

Photosensitization of Tetrakis(amine)rhodium(III) Complexes $[\text{Rh}(\text{L})_4\text{XY}]^+$ Mariel M. Muir* and Hector M. Torres¹

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Photosensitization by biacetyl was observed for complexes of the type $\text{trans}-[\text{Rh}(\text{L})_4\text{X}_2]^+$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-$; $\text{L} = \text{heterocyclic amine}$) or $\text{trans}-[\text{Rh}(\text{py})_4\text{ClY}]^+$ ($\text{Y} = \text{Br}^-, \text{CN}^-$) in aqueous solution. The quantum yields for the direct photoaquation of halide or CN^- and of amine were nearly the same as the limiting sensitization quantum yields for these complexes, which were of the order of magnitude of 0.01–0.3 mol/einstein. Measurements of the quenching of the biacetyl emission showed that all the complexes quenched the phosphorescence of biacetyl but not its fluorescence. The bimolecular quenching rate constants k_q varied from about 1.1×10^8 to $2.0 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ and decreased as the field strength of the ligands increased.

Introduction

Complexes of the type $\text{trans}-[\text{Rh}(\text{L})_4\text{XY}]^+$, where X and Y are halide or pseudohalide and L is a heterocyclic amine, undergo photoaquation in aqueous solution to give the corresponding aquo complex and free X^- , Y^- , or L .^{2–4} The distribution of photo-products and the geometrical course of the reaction differ significantly from those of the reaction of analogous complexes in which L is NH_3 .^{5,6} For some of the complexes with heterocyclic amines, the major reaction is photoaquation of amine, while the NH_3 complexes give only minor amounts of NH_3 . The stereomobility observed for the NH_3 complexes has not been observed for the complexes with heterocyclic amines.⁴ Thus, it seemed of interest to probe the nature of the excited states of the complexes with heterocyclic amines for comparison with those of the NH_3 complexes. Since the triplet state has been shown⁷ to be important for the NH_3 complexes of Rh(III), the triplet sensitizer biacetyl was selected for indirect photolysis and quenching experiments.

Experimental Section

Materials. The materials $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{RhBr}_3 \cdot 2\text{H}_2\text{O}$ (Strem Chemicals), pyridine (py), and 1-methylimidazole (mim) (Fisher Scientific Co.), thiazole (tz) (Aldrich Chemicals), and biacetyl and pyrazole (pz) (Fluka) were used as received, except biacetyl. Biacetyl was distilled under N_2 using an Auto Annular Teflon spinning-band distillation column, Perkin-Elmer Model 251. The purity of the distilled biacetyl was greater than 99.9% by capillary GC analysis. The water used as a solvent for the photolyses was triply distilled.

The following complexes were prepared and characterized by methods from the literature: $\text{trans}-[\text{Rh}(\text{py})_4\text{Cl}_2]\text{Cl} \cdot 5\text{H}_2\text{O}$,⁸ $\text{trans}-[\text{Rh}(\text{py})_4\text{Br}_2] \cdot \text{Br} \cdot 6\text{H}_2\text{O}$,^{8,9} $\text{trans}-[\text{Rh}(\text{py})_4\text{I}_2] \cdot \text{I} \cdot 2\text{H}_2\text{O}$,⁴ $\text{trans}-[\text{Rh}(\text{py})_4\text{CN}_2] \cdot \text{CN} \cdot 2\text{H}_2\text{O}$,⁴ $\text{trans}-[\text{Rh}(\text{py})_4\text{ClBr}]\text{Cl} \cdot 3\text{H}_2\text{O}$,⁴ $\text{trans}-[\text{Rh}(\text{py})_4\text{Cl}(\text{CN})]\text{Cl} \cdot \text{H}_2\text{O}$,⁴ $\text{trans}-[\text{Rh}(\text{tz})_4\text{Cl}_2]\text{ClO}_4$,^{8,10} $\text{trans}-[\text{Rh}(\text{pz})_4\text{Cl}_2]\text{NO}_3 \cdot \text{H}_2\text{O}$,⁸ and $\text{trans}-[\text{Rh}(\text{nmiz})_4\text{Cl}_2]\text{Cl} \cdot 3\text{H}_2\text{O}$.⁸ These complexes were converted to nitrate salts by dissolving 0.30 g of the halide salt of the complex in boiling 30% water-ethanol (10 mL) and filtering the hot solution with suction over 1 g of NaNO_3 . All of the complexes were recrystallized from methanol, and

