Mechanistic Photochemistry of Transition Metal β-Diketonate Complexes. The Case of *trans*-Tris(1,1,1-trifluoro-2,4-pentanedionato)rhodium(III)

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Abstract: A photochemical study of *trans*-Rh(tfa)$_3$ (tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione) has revealed the occurrence of two photoinduced processes whose relative quantum efficiencies exhibit a striking dependence upon the solution environment. Thus trans to cis isomerization is the sole observable photoprocess in cyclohexane, whereas only decomposition of the complex occurs in ethanol and 2-propanol. The key role of solvent in regulating the photochemical behavior is particularly evident in mixed cyclohexane-2-propanol systems where both photoprocesses can be observed. Oxygen quenching and wavelength-dependence studies provide strong evidence for the existence of two photoactive excited states in *trans*-Rh(tfa)$_3$. The enhanced photoreactivity in the presence of hydrogen atom donors suggests that one or both of these photoactive states imparts considerable radical character to the complex. Flash photolysis results obtained under a variety of experimental conditions support this suggestion and allow a more precise delineation of several steps in the overall reaction sequence.

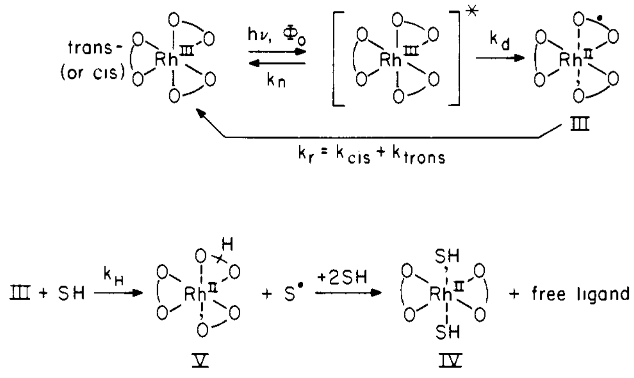
Introduction

Metal chelate complexes of general formula M(dik)$_n$ (where dik denotes the anion of a β-diketone and n = 2, 3, or 4) have been reported for the majority of d transitional elements.[2a] These complexes display several physical characteristics which can be profitably exploited in studies of transition-metal photochemistry. Thus the ready solubility of the compounds in a broad range of polar and nonpolar solvents offers the flexibility of examining the effects of systematic variations in the solution environment upon photoreactivity patterns. Furthermore, complexes containing fluorinated ligands are sufficiently volatile and stable at moderate temperatures to permit gas-phase photochemical studies in the complete absence of solvent. The enhanced volatility also enables the separation and identification of nanogram (or lower) quantities of closely related complexes by gas chromatography.[2b] This capability is especially crucial when the steric course of a reaction needs to be monitored as, for example, in the trans (I)–cis (II) isomerization of a trischelate containing unsymmetrical ligands.[3] The spectral characteristics of β-diketonate complexes will, of course, depend upon the particular metal–ligand combination, but generally metal localized (ligand field), metal–ligand charge transfer, and ligand localized excited states are all accessible to light in the visible or near-ultraviolet spectral region.[4-7] This richness of excited states can result in varied and often complex reaction schemes depending upon the wavelength of irradiation.

Despite the attractive characteristics noted above, fewer than 12 mechanistic photochemical studies of transition metal β-diketonate complexes have been reported, and, until recently, these have dealt exclusively with first-row metals. The salient features of these previous investigations can be summarized as follows: (1) visible or near-ultraviolet irradiation induces either stereochemical rearrangement (Cr) or redox decomposition (Mn, Fe, Co, Ni, Cu), and (2) the quantum yield for the latter pathway is generally quite sensitive to the solvent environment. In his review[8] of β-diketonate photochemistry, Lintvedt attributed this solvent dependence (specifically for alcohols) to the chemical participation of solvent via hydrogen atom donation to a metal-bound ligand radical formed in the primary photochemical step. A generalized version of this mechanism applicable to any hydrogen atom donor, SH, is outlined in Scheme I, where ϕ_0 is the efficiency of forming the reactive excited state and the k's represent rate constants for the indicated processes. The quantum yield for photoredox decomposition, ϕ_{dec}, can be defined in terms of these quantities by

$$\phi_{dec} = \phi_0 \left(\frac{k_d}{k_n + k_d}\right)\left(\frac{k_H[SH]}{k_r + k_H[SH]}\right) \qquad (1)$$

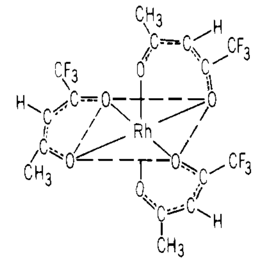
Scheme I



Accordingly, the origin of the solvent dependence resides in the last term, which expresses the partitioning of an intermediate (III) between reactive (k_H[SH] term) and nonreactive (k_r term) paths.

The foregoing analysis focuses upon the chemical role of solvent as a reaction partner. There is the additional possibility, however, that solvent can influence ϕ_{dec} through its effect upon one or more of the "nonchemical" processes (those characterized by ϕ_0, k_n, k_d, and k_r) in Scheme I. In several recent studies,[9-12] evidence for the operation of this type of solvent effect has been presented.

