiative decay processes. Dissociation apparently requires considerable enthalpy input, albeit far less than is required for the thermal substitution processes. For *trans*-$[Rh(en)_2Br_2]^+$, the activation entropy is negative: there is some increased ordering necessary to form the transition state, but the effect is not too restrictive. In that complex the photochemical substitution is $Br^-$ aquation. In contrast, in $Rh(NH_3)_5Br^{2+}$, the photochemical substitution is $NH_3$ aquation and for the latter process, which does not involve the same charge separation, the activation entropy appears to be positive, although the uncertainty is sufficiently large that one cannot be certain. In contrast, nonradiative decay, in these systems near room temperature, is dominated by a process that requires some enthalpy, but less than is needed for the photoaquation reaction; however, it occurs through a rather highly ordered transition state that involves a decrease of entropy that is significantly greater than what is required for photoaquation. Of course, much of the entropy contribution to both processes is expected to relate to ordering the surrounding solvent shell. When the two different complexes are compared, it seems that the difference in their nonradiative rates is predominately an enthalpic effect.

We conclude with the observation that excited electronic states with lifetimes as short as 1 ns are true metastable chemical species. They exhibit a chemistry that is distinctly different from that of the ground state of the same molecules, but that chemistry can be subjected to the same systematic investigation and thermodynamic interpretation.

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Contribution No. 7759 from the A. A. Noyes Laboratory
of Chemical Physics, California Institute of Technology,
Pasadena, California 91125

## Two More Space Group Revisions

Richard E. Marsh

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The space groups (and atom coordinates) of two crystal structures reported in a recent issue of *Inorganic Chemistry* (Vol. 27, No. 4; Feb 24, 1988) should be revised. In both cases the structures were reported as triclinic, and the revised structures are *C*-centered monoclinic, one in space group $C2/m$ and the other in $C2/c$.

**Table I.** Coordinates (×10$^4$ for Cu, Cl, and N; ×10$^3$ for C) for TMCuC in Space Group $C2/m$[a]

| | $x'$ | $y'$ | $z'$ | $x'$ | $y'$ | $z'$ |
|---|---|---|---|---|---|---|
| Cu(1) | 0 | 0 | 0 | 0 | 0 | 0 |
| Cu(2) | 0 | 0 | 5000 | 0 | 0 | 5000 |
| Cl(1) | 1222 (2) | −4 (4) | 2079 (4) | 1222 | 0 | 2079 |
| Cl(2a) | −550 (3) | −1628 (7) | 2409 (8) | −551 | 1640 | 2358 |
| Cl(3a) | −552 (4) | 1651 (8) | 2306 (9) | | | |
| Cl(2) | −640 (4) | −1945 (6) | 3077 (7) | −632 | 1926 | 3050 |
| Cl(3) | −623 (3) | 1907 (6) | 3024 (7) | | | |
| N | −1672 (4) | −4992 (7) | 7500 (9) | −1672 | 5000 | 7500 |
| C(1) | −202 (2) | −369 (4) | 845 (6) | −204 | 370 | 843 |
| C(2) | −205 (2) | −628 (3) | 841 (6) | | | |
| C(3) | −186 (3) | −498 (6) | 533 (3) | −186 | 500 | 533 |
| C(4) | −77 (1) | −503 (6) | 796 (7) | −77 | 500 | 796 |
| C(1a) | −153 (2) | −498 (6) | 970 (3) | −153 | 500 | 970 |
| C(2a) | −214 (2) | −627 (2) | 687 (7) | −215 | 372 | 687 |
| C(3a) | −216 (2) | −372 (4) | 687 (7) | | | |
| C(4a) | −88 (2) | −497 (5) | 652 (6) | −88 | 500 | 652 |

[a] The values on the left are obtained by transforming the coordinates in Table III, ref 1, as described in the text; values on the right are obtained by symmetrizing and averaging according to $C2/m$.

**(1) Tetramethylammonium Trichlorocuprate(II) (TMCuC) at 323 K.**[1] The structure was described in space group $P\bar{1}$, with $a$ = 9.082 (5) Å, $b$ = 9.073 (5) Å, $c$ = 6.442 (3) Å, $\alpha$ = 90.05 (4)°, $\beta$ = 92.40 (4)°, $\gamma$ = 119.99 (3)°, and $Z$ = 2. The lattice vectors [210], [010], and [001] define a *C*-centered cell with $a'$ = 15.732 Å, $b'$ = 9.073 Å, $c'$ = 6.442 Å, $\alpha'$ = 90.05°, $\beta'$ = 92.80°, $\gamma'$ = 90.02°, and $Z$ = 4; the corresponding transformations $x' = {}^1/_2x$, $y' = y - {}^1/_2x$, and $z' = z$ lead to the coordinates in the left-hand columns of Table I. When these coordinates are symmetrized and, in some cases, averaged so as to conform to space group $C2/m$, the values in the right-hand columns of Table I result.

Except for the four disordered atoms Cl(2a), Cl(3a), Cl(2), and Cl(3), none of the symmetrizing shifts is larger than expected from the reported esd's. For these four chlorine atoms, the necessary shifts are much greater than the esd's, ranging up to 0.035 Å. However, the proposed disorder[1] is such that pairs of disordered atoms are separated by only 0.53 Å; the electron density associated with these sites is undoubtedly diffuse and can probably be modeled in several ways. (The carbon atoms are also disordered, but for them the separations are about 1.0 Å or more so resolution is complete.)

Space group $C2/m$ is more attractive than $P\bar{1}$ on the general grounds of symmetry relationships in phase transitions. The structure represents an intermediate-temperature (323 K) phase that undergoes a transition (probably first order) at 319 K to a low-temperature phase with space group $P2_1$ and another transition (probably second order) at about 373 K to a high-temperature phase with space group $P6_3/mmc$.[1] Symmetry $C2/m$ for the intermediate phase is then far more logical than symmetry $P\bar{1}$, in view of the transition to the low-temperature and (presumably) lower symmetry phase with space group $P2_1$: a $2_1$ axis is contained within the symmetry elements of $C2/m$ but not of $P\bar{1}$.

**(2) $Fe(C_6H_8N_2S_2)_2(NCS)_2$. Polymorph B.**[2] The structure of this crystalline form of bis(2,2′-bis-2-thiazoline)bis(thiocyanato)iron(II) was also described in space group $P\bar{1}$, with $a$ = 10.846 (3) Å, $b$ = 10.847 (3) Å, $c$ = 12.526 (4) Å, $\alpha$ = 115.72 (2)°, $\beta$ = 93.92 (2)°, $\gamma$ = 119.97 (2)°, and $Z$ = 2. The vectors [210], [0$\bar{1}$0], [$\bar{1}\bar{1}\bar{1}$] define a *C*-centered cell with $a'$ = 18.792 Å, $b'$ = 10.847 Å, $c'$ = 11.754 Å, $\alpha'$ = 90.03°, $\beta'$ = 116.65°, $\gamma'$ = 90.03°, and $Z$ = 4; the corresponding transformations $x' = {}^1/_2(x - z) + 0.25$, $y' = -y + {}^1/_2(x + z) - 0.25$, and $z' = 1 - z$ (the translations of 0.25 in $x'$ and $y'$ are necessary to place the origin at a conventional center of symmetry) lead to coordinates that are compatible with space group $C2/c$ within their esd's. These

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