their elemental analyses for C, H, and N or halogen gave satisfactory agreement with the calculated values. Preparation of the Reinecke actinometer was carried out under weak red light. $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ (10.0 g, Fisher Scientific Co.) was dissolved in 20 mL of warm distilled water (40–50 °C), and an excess of KNO_3 (3.6 g) was added to the solution. The solution was cooled in an ice bath and filtered. The precipitate was recrystallized 10 times from a 10% KNO_3 aqueous solution (50 °C). The final precipitate was washed with cold distilled water and kept over P_2O_5 in the dark until use.

Physical Measurements. UV-vis absorption spectra were measured on a Perkin-Elmer Lambda 4B spectrophotometer. Steady-state emission spectra were measured with a Perkin-Elmer MPF-3 fluorescence spectrometer. The concentrations of halide (Cl^- , Br^- , I^-) and CN^- released during photolysis were measured with the corresponding Markson ion-selective electrode, a Markson double-junction reference electrode, and a Radiometer PHM84 pH meter.

Direct Photolysis. The apparatus and conditions for the direct photolyses of the complexes have been described previously.^{3,4} In order to maintain a relatively constant ionic strength, 30 μL of 1 M NaNO_3 was added to 3.0 mL of the complex in aqueous solution. The concentration of complex ranged from 0.5 to 3 mM. The Reinecke actinometer¹¹ was used to determine the intensity of the incident light. The duration of photolysis was adjusted so that the maximum extent of reaction was less than 20%. The wavelength of photolysis corresponded to the absorption maximum of longest wavelength, as reported previously.⁴ Changes in UV-vis absorption spectra were followed by stopping the photolyses and recording the spectrum.

Quantum yields were determined from the amount of light absorbed and the amount of each ligand liberated during the photolysis. The concentration of halide or cyanide was determined from potentiometric measurements with the appropriate ion-sensitive electrode and double-junction reference electrode. A calibration curve for that ion was used to convert the potential to concentration. The minimum concentration that could be detected was 105 ppb for Cl^- , 40 ppb for Br^- , 1 ppb for I^- , and 2 ppb for CN^- . The amount of heterocyclic amine released during the photolyses was measured by a modification of the Fritz method.^{4,12} Aliquots of the reaction mixture were kept in the dark in order to provide a blank correction to the measurements of free-ligand concentration and the absorbance.

Indirect Photolysis.¹³ The aqueous solutions were prepared to be 0.4 M in biacetyl, and the concentration of the complex ranged from 0.1 to 3 mM. In this range of concentration, the absorbance of the complex at the photolysis wavelength was less than 5% of the total absorbance, so that direct photolyses of the complexes could be neglected. The only exception to this was $\text{trans}-[\text{Rh}(\text{py})_4\text{I}_2]^+$, where the absorbance was about 50% of the total absorbance, so that the contribution of the direct photolysis of the complex was subtracted from the amounts of ligand liberated. The ionic strength of the solutions was maintained nearly constant with $\mu = 0.01 \text{ M}$ by using 0.01 M NaNO_3 to prepare the solutions. Solutions

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Table I. Quantum Yields for Direct Photoaquation and Sensitized Photoaquation, Bimolecular Quenching Rate Constants k_q , and Stern–Volmer Intercepts for *trans*- $[\text{Rh}(\text{L})_4\text{XY}]^+$