To broaden the presently limited scope of transition metal β-diketonate photochemistry to encompass complexes of



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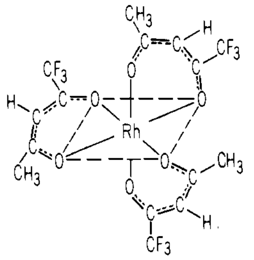

II

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second-row metals, we have undertaken a detailed photochemical investigation of *trans*-Rh(tfa)$_3$ (I) (tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione) in several nonaqueous solvents. Both continuous and flash photolysis experiments performed under a variety of conditions have yielded some valuable mechanistic insights, particularly with regard to the role played by solvent. Our detailed studies, which expand upon some preliminary observations communicated previously,[13,14] are reported here.

Experimental Section

A. Reagents. Rh(tfa)$_3$ was prepared from RhCl$_3$·3H$_2$O and the commercially available ligand (Eastman) according to a published procedure.[15] Separation into trans and cis isomers was accomplished by chromatography on a 70 × 3 cm glass column packed with silica gel (60–200 mesh), using 70:30 v/v hexane-benzene as the eluant at a flow rate of 15 drops/min. The trans isomer elutes first and can be obtained in >99% isomeric purity. Anal. Calcd: C, 32.05; H, 2.15. Found for trans isomer: C, 32.17; H, 2.12. The melting point was 187–189 °C (lit. 189.5–190 °C). Tri(*n*-butyl)stannane was prepared by the method of van der Kerk et al.[16] and stored under nitrogen. Solvents employed in the photochemical studies were rigorously purified and dried by standard techniques[17] and stored under an inert atmosphere.

B. Continuous Photolysis Procedures. Photolyses at 254 nm were performed using a Pen-Ray lamp (Ultraviolet Products), whose unfiltered output is 92% at this wavelength. Higher wavelength irradiations were provided by a 200-W high-pressure mercury arc lamp (Illumination Industries) in conjunction with suitable blocking and interference filters. Light intensity was determined by ferrioxalate actinometry.[18]

In a typical photochemical experiment, a nitrogen-purged[19] solution of ~3.3 × 10^{-4} M *trans*-Rh(tfa)$_3$ was irradiated in a tightly stoppered 1-cm quartz cell. The extent of reaction was generally <10% to avoid secondary photolysis or inner filter effects. A 1-2-μL sample of the photolyte was analyzed by gas chromatography using a Varian Model 1440 chromatograph equipped with a scandium tritide electron capture detector. The operating temperatures of the instrument follow: injector port, 130 °C; column, 105 °C; detector, 150 °C. Separation of cis-trans isomers was accomplished on a 12-in. glass column (4 mm i.d.) containing open pore polyurethane.[3] At a nitrogen carrier gas flow rate of 30 mL/min, the retention times were ~6 min for the trans compound and ~8.5 min for its cis companion. Since the electron capture detector response was determined experimentally to be virtually identical for both isomers, the ratio of peak areas (integrated by planimetry) is a direct measure of the extent of isomerization. Decomposition was monitored by comparing the total (trans + cis) peak area of an irradiated sample with that of an unirradiated standard.

Electronic absorption spectra were measured using a Cary 15 spectrophotometer. Identification of free H(tfa) in photolyzed solutions was accomplished by high-pressure liquid chromatography on a Varian Model 8500 chromatograph containing a 25 cm × 2 mm column packed with Micropore SI-10. A methylene chloride-hexane mixture constituted the eluant.

C. Flash Photolysis Procedures. Flash irradiations were performed using an apparatus described previously.[20] Pulses of polychromatic light of ~30 μs half-life were obtained for stored electrical energies between 40 and 250 J/flash. Cutoff filters placed in the path of the exciting light were used to isolate appropriate spectral regions. The results of time-resolved optical detection were analyzed by already reported methods.[20,21]

Sample solutions were prepared by dissolving pure *trans*-Rh(tfa)$_3$ in solvents which had been previously deaerated by three freeze-thaw cycles followed by saturation with argon at 1 atm. All additional manipulations were carried out under an argon atmosphere in a gas-tight apparatus. Fresh samples of a given solution were used for each flash irradiation.

Results and Discussion

A. Spectral Considerations. The electronic absorption spectra of H(tfa), Al(tfa)$_3$, and *trans*-Rh(tfa)$_3$ in cyclohexane are compared in Figure 1. The characteristic $^1(\pi-\pi^*)$ transition at 283 nm in the free ligand shifts to 293 nm in the Al complex and develops a slight shoulder on the long-wavelength side. This small splitting of the $\pi-\pi^*$ band has been attributed to interligand interactions within the complex.[4,22]

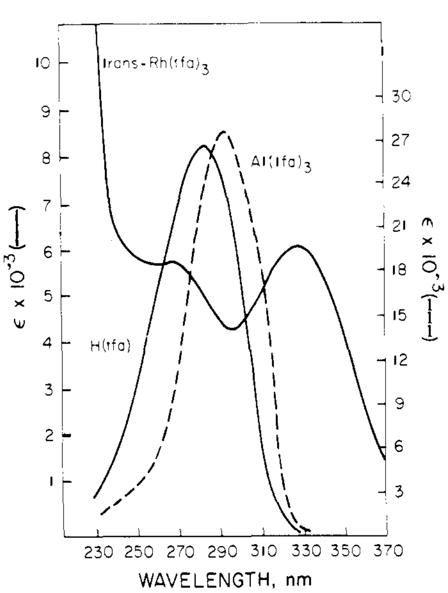

Figure 1. Electronic absorption spectra of H(tfa), Al(tfa)$_3$, and *trans*-Rh(tfa)$_3$ in cyclohexane.

