A Photochemical Investigation of *trans*-Tris(1,1,1-trifluoro-2,4-pentanedionato)rhodium(III) in the Gas Phase[1a]

Xiucen Yang[1b] and Charles Kutal*

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602.

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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) in the gas phase at 150 °C is reported. The complex undergoes both decomposition and geometrical isomerization when irradiated at 366 nm under vacuum, under a N_2 atmosphere, or in the presence of benzene vapor. In contrast, the complex is photoinert in benzene or mesitylene solution under identical conditions of irradiation wavelength and temperature. Some possible explanations for this disparity are presented. Addition of a good hydrogen atom donor such as 2-propanol or tri-*n*-butyltin hydride to the system markedly enhances the gas-phase photodecomposition of *trans*-Rh(tfa)$_3$. The kinetics of this bimolecular process can be analyzed in terms of simple gas-phase collision theory to provide a lower limit of $\sim 2 \times 10^{-10}$ s for the lifetime of a photogenerated rhodium(II)-ligand radical intermediate.

Modern inorganic photochemistry has its origins in the pioneering studies of several groups in the mid 1960s.[2] Earlier suggestions that the photochemical reactions of transition-metal complexes are merely photon-assisted thermal processes were shown to be incorrect and, instead, a distinct chemistry of electronically excited states began to unfold. Empirical observations of photoreactivity patterns were correlated with the electronic transitions in the complexes, leading to the useful generalizations that ligand field (metal-localized) excited states are precursors to ligand labilization and solvolysis, whereas charge-transfer excited states favor oxidation-reduction processes. Guided by these results, a number of workers[3-5] began to model excited-state reactivity within the context of current bonding theories. While the predictive power of these models attests to the importance of electronic factors in determining the photoreactivity of transition-metal complexes, there is increasing evidence that the reaction medium plays a noninnocent role in solution photochemical processes. Consider, for example, the effects of the cage of solvent molecules that completely surround the complex. Since the efficiency of separation of any fragments produced in the primary photochemical act depends upon the properties of this solvent cage, the observed quantum yield for product formation can be influenced by changes in solvent viscosity,[6,7] dielectric relaxation time,[8] or solvating ability.[9,10] Moreover, the enormous excess of solvent molecules may completely swamp out any bimolecular reactions of the excited complex with other (nonsolvent) species in solution.

Clearly, these effects that are encountered in solution photochemical studies arise from the ubiquitous presence of solvent molecules in the system. An attractive, yet virtually unexplored alternative for obtaining information about the excited-state reactivity of transition-metal complexes involves the study of photochemical behavior in the gas phase where many of the complications arising from solvent-solute interactions can be avoided. In cases where a complex has also been examined in solution, a comparison of the respective quantum yields or excited-state rate constants may provide valuable insight as to the mechanistic role of solvent. Equally intriguing is the possibility of observing photochemical reactivity patterns in the gas phase that have no counterpart in solution. In some systems new classes of reactions, perhaps leading to unusual or otherwise difficult to synthesize products, may be found. Bimolecular photoreactions between a transition-metal complex and reactive substrates should be especially prominent in the gas phase.

With these prospects in mind, we undertook an exploratory study of the photochemical behavior of *trans*-Rh(tfa)$_3$ (tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione; see Figure 1) in the gas phase. The exceptional volatility and thermal robustness of this complex make it ideally suited for such an undertaking. Moreover, a detailed investigation of the solution photochemistry of *trans*-Rh(tfa)$_3$ was described recently,[11] thereby facilitating a direct comparison with the gas-phase results reported here.

Experimental Section

(a) Reagents. Analytically pure *trans*-Rh(tfa)$_3$ was prepared according to published procedures.[11,12] Commercially available tri-*n*-butyltin hydride (Alfa) was purified by vacuum distillation (78 °C (0.8 torr)) and was kept refrigerated under nitrogen when not in use. Spectral grade benzene (Burdick and Jackson) and cyclohexane (Fisher) and reagent grade mesitylene (Aldrich) and 2-propanol (Fisher) were used as received.