X	Y	L	$10^2\Phi(\text{X})$		$10^2\Phi(\text{Y})$		$10^2\Phi(\text{L})$		$10^{-8}k_q^a$	intercept ^b
			dir ^c	lim ^d	dir	lim	dir	lim		
Cl	Cl	py	1.07 (3)	1.06 (1)			4.04 (9)	3.92 (1)	1.2 (1)	0.97 (6)
Br	Br	py	3.5 (1)	3.44 (2)			2.7 (1)	2.70 (1)	1.71 (7)	1.08 (5)
I	I	py	3.7 (4)	3.67 (3)			3.62 (7)	3.58 (1)	2.0 (1)	1.2 (1)
CN	CN	py	11.7 (9)	10.9 (1)			4.10 (5)	3.88 (1)	1.11 (6)	1.01 (3)
Cl	Br	py	31.5 (9)	30.6 (2)	2.7 (6)	2.8 (2)	1.47 (4)	1.52 (2)	1.32 (6)	0.99 (3)
Cl	CN	py	33.4 (9)	32.0 (7)	8.6 (8)	8.2 (1)	5.14 (7)	5.07 (5)	1.15 (3)	1.09 (3)
Cl	Cl	tz	0.65 (6) ^e				8.7 (5)	8.37 (1)	1.32 (5)	1.03 (4)
Cl	Cl	pz	0.40 (1) ^f				8.6 (1)	8.50 (1)	1.12 (6)	0.99 (3)
Cl	Cl	mim	3.42 (9)	3.32 (4)			1.13 (8)	1.21 (1)	1.19 (5)	0.98 (3)

^a Values in $\text{L mol}^{-1} \text{s}^{-1}$ calculated from the slope K_{SV} of the Stern–Volmer quenching plot and $\tau_0 = 0.001$.¹⁴ ^b Intercepts of the Stern–Volmer plots for quenching of triplet biacetyl. ^c Values of the quantum yield for direct photoaquation. ^d Values of limiting quantum yields for sensitized photoaquation were obtained from a plot of $1/\Phi_s$ vs $1/[\text{complex}]$. ^e Value taken from ref 4. ^f Value taken from ref 3.

of biacetyl were allowed to stand for 1 day before use so that equilibrium between biacetyl and its hydrate was achieved.

The photolysis apparatus used in the indirect photolysis was the same as that used in the direct photolysis experiments. The emission slit of the monochromator was set at 3.00 nm, and the bandwidth of the incident light was ± 5 nm. A sample of 3.00 mL of the solution was placed in a long-neck 1.00-cm quartz spectrophotometer cell sealed with a rubber septum. The solutions were deaerated for 10 min by passing Cr^{2+} -scrubbed Ar through them, since the biacetyl triplet is quenched very efficiently by oxygen.¹⁴ Following the bubbling of Ar, the sample top was wrapped with paraffin film. The solutions were irradiated at 400 nm, in the biacetyl $\text{S}_1 \leftarrow \text{S}_0$ band. Quantum yields for the various photoaquation processes as a function of the concentration of the complex were determined from the amount of the various ligands liberated from the complex and the amount of light absorbed by biacetyl. The absorption spectra of the irradiated solutions were compared to that of an aliquot which had been kept in the dark for at least 1 h.

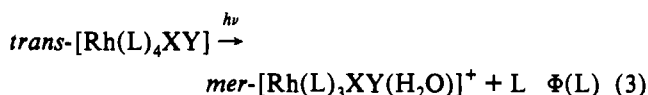
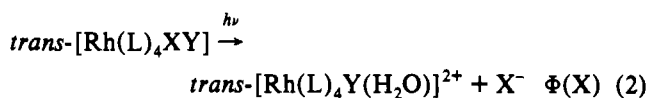
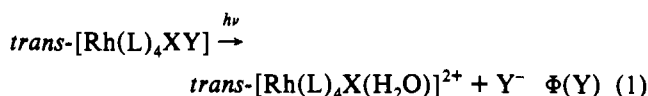
The concentrations of the halide, cyanide, or amine liberated were measured in the same manner as in the direct photolyses. The measurements for the solution of biacetyl and complex were compared with measurements on an aliquot of the same solution which had been kept in the dark for at least 1 h during the photolysis experiments.