trans-Rh(tfa)$_3$ displays a more complicated spectrum with two maxima of comparable intensity at 324 and 265 nm and a sharply rising absorption which extends below 210 nm. While these transitions are reasonably assigned as symmetry and multiplicity allowed on the basis of their high extinction coefficients, their orbital designations are less obvious.[23] Clearly, the absence of a peak in the 280–300-nm spectral region suggests that the lowest $^1(\pi-\pi^*)$ transition in the ligand has been strongly perturbed upon coordination. It may be that the 324- and 265-nm bands in *trans*-Rh(tfa)$_3$ correspond to the split components of this transition,[24] although such an assignment would require an appreciably larger interligand interaction than exists in Al(tfa)$_3$. Alternatively, the proximity in energy of $\pi-\pi^*$ and charge transfer excited levels of appropriate symmetry can give rise to extensive configuration interaction.[25] Under such circumstances, the use of "pure" orbital labels to describe electronic distributions has limited validity in that the actual excited states would be of *mixed* $\pi-\pi^*$/charge transfer character and would possess energies which are shifted from the parent (unmixed) set. Since the possibility of some configurational mixing in *trans*-Rh(tfa)$_3$ cannot be discounted, we adopt the most general view that the excited states directly populated in absorption can contain contributions (though not necessarily equal in magnitude) from both $\pi-\pi^*$ and charge-transfer configurations. Additional spectroscopic and theoretical studies are needed to define more precisely the nature of these states.

Two orbitally forbidden transitions in *trans*-Rh(tfa)$_3$ which are expected to lie in the near-ultraviolet region deserve brief mention. Thus the first spin-allowed ligand field transition, $^1A_{1g} \rightarrow {}^1T_{1g}$ (labels refer to O_h symmetry), can be estimated to occur at 350 nm.[7,26] The position of the ligand localized $^1(n-\pi^*)$ transition is less certain, although photoelectron spectroscopy indicates that in Al(tfa)$_3$ it lies to the high-energy side of the lowest $^1(\pi-\pi^*)$ band.[27] Since both transitions (ligand field, $n-\pi^*$) possess low extinction coefficients, they presumably are hidden under the intense absorption bands which dominate the spectrum of the complex (vide supra). A similar situation must also exist for transitions involving a change in spin multiplicity (e.g., $^3n-\pi^*$).

B. Continuous Photolysis Studies. A detailed study of the solution photochemistry of *trans*-Rh(tfa)$_3$ is summarized in

Table I. Photochemical Quantum Yields for the Isomerization and Decomposition of *trans*-Rh(tfa)$_3$ in Various Solvents

irradiation wavelength, nm	cyclohexane		2-propanol		ethanol	
	ϕ_{isom}	ϕ_{dec}	ϕ_{isom}	ϕ_{dec}	ϕ_{isom}	ϕ_{dec}
366	$<3 \times 10^{-6}$	$<1.5 \times 10^{-5}$	$<3 \times 10^{-6}$	$<1.5 \times 10^{-5}$	$<3 \times 10^{-6}$	$<1.5 \times 10^{-5}$
302	$<5.9 \times 10^{-6}$	$<1.5 \times 10^{-5}$	$<3.2 \times 10^{-6}$	$4.4 \pm 0.3 \times 10^{-4}$	$<3 \times 10^{-6}$	$<1.5 \times 10^{-5}$
254	$9.2 \pm 0.4 \times 10^{-5}$	$<6 \times 10^{-5}$	$<2 \times 10^{-5}$	$2.3 \pm 0.2 \times 10^{-3}$	$<3.3 \times 10^{-6}$	$4.5 \pm 0.2 \times 10^{-4}$

Table II. Effect of Added HSn(n-Bu)$_3$ on ϕ_{dec}

[HSn(n-Bu)$_3$], M	ϕ_{dec}[a]	[HSn(n-Bu)$_3$], M	ϕ_{dec}[a]
0	$<6 \times 10^{-5}$	2.6×10^{-3}	0.043
1.1×10^{-4}	0.0025	3.8×10^{-3}	0.068
3.8×10^{-4}	0.0052	7.6×10^{-3}	0.12
1.4×10^{-3}	0.021	1.1×10^{-2}	0.13

[a] Irradiations performed at 254 nm in cyclohexane solution.

Table I. Two distinct photoinduced processes can be detected, depending upon the nature of the solvent employed. Irradiation of the complex at 254 nm in pure cyclohexane induces only trans to cis isomerization, while at wavelengths ≥302 nm the complex is photoinert within our detection limits.[28] Photolysis in alcoholic solvents, on the other hand, results in photodecomposition with release of free H(tfa).[29] The quantum efficiency of this pathway drops sharply at longer excitation wavelengths, but is unaffected (at 254 nm) upon addition of inorganic salts (LiCl, NH_4Cl) or acid (H_2SO_4).