(b) Measurements. Photolyses were performed with a 200-W high-pressure mercury arc lamp (Illumination Industries). The 366-nm mercury line was isolated with a half-width of 21 nm by means of interference and blocking filters. Light intensity was determined by ferrioxalate actinometry.[13]

Samples were irradiated in a 2-cm jacketed cylindrical cell fitted with a Rotaflo stopcock (Corning) that could be sealed tightly. Light entered and exited the cell through double-walled windows. The space between the inner and outer walls of each window was evacuated so as to minimize heat loss and the resulting formation of cold spots. The inside surface of the cell was treated overnight with a 40:60 v/v 1,1,1,3,3,3-hexamethyldisilizane-benzene solution, then rinsed several times with benzene, and finally dried in a stream of N_2. This treatment converts potentially reactive surface O-H groups to O-Si(CH$_3$)$_3$ linkages and thereby reduces the likelihood that *trans*-Rh(tfa)$_3$ will interact with the cell walls.

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[1] (a) Mechanistic Photochemistry of Transition-Metal β-Diketonate Complexes. 4. Part 3: Ferraudi, G.; Grutsch, P. A.; Kutal, C. *Inorg. Chim. Acta* **1982**, *59*, 249. (b) Visiting scholar on leave from the Medical Chemistry Department, Sichuan Medical College, Peoples' Republic of China.

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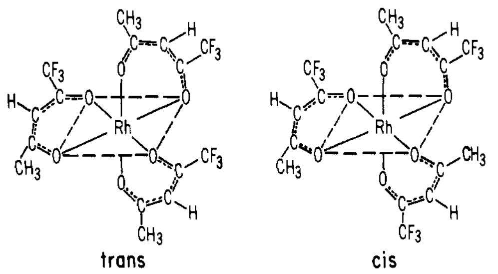

Figure 1. Structures of *trans*- and *cis*-Rh(tfa)$_3$.

The method of sample preparation depended upon the nature of the reaction medium. For gas-phase photolyses conducted at reduced pressure, a known volume of a stock solution of *trans*-Rh(tfa)$_3$ in benzene was pipetted into the cell; thereafter the cell was purged with N_2 gas for 20 min and then was evacuated to <1 torr. When a N_2 atmosphere was desired, the solvent was evaporated by flushing the cell with a gentle stream of the gas for 30 min. Reagents such as 2-propanol or HSn(*n*-Bu)$_3$ (dissolved in a small volume of deaerated benzene) could be added at this point. For liquid-phase photolyses, *trans*-Rh(tfa)$_3$ was dissolved in deaerated benzene or mesitylene. This solution was transferred by pipet to the cell and then purged with a gentle stream of N_2 for 0.5 min.

The cell was heated to and maintained at the desired temperature (150 ± 1 °C) by circulating oil from a thermostated bath through the outer jacket. The system was allowed to equilibrate for 15 min prior to irradiation. After photolysis, the cell was cooled to room temperature and its contents were analyzed by gas chromatography.[14] The instrument and operational conditions employed were very similar to those reported previously.[11] The areas of the *trans*- and *cis*-Rh(tfa)$_3$ peaks (integrated by planimetry) were converted to concentration units by comparison with calibration curves constructed from standard solutions of the isomers. Control experiments indicated that *trans*-Rh(tfa)$_3$ is thermally stable under the following conditions: (i) in benzene or mesitylene solution at 150 °C for at least 30 min; (ii) in the gas phase at 150 °C for up to 6 h in the presence of N_2, 0.05 M benzene, or 0.05 M 2-propanol; (iii) in the gas phase at 150 °C for 10 min in the presence of 10^{-5} M HSn(*n*-Bu)$_3$. In contrast, appreciable decomposition of the complex occurs within 3 min at 150 °C in the presence of 10^{-4} M HSn(*n*-Bu)$_3$.

The electronic absorption spectrum of *trans*-Rh(tfa)$_3$ in room-temperature solution was recorded on a Cary 15 spectrophotometer. The same instrument was used to obtain absorbance readings at 360 and 366 nm on gas-phase samples of the complex at elevated temperatures. Samples were contained in the 2-cm photolysis cell described above. Gas-phase spectra in the range 310–360 nm were measured point by point with a Beckman DU spectrometer whose detector assembly was modified to accept a 30-cm jacketed cylindrical cell fitted with a Rotaflo stopcock; the windows on this cell were of the double-wall design described above. Absorbance readings were first taken at several wavelengths with the vacuumized, heated cell in the light beam. The complex was then added to the cell, and the absorbance measurements were repeated. The difference between the two sets of readings corresponds to absorption by the complex. Five independent determinations of the spectrum provided extinction coefficients that agreed to within ±2% at most wavelengths (the largest deviation was 8% at 360 nm).