Luminescence Quenching.¹³ Emission spectra were recorded with a Perkin-Elmer MPF-3 spectrometer. The exciting wavelength was 400 nm, and the emission intensity was monitored at 513 nm. The ionic strength of the solution was adjusted to 0.01 M by using aqueous 0.01 M NaNO_3 as the solvent. In a typical experiment, the biacetyl solution (270 μL of distilled biacetyl diluted to 25 mL with aqueous NaNO_3) was placed in a quartz cuvette and closed by a rubber septum cap. The solution was degassed by bubbling Cr^{2+} -scrubbed Ar for at least 20 min. Then, the solution was irradiated at 400 nm to consume the residual oxygen concentration.^{15,16} The irradiation at 400 nm was stopped when the phosphorescence to fluorescence peak ratio was at least 6:1. Then the quencher, a 1 mM solution of the rhodium complex, was added in 1- μL increments to the biacetyl solution. For each complex, the emission intensity was measured with at least five different quencher concentrations. Quenching experiments were carried out in triplicate, and the quenching constants are averages obtained from the separate experiments. The observed ratio of the luminescence intensity in an unquenched solution to that in a quenched solution (I_0/I) was corrected for absorption of incident light by the quenchers^{17,18} to give $(I_0/I)_{\text{cor}}$, although such internal filter effects were very small for the very small concentrations of quencher used.

Results

Direct Photolyses. The products and quantum yields for direct irradiation of each complex at the longest wavelength absorption band have been reported previously.⁴ The values obtained in this work were all in agreement with the previous values and are summarized in Table I. Complexes of the type *trans*- $[\text{Rh}(\text{L})_4\text{X}_2]^+$

gave photoaquation of both X⁻ and L, and the complexes *trans*- $[\text{Rh}(\text{py})_4\text{ClY}]^+$ gave photoaquation of py, X⁻ (=Cl⁻), and Y⁻. The reactions and corresponding quantum yields are given in eqs 1–3.



Indirect Photolyses. When 0.4 M biacetyl solutions which contained the complexes in concentrations from 3×10^{-3} to 1×10^{-4} M were irradiated at 400 nm in the $\text{S}_1 \leftarrow \text{S}_0$ biacetyl band, most of the incident radiation was absorbed by biacetyl and photoaquation reactions characteristic of the complexes were observed. No change in absorbance of biacetyl was observed during the photolysis, which suggests that photodecomposition of biacetyl was not a complication. No thermal reactions were observed for solutions that had been kept in the dark at room temperature for at least 1 h. Since relatively nonabsorbing quantities of all the complexes were used and no detectable photoproducts were obtained when the complexes at the concentrations used for indirect photolyses were irradiated directly at 400 nm, no corrections were needed for the contribution of direct photolysis. The apparent quantum yield for the sensitized reaction, Φ_s , was obtained from the amount of the ligand released and the number of photons absorbed by biacetyl. Photosensitization Stern–Volmer plots of $(\Phi_s)^{-1}$ as a function of the reciprocal of the complex concentration gave straight lines with good correlation coefficients (≥ 0.97) for all the photoaquation reactions observed. The plots for the biacetyl-sensitized aquation of both chloride and pyridine from *trans*- $[\text{Rh}(\text{py})_4\text{Cl}_2]^+$ are shown in Figure 1. The intercepts of the photosensitization Stern–Volmer plots were taken to be $(\Phi^{\text{lim}})^{-1}$, where the limiting quantum yield, Φ^{lim} , is the apparent quantum yield for infinite complex concentration. Values of Φ^{lim} for photoaquation of X⁻, Y⁻, and L are listed in Table I. For all the Rh(III) complexes studied, the quantum yield for direct photolysis and the limiting quantum yield for the photosensitized reaction are the same within experimental error.

Luminescence Quenching. The emission spectra of deoxygenated solutions of biacetyl in the absence and in the presence of the complexes show that the complexes quench the biacetyl phosphorescence but not its fluorescence. Stern–Volmer quench-

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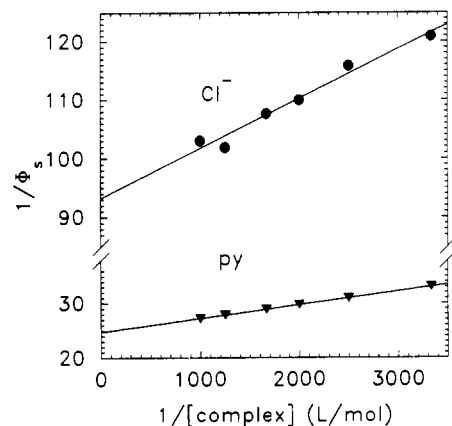


Figure 1. Stern-Volmer plots of the reciprocals of the sensitized quantum yields as a function of the reciprocal of the complex concentration for the photosensitization of *trans*-[Rh(py)₄Cl₂]⁺ by 0.4 M aqueous biacetyl at 400 nm to give photoaquation of Cl⁻ (●) and photoaquation of pyridine (▼). The intercept for each plot is (Φ^{lim})⁻¹, the reciprocal of the limiting quantum yield Φ for the corresponding sensitized reaction.