The solvent-dependent photochemical behavior of *trans*-Rh(tfa)$_3$ was probed in more detail using mixed solvent systems. We find that *both* isomerization and decomposition of the complex occur upon 254-nm irradiation of cyclohexane solutions containing up to 0.065 M (0.7 mol %) 2-propanol. The processes are competitive as evidenced by the opposite responses of ϕ_{isom} (decreases) and ϕ_{dec} (increases) to increasing alcohol content.[30] Isomerization is completely suppressed within our detection limits by 0.24 M (2.6 mol %) 2-propanol, at which point the value of ϕ_{dec} is experimentally indistinguishable from that measured in the pure alcohol. Both photoreactions are quenched by oxygen, with decomposition being affected to the larger extent. Thus the ratio, ϕ_{dec}/ϕ_{isom}, measured in a cyclohexane solution containing 0.013 M (0.14 mol %) 2-propanol decreases from 5.8 to 3.8 upon bubbling the sample with oxygen. Moreover, this ratio is wavelength dependent, increasing from 5.8 at 254 nm to ≥14.7 at 302 nm in deaerated solutions.

Table II summarizes the effect of added tri(n-butyl)stannane on the photochemical behavior of *trans*-Rh(tfa)$_3$ in cyclohexane. Even extremely low concentrations of this potent hydrogen atom donor[31,32] dramatically enhance photodecomposition of the complex upon 254-nm irradiation. Under the experimental conditions, we were unable to detect any concomitant trans to cis isomerization.

The spectral changes observed upon 254-nm photolysis of *trans*-Rh(tfa)$_3$ in 2-propanol are depicted in Figure 2. At short irradiation times the absorbance of the long-wavelength band of the complex diminishes and isosbestic points are observed at 304 and 357 nm. Upon prolonged irradiation, however, the former isosbestic point is lost and a new absorption rapidly grows in the 270-nm region. This feature signals the formation of some secondary photolysis product(s), whose high extinction coefficient at 254 nm clearly dictates that short irradiation times be employed in quantum yield determinations.

C. Flash Photolysis Studies. No spectral changes occur upon flashing a deaerated[23] cyclohexane solution of *trans*-Rh(tfa)$_3$ with polychromatic light, whereas comparable irradiation in deaerated alcoholic solvents produces a transient absorption which decays in two successive stages well separated in time. By employing suitable blocking filters to isolate various spectral regions, we have established that the photogenerated intermediates responsible for this behavior result from excitation with wavelengths ≤320 nm.[34]

The absorption spectrum of the short-lived intermediate, X, exhibits a maximum at 360 ± 5 nm in either 2-propanol or ethanol (Figure 3). By monitoring the initial absorbance change at this wavelength,[35] we can directly determine the amount of X produced by the flash. This initial yield of X varies linearly with the flash intensity (Figure 4), indicating that X is generated neither in the disproportionation nor the dimerization of a precursor species. Moreover, the yield depends upon both the concentration and identity of the alcohol component in mixed alcohol-cyclohexane solvents (Figure 5). For comparable concentrations of *trans*-Rh(tfa)$_3$, X is produced 6 ± 0.7 (four determinations) times more efficiently in pure 2-propanol than in pure ethanol. The rate law describing the decay of X is

$$\frac{-d[X]}{dt} = k_{ob}[X] \qquad (2)$$

The observed first-order rate constant, k_{ob}, depends upon the identity but not the concentration of the alcohol employed, and is unaffected by the addition of acid (Table III).

Kinetic analysis of the long-lived intermediate, Y, reveals that its decay obeys a first-order rate expression analogous to eq 2. The observed rate constant, $k_{ob'}$,[36] does not appear to be particularly sensitive to the identity of the alcoholic solvent, but exhibits a linear dependence upon the concentration of added acid (Table III).

To determine whether the two intermediates observed in flash photolysis studies of *trans*-Rh(tfa)$_3$ are characteristic of β-diketone compounds, we flashed alcoholic solutions of free H(tfa), *trans*-Co(tfa)$_3$, and *trans*-Cr(tfa)$_3$. Since none of the latter systems exhibited transient behavior resembling that described above, it appears reasonable to assign both X and Y as Rh-containing species (vide infra).

D. Mechanistic Interpretations. The key observations which any proposed mechanism must accommodate can be summarized as follows: (1) *trans*-Rh(tfa)$_3$ undergoes two competing photochemical processes—isomerization to the corresponding cis complex and decomposition with production of free H(tfa); (2) the relative importance of these pathways as reflected in the ratio ϕ_{dec}/ϕ_{isom} exhibits a pronounced solvent dependence;[37] (3) the magnitude of ϕ_{dec} correlates well with the hydrogen atom donor ability of the solvent (HSn(n-Bu)$_3$-cyclohexane > 2-propanol > ethanol > cyclohexane); (4) ϕ_{dec} is insensitive to the addition of inorganic salts or acid; (5) ϕ_{dec}/ϕ_{isom} varies with the wavelength of irradiation and the concentration of dissolved oxygen.

Observation (5) deserves special note, since it is diagnostic of the presence of more than one photoactive excited state in *trans*-Rh(tfa)$_3$.[38] Consequently, the mechanism outlined in Scheme I cannot, *by itself*, adequately account for the photochemical behavior of the complex. This conclusion is compelled especially strongly by an analysis of ϕ_{dec} values measured in mixed solvent systems. Thus the quantum yield for decomposition originating from the single reactive state in Scheme I is given by eq 1. The reciprocal of this expression gives

$$\frac{1}{\phi_{dec}} = \frac{k_d + k_n}{\phi_0 k_d}\left(1 + \frac{k_r}{k_H[SH]}\right) \qquad (3)$$