Results

The electronic absorption spectrum of *trans*-Rh(tfa)$_3$ in room-temperature cyclohexane contains two bands of comparable intensity at 325 and 265 nm (Figure 2). Both bands are thought to result from spin-allowed transitions to excited states of mixed $\pi-\pi^*$/charge-transfer character.[11,15] The energies of these transitions are nearly insensitive to changes in the polarity or hydrogen-bonding ability of the solvent. Thus the 325-nm band observed in cyclohexane appears at 323 nm in ethanol and 327 nm in benzene.

Quantitative measurement of the spectral and photochemical properties of *trans*-Rh(tfa)$_3$ in the gas phase requires accurate knowledge of the complex concentration. Since our method of sample preparation (see Experimental Section) involved the addition of a known amount of complex to a cell of known volume, the vapor-phase concentration of *trans*-Rh(tfa)$_3$ can be calculated in a straightforward manner if complete volatilization occurs upon heating. On the basis of the vapor-pressure measurements of Wolf et al.[16] and the empirical observation that complexes containing fluorinated β-diketonate ligands are appreciably more volatile than their non-fluorinated analogues,[17] we estimated that a concentration of *trans*-Rh(tfa)$_3$ on the order of 10^{-5}–10^{-6} M should exist entirely in the gas phase at 150 °C. This estimate was tested by measuring the absorbance of the complex as a function of temperature. In the most comprehensive experiment, sufficient complex was added to the cell to provide a maximum vapor phase concentration of 4.1×10^{-6} M. Absorbance values at several wavelengths were then measured at 150 and 160 °C. The close agreement between the corresponding values indicates that complete volatilization of the complex had occurred at these temperatures.[18] This conclusion receives further support from the observation that the absorbance of the complex at 150 °C obeys Beer's law in the concentration range $(3-4.1) \times 10^{-6}$ M.

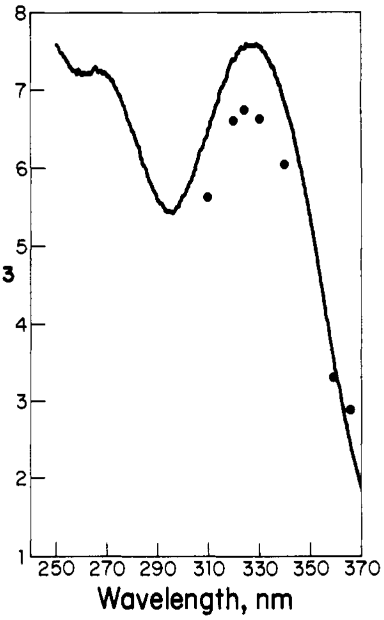

Figure 2. Electronic absorption spectra of *trans*-Rh(tfa)$_3$: (–) spectrum measured in cyclohexane at room temperature; (···) spectrum measured in the gas phase at 150–160 °C.

The gas-phase absorption spectrum of *trans*-Rh(tfa)$_3$ in the wavelength interval 310–366 nm is plotted in Figure 2. Each point represents the average of two independent determinations of the absorbance 150 °C and three at 160 °C. No significant change in the spectrum occurs as the pressure in the system is increased from <0.1 torr (vacuum) to >10^3 torr (added N_2). The most important conclusion to be derived from Figure 2 is that the gas-phase spectrum of *trans*-Rh(tfa)$_3$ corresponds closely to that measured in solution. Consequently, we expect that irradiation at a fixed wavelength (e.g., 366 nm) will result in the initial population of the same excited state(s) of the complex in both environments.

The gas-phase photochemical behavior of *trans*-Rh(tfa)$_3$ at 150 °C is summarized in Table I. Two processes are observed upon irradiation at 366 nm: decomposition[19] and isomerization to the cis complex (structure shown in Figure 1). These pathways occur with comparable quantum efficiencies under vacuum, under an atmosphere of N_2, or in the presence of a small amount of

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(14) For gas-phase samples, 5 mL of benzene was added to the cell to dissolve the contents.

(15) These intense bands undoubtedly mask several orbitally and/or spin-forbidden transitions expected to lie in this wavelength region.[11]

(16) Wolf, W. R.; Sievers, R. E.; Brown, G. H. *Inorg. Chem.* **1972**, *11*, 1995.

(17) Sievers, R. E. In "Coordination Chemistry"; Kirschner, S.; Ed.; Plenum Press: New York, 1969; p 270.

(18) In another experiment, the