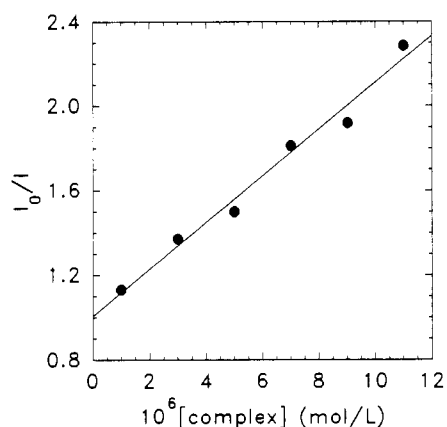


Figure 2. Stern-Volmer plot of the ratio of unquenched to quenched phosphorescence intensity as a function of complex concentration for quenching of 0.4 M biacetyl by *trans*-[Rh(py)₄(CN)₂]⁺ in aqueous solution. The bimolecular quenching rate constant k_q was obtained by dividing the slope, K_{SV} , by τ_0 , the lifetime for biacetyl in the absence of quencher.

ing plots of $(I_0/I)_{cor}$ as a function of concentration of the complex gave straight lines with very good correlation coefficients, 0.97 or higher. The plot shown in Figure 2 is for the quenching of biacetyl phosphorescence by *trans*-[Rh(py)₄(CN)₂]⁺. The bimolecular quenching rate constants, k_q , were obtained from the slope K_{SV} of the Stern-Volmer quenching plot, according to the expression

$$k_q = K_{SV}/\tau_0 \quad (4)$$

where τ_0 , the relaxation lifetime of biacetyl in the absence of quencher, was assumed to be 0.001 s.¹⁴ The bimolecular quenching rate constants and the intercepts of the Stern-Volmer quenching plots are listed in Table I.

Discussion. The syntheses, characterizations, and results of direct photolyses of these complexes have been discussed elsewhere.^{3,4} The results of direct photolyses which are reported here all agreed with the previous values, within experimental error, although the concentrations used in this study were generally somewhat smaller (0.5–3 mM) than the range of 1–8 mM reported in the previous studies. The lower concentrations were used in order to avoid direct photolysis of the complex during photolysis of the biacetyl. Values reported were averages of three or more determinations, and the average deviations were within 10% or 15% of the values. For the complexes with thiazole and pyrazole, the yield of chloride was very low, so it was not possible to determine the quantum yields for photoaquation of halide for the

small concentrations of complex used in the photosensitization experiments. The values reported in these cases were the literature values,^{3,4} as indicated in Table I.

The agreement between quantum yields for direct and for sensitized photolyses is remarkably close for all the rhodium complexes. This suggests that the excited states from which photoreactions occur are the same for the sensitized complexes as for the complexes which undergo direct photolysis. One of the surprising features of the direct photolysis experiments was the distribution of photoproducts in the dicyano and chloro cyano complexes. Predictions based on AOM would suggest that a complex in which Y is a strong-field ligand such as CN⁻ should give labilization of X and isomerization to the *cis* complex, as observed for complexes with L = NH₃.^{19,20} One possible explanation for the direct photolysis results was that there is overlap between ligand-field and charge-transfer bands in the cyano complexes, which would account for deviation from predictions based on ligand-field transitions. However, the photosensitization of the cyano complexes was carried out by exciting biacetyl at 400 nm, which is at lower energy than the energies used for direct photolysis (309 nm for the dicyano complex and 349 nm for the chloro cyano complex).⁴ In other words, the energy from the biacetyl should not be sufficient to excite a charge-transfer transition. Since the quantum yields are nearly identical for direct and indirect photolysis, the direct photolysis is probably also occurring from a low-energy state.