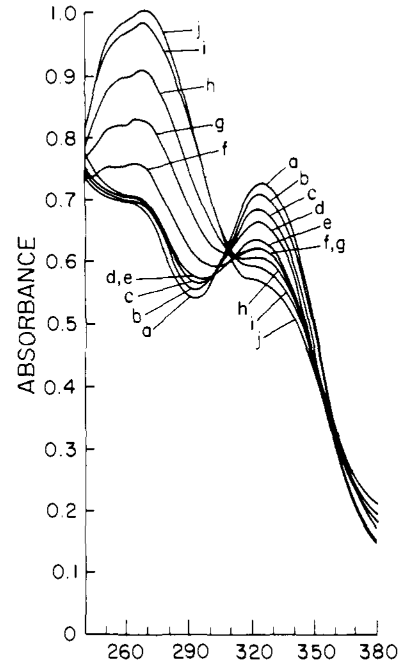

Figure 2. Spectral changes observed upon 254-nm irradiation of *trans*-Rh(tfa)$_3$ in 2-propanol; spectra a-j taken at successively longer times.

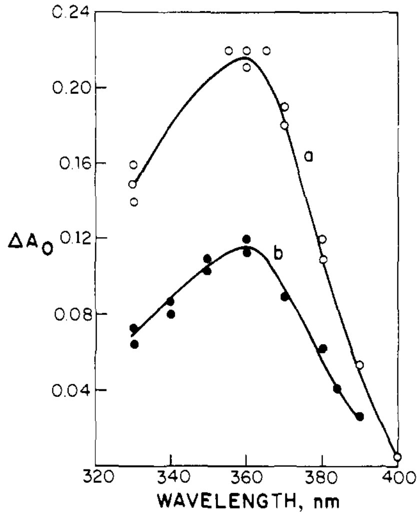

Figure 3. Spectrum of short-lived transient, X, generated in the flash photolysis of (a) 2.0×10^{-6} M *trans*-Rh(tfa)$_3$ in 2-propanol, (b) 5.0×10^{-6} M *trans*-Rh(tfa)$_3$ in ethanol.

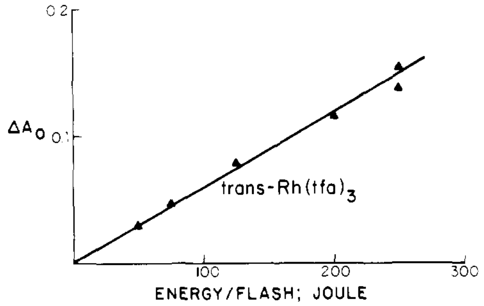

Figure 4. Initial yield (ΔA_0) of the short-lived intermediate, X, as a function of flash intensity.

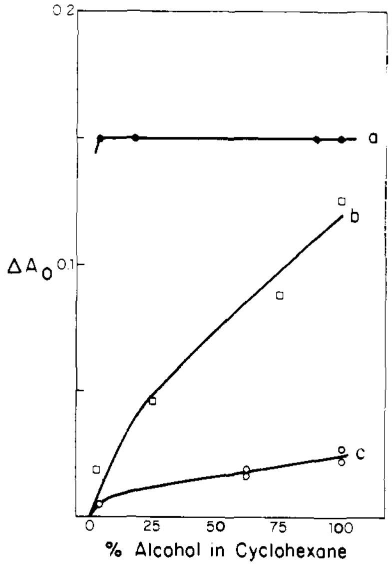

Figure 5. Dependence of initial yield (ΔA_0) of the short-lived intermediate, X, on alcohol concentration: (a) 2.0×10^{-6} M *trans*-Rh(tfa)$_3$ in 2-propanol-cyclohexane, (b) 5.0×10^{-6} M *trans*-Rh(tfa)$_3$ in ethanol-cyclohexane, (c) 2.0×10^{-6} M *trans*-Rh(tfa)$_3$ in ethanol-cyclohexane.

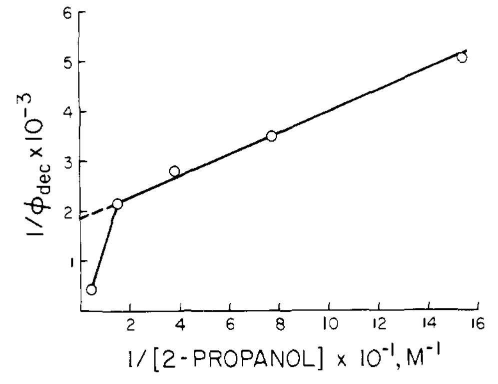

Figure 6. Reciprocal plot of ϕ_{dec} vs. alcohol concentration in 2-propanol-cyclohexane solvent mixtures.

A plot of $1/\phi_{dec}$ vs. $1/[SH]$ should yield a straight line with an intercept equal to $(k_d + k_n)/(\phi_0 k_d)$. The reciprocal of the intercept defines the limiting value of ϕ_{dec} attained at high concentrations of the hydrogen atom donor, SH. Using data obtained in cyclohexane-2-propanol solvent mixtures, we find that such a plot (Figure 6) is indeed linear at low alcohol concentrations, but curves sharply at higher concentrations.[39] This behavior is expected if decomposition occurs from *two* excited states, hereafter designated A and B. If we assume that the linear portion of the plot in Figure 6 represents decomposition originating solely from state A, then the reciprocal of the intercept of the extrapolated (dotted) line yields a limiting ϕ^A_{dec} value of 5.3×10^{-4}. Since the total quantum yield for decomposition of *trans*-Rh(tfa)$_3$ in 2-propanol upon 254-nm irradiation is 2.3×10^{-3}, we infer that 23% of this pathway originates in state A and 77% in state B under these conditions. Analysis of the corresponding ϕ_{isom} values measured in cyclohexane-2-propanol solvent mixtures reveals that the percent quenching of this pathway by alcohol closely matches the percent enhancement of decomposition from state A (Table IV). This parallel response of the two processes would be expected if isomerization occurs exclusively from A and is competitive with decomposition (see Appendix).

Based upon the preceding analyses, the simplest mechanistic picture which can accommodate the photochemical behavior of *trans*-Rh(tfa)$_3$ has, as its main feature, the presence of two reactive excited states (see Figure 7). The higher energy state, A,[40] is characterized by a competition between decomposition and isomerization, while state B strongly favors decomposition.

Table III. Rate Constants for Decay of the Intermediates Produced in Flash Irradiations of *trans*-Rh(tfa)$_3$

short-lived transient, X k_{ob}, s^{-1} [a]	conditions
$(5.3 \pm 0.5) \times 10^3$	100% ethanol; 250 J/flash
$(5.0 \pm 0.6) \times 10^3$	100% ethanol; 122 J/flash
$(5.4 \pm 0.3) \times 10^3$	100% ethanol; 63 J/flash
$(5.6 \pm 0.6) \times 10^3$	50% ethanol in cyclohexane; 250 J/flash
$(5.4 \pm 0.4) \times 10^3$	25% ethanol in cyclohexane; 250 J/flash
$(2.0 \pm 0.8) \times 10^3$	90% 2-propanol in cyclohexane; 500 J/flash
$(1.6 \pm 0.6) \times 10^3$	90% 2-propanol in cyclohexane; 400 J/flash
$(8.3 \pm 0.3) \times 10^2$	100% *tert*-butyl alcohol; 250 J/flash
$(8.7 \pm 0.5) \times 10^2$	100% *tert*-butyl alcohol; 122 J/flash
$(8.5 \pm 0.6) \times 10^2$	100% *tert*-butyl alcohol; 90 J/flash
$(8.8 \pm 0.5) \times 10^2$	100% *tert*-butyl alcohol; 5×10^{-3} M HClO$_4$;[b] 250 J/flash
long-lived transient, Y $k_{ob'}$, s^{-1} [a]	**conditions**
(1.5 ± 0.6)	100% ethanol; 250 J/flash; 90 J/flash
$(3.7 \pm 0.4) \times 10$	100% ethanol; 10^{-3} M HClO$_4$; 250 J/flash
$(3.0 \pm 0.3) \times 10^2$	100% ethanol; 10^{-2} M HClO$_4$; 250 J/flash
(2.0 ± 0.3)	100% *tert*-butyl alcohol; 250 J/flash
(20 ± 5)	100% *tert*-butyl alcohol; 5×10^{-3} M HClO$_4$; 250 J/flash
(63 ± 3)	100% *tert*-butyl alcohol; 1×10^{-2} M HClO$_4$; 250 J/flash
(90 ± 5)	100% *tert*-butyl alcohol; 2×10^{-2} M HClO$_4$; 250 J/flash

[a] Average of four to ten determinations. [b] Acidic solutions were obtained by dilution of 70% HClO$_4$ with the appropriate alcohols.

Table IV. Evidence for Competitive Isomerization and Quenching from State A in *trans*-Rh(tfa)$_3$[a]

[2-propanol], M[b]	$(1 - (\phi_{isom}{}^{mixed}/\phi_{isom}{}^{C_6H_{12}}))$[c]	$(\phi_{dec}{}^{mixed}/\phi_{dec}{}^{alc})_A$[d]
6.5×10^{-3}	0.36	0.38
1.3×10^{-2}	0.46	0.54
2.6×10^{-2}	0.66	0.68
6.5×10^{-2}	0.92	0.89

[a] See Appendix for derivation. [b] Concentration of 2-propanol in cyclohexane. [c] Percent quenching of isomerization from state A caused by 2-propanol. [d] Percent enhancement of decomposition from state A caused by 2-propanol.

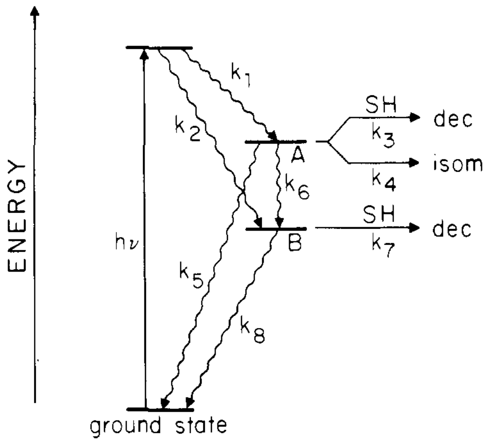

Figure 7. Excited state scheme for the photochemical behavior of *trans*-Rh(tfa)$_3$.

Consideration of the photoreactivity of the complex as a function of wavelength (Table I) reveals that both states are populated, either directly or following relaxation from some higher level, via irradiation in the spectral region where the 265-nm band overlaps the sharply rising absorption extending below 210 nm (Figure 1). In contrast, neither state appears to be reached upon irradiating the 324-nm band. Since the efficiency of decomposition correlates with the ease of hydrogen atom abstraction from the solvent (observation 3), we infer that the population of one or both excited states imparts considerable radical (and thus hydrogen atom abstracting) character to *trans*-Rh(tfa)$_3$. The independence of ϕ_{dec} to changes in ionic strength or pH (observation 4) lends support to this premise, since any probable metal- or ligand-centered radicals are not likely to develop significant charge separation or function as good Brønsted bases.