Bimolecular quenching could occur by several different mechanisms,^{21,22} including electronic energy transfer, chemical reaction, spin-catalyzed deactivation, external heavy-atom effects, and exciplex or excimer formation. Of these, the most likely for the Rh(III) complexes is electronic energy transfer. Quenching by a chemical reaction would require that the chemical process be able to compete with the physical deactivation processes of the excited-state complex. This possibility cannot be completely discarded, but the behavior observed here is consistent with that for halo pentaammine Rh(III) systems¹³ for which electronic energy transfer was reported for the quenching mechanism. Only the triplet excited states of biacetyl show quenching by the complexes. The ground state of these Rh(III) d⁶ complexes can be considered to be singlets. (Although spin-orbit coupling for Rh(III) is not negligible, states *s* will be designated here as singlets or triplets for convenience.) Then, spin-catalyzed quenching of triplet biacetyl would be forbidden by the spin conservation rules.²³ The $n-\pi^*$ configuration of triplet biacetyl has an inherent spin-orbit coupling stronger than that which can be induced by external effects, so no external heavy-atom effect on biacetyl is expected.²⁴ Exciplex formation can be ruled out as a probable contributor to the quenching. The high polarity of water and the electroneutrality of biacetyl imply relatively low intermolecular attractive forces between the cationic complex and biacetyl.

The electronic energy transfer presumably occurs by a collisional exchange mechanism, rather than by a dipole-dipole (Coulombic) mechanism, since the latter is forbidden for triplet-triplet energy transfer²⁵ and should not be important in any case for transition metal complexes with Laporte- and spin-forbidden transitions.

For all the Rh(III) complexes studied, quenching only of the biacetyl phosphorescence and not of the fluorescence was observed. The energy transfer between triplet biacetyl and the quencher complex should produce a triplet excited state of the quencher

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complex, assuming these systems follow the spin selection rules for energy transfer by exchange. The values of Table I of the bimolecular quenching constants for $\text{trans}-[\text{Rh}(\text{py})_4\text{X}_2]^+$ varied to a limited extent with X in the order $\text{CN}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$, and those for $\text{trans}-[\text{Rh}(\text{py})_4\text{ClY}]^+$ varied with Y in the order $\text{CN}^- \sim \text{Cl}^- < \text{Br}^-$. Very little variation in k_q with change in the amine L occurred in the series $\text{trans}-[\text{Rh}(\text{L})_4\text{Cl}_2]^+$. All the amines used had similar field strengths, since for a given X and Y the spectrum changed very little as L was varied. The higher the ligand-field strength of the ground-state complex, the lower the bimolecular quenching rate constant. This is reasonable if a ligand with a higher field strength leads to a higher excited-state energy. In other words, the variation in k_q as the ligands X⁻ and Y⁻ varied suggests that the energies of the triplet excited states follow the same order as those of the ground-state complexes. The values of the emission maxima for the transition labeled as $^1\text{A}_{1g} \leftarrow ^3\text{E}_g$ at 77 K in water-methanol (1:4) for the complexes $\text{trans}-[\text{Rh}(\text{py})_4\text{X}_2]^+$ have been reported²⁶ to be $15.3 \times 10^3 \text{ cm}^{-1}$ for X =

Cl and $14.7 \times 10^3 \text{ cm}^{-1}$ for X = Br, which is consistent with this conclusion.

The nearly identical results from the sensitized photolyses and direct photolyses suggest that the limiting energy-transfer efficiency from triplet biacetyl to these complexes is nearly 1. The commonly accepted mechanism for photoreaction of these complexes is for formation of a triplet excited state which can undergo photodissociation of one ligand to give a triplet square pyramidal excited-state species (SP^*).^{4,7} The observation in this work that both the photoaquation of halide and the photoaquation of amine are the same whether produced by direct or indirect photolysis is strong support for the mechanism in which the various photoaquation reactions start from the same triplet excited state. The lack of quenching of the biacetyl fluorescence is additional support for the importance of the triplet state in the photochemistry of these complexes.

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