The reactivity pattern associated with A is just that expected for a state which possesses appreciable ligand to metal charge transfer character and undergoes the sequence of reactions presented in Scheme I. Thus the immediate consequence of populating this state would be the production of a short-lived (<1 μs) Rh(II)-ligand radical species, III. In a period short compared to the time resolution of the flash photolysis equipment (~30 μs), III can undergo either of two competing processes:[41] (1) back electron transfer to the ligand with no net change in the stoichiometry of the complex; the distorted Rh(II) complex can rearrange (albeit with low efficiency) prior to this back transfer as evidenced by the production of some cis isomer; (2) reaction with the solvent to yield V, which subsequently releases free H(tfa) to form the solvated intermediate, IV.[42] Process 1 should be favored in an inert (noncoordinating, poor hydrogen atom donating) solvent, whereas process 2 is facilitated by a good hydrogen atom donor solvent which is able to capture the Rh(II)-ligand radical moiety, III, prior to back electron transfer.

State B could also possess charge transfer to metal character and react according to Scheme I, but with diminished tendency (relative to state A) to undergo rearrangement. An alternative assignment of B is a ligand localized n-π* state arising from the transfer of a nonbonding electron on oxygen to a π* molecular orbital. Hydrogen atom abstraction is a characteristic pathway for this type of excited state[31,32] and would initially produce a Rh(III) complex formally containing a coordinated ligand radical anion. Subsequent intramolecular electron transfer from this radical anion to the metal[43] would yield a labile Rh(II) species similar to III which could eliminate free H(tfa) and form IV. Based upon this scenario, charge transfer and n-π^* states are expected to exhibit comparable reactivity patterns and no distinction between the two can be made on the basis of the available data.

E. Reconciliation of Continuous and Flash Photolysis Observations. The continuous photolysis results strongly implicate hydrogen atom abstraction from the solvent as a key step in the photodecomposition of *trans*-Rh(tfa)$_3$. Moreover, we have inferred from such behavior that the population of one or both of the photoexcited states, A and B, imparts considerable radical character to the complex. Flash photolysis studies lend support to these ideas and also provide the details of several key steps in the overall reaction sequence.

There is precedent[41] to suggest that the solvated Rh(II) species, IV, possesses a substantially greater lifetime (milliseconds) than its immediate precursors such as III and V in Scheme I. It should therefore be possible to detect this species with the flash photolysis apparatus employed in the present study, and we, in fact, identify IV as the short-lived intermediate, X.[44] This assignment is justified on grounds that X exhibits just those characteristics expected of IV by virtue of its involvement in the decomposition of *trans*-Rh(tfa)$_3$. Thus the solvent dependence of the initial yields of X produced during the flash (Figure 5) parallels that of ϕ_{dec} measured under comparable conditions. Moreover, the ratio of the flash-induced yield of X in 2-propanol to that in ethanol (6 ± 0.7) matches the ratio of ϕ_{dec} values in these solvents (5.1 ± 0.5).

The decay of X by a first-order process produces the long-lived intermediate, Y, which we tentatively identify as a Rh(III)-hydride (eq 4). This intramolecular hydrogen atom

$$\underset{\text{X}}{\text{Rh}^{\text{II}}(\text{tfa})_2(\text{ROH})_2} \rightarrow \underset{\text{Y}}{\text{Rh}^{\text{III}}(\text{tfa})_2(\text{ROH})(\text{H}^-)} + \text{alcohol radical} \tag{4}$$

transfer from a coordinated alcohol molecule to Rh(II) should be independent of the alcohol concentration in solution (Table III). The rate constant (k_{ob} in eq 2) for this process, on the other hand, reflects the characteristic ease with which the coordinated alcohol donates a hydrogen atom. While additional evidence is needed to substantiate the assignment of Y as a hydride, it is consistent with the observed acid-dependent decay of this species (Table III) and the reported behavior of some Rh(III)-hydride complexes.[45,46]

F. Concluding Remarks. The preceding discussion has emphasized the chemical role of solvent in the photochemical behavior of *trans*-Rh(tfa)$_3$. A more detailed analysis should also include consideration of the influence of solvent on the "nonchemical" processes (e.g., ϕ_0, k_n, k_d, and k_r in Scheme I) associated with the reactive excited states and intermediates generated during photolysis. Two observations suggest that effects of this type are probably small in the present study: (1) values of ϕ_{dec} correlate well with the hydrogen atom donor ability (a chemical property) of the solvent, and (2) in mixed solvents small concentrations of one component cause extraordinarily large effects on the photoreactivity of *trans*-Rh(tfa)$_3$ without significantly altering the physical properties (e.g., viscosity, hydrogen-bonding ability) of the solution. A particularly dramatic example of this latter situation is provided by the HSn(n-Bu)$_3$-cyclohexane system, where as little as 1.1×10^{-4} M hydride enhances ϕ_{dec} by a factor of >40.[47] For these reasons we feel that the key role of solvent in regulating the photochemical behavior of *trans*-Rh(tfa)$_3$ resides mainly in its ability to react with and solvate the various excited states and intermediates produced.

Finally, we have noted previously[13] that, while the photodecomposition of *trans*-Rh(tfa)$_3$ is generally less efficient than that of its Co(III) analogue, it is also considerably more sensitive to changes in solvent environment. The former result is explicable in terms of the greater tendency of Rh(II) (relative to Co(II)) and the oxidized ligand radical (Scheme I) to recombine before net reduction can occur. Likewise the greater sensitivity of *trans*-Rh(tfa)$_3$ to changes in the solvent environment reflects the need for a solvent molecule to intercept the short-lived Rh(II)-ligand radical species, III, prior to back electron transfer. Such solvent participation is less crucial in the case of *trans*-Co(tfa)$_3$, since the Co(II) photoproduct (Co(tfa)$_2$) is stable in solution.[48]

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Appendix

Shown in Figure 7 is a generalized scheme for the photoreactivity of *trans*-Rh(tfa)$_3$ which presumes the presence of two photoactive excited states. State A leads to both isomerization and decomposition via hydrogen atom abstraction from some substrate, SH, whereas state B leads solely to decomposition. While only nonradiative processes are shown, the inclusion of radiative transitions would add nothing substantive to the analysis presented below.

The quantum efficiency of isomerization in a poor hydrogen atom donating solvent such as cyclohexane is given by

$$\phi_{\text{isom}}{}^{\text{C}_6\text{H}_{12}} = \left(\frac{k_1}{k_1 + k_2}\right)\left(\frac{k_4}{k_4 + k_5 + k_6}\right) \tag{i}$$

In cyclohexane-2-propanol mixtures the efficiency of isomerization, defined by

$$\phi_{\text{isom}}{}^{\text{mixed}} = \left(\frac{k_1}{k_1 + k_2}\right)\left(\frac{k_4}{k_4 + k_5 + k_6 + k_3[\text{SH}]}\right) \tag{ii}$$

contains a term reflecting hydrogen atom abstraction from the alcohol. The ratio of the two quantum efficiencies is given in

$$\frac{\phi_{\text{isom}}{}^{\text{mixed}}}{\phi_{\text{isom}}{}^{\text{C}_6\text{H}_{12}}} = \left(\frac{k_4 + k_5 + k_6}{k_4 + k_5 + k_6 + k_3[\text{SH}]}\right) \tag{iii}$$

while eq iv represents the percent quenching of isomerization caused by the addition of alcohol.

$$1 - \frac{\phi_{\text{isom}}{}^{\text{mixed}}}{\phi_{\text{isom}}{}^{\text{C}_6\text{H}_{12}}} = \frac{k_3[\text{SH}]}{k_4 + k_5 + k_6 + k_3[\text{SH}]} \tag{iv}$$

The quantum efficiency characterizing decomposition from state A in mixed solvents is given by eq v, which reduces to eq vi in pure alcohol.

$$\phi_{\text{dec}}{}^{\text{mixed}} = \left(\frac{k_1}{k_1 + k_2}\right)\left(\frac{k_3[\text{SH}]}{k_4 + k_5 + k_6 + k_3[\text{SH}]}\right) \tag{v}$$

$$\phi_{\text{dec}}{}^{\text{alc}} = \left(\frac{k_1}{k_1 + k_2}\right) \tag{vi}$$

The ratio of the two efficiencies

$$\left(\frac{\phi_{\text{dec}}{}^{\text{mixed}}}{\phi_{\text{dec}}{}^{\text{alc}}}\right)_{\text{A}} = \frac{k_3[\text{SH}]}{k_4 + k_5 + k_6 + k_3[\text{SH}]} \tag{vii}$$

defines the percent enhancement of decomposition caused by increasing the alcohol concentration. The equality of eq iv and vii is expected, since isomerization and decomposition are competitive processes originating from the same excited state.

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(29) A quantitative determination of released H(tfa) was precluded by its photochemical and/or thermal reactivity in alcohols.

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(33) It is imperative to deaerate the sample solutions, since oxygen strongly quenches the transient absorption.

(34) Identical transient absorptions are produced by excitation wavelengths >210 and >240 nm. Thus no new photochemical features are added for photolysis in the 210–240-nm region.

(35) More precisely, the initial change in absorbance is extrapolated back to zero time using a first-order plot.

(36) Since k_{ob}' was determined at only one alcohol concentration, no distinction can be made as to whether it is a true or a pseudo-first-order rate constant.

(37) A reviewer has raised the question as to whether the entire solvent dependence of ϕ_{dec} may be related to the presence of solvent impurities. Several observations can be cited to discount this possibility. Thus the absence of decomposition in highly purified cyclohexane (Table I) clearly establishes that the effects of impurities (notably peroxides, footnote 28) have been minimized. Consequently, the marked enhancement of ϕ_{dec} upon addition of HSn(n-Bu)$_3$ to cyclohexane (Table II) must reflect entirely the effect of this potent hydrogen atom donor. In alcohols, we find that ϕ_{dec} is relatively insensitive to whether or not the solvent is purified, suggesting that impurity-induced decomposition constitutes a minor pathway in these systems as well. One final point relates to the excellent reproducibility of the ϕ_{dec} values measured in different batches of purified solvent. If decomposition were sensitive to adventitious traces of impurities, such reproducibility would seem unlikely.

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(39) Qualitatively similar behavior is observed for a plot of $1/\phi_{dec}$ vs. $1/[\mathrm{HSn(n\text{-}Bu)_3}]$ using the data in Table II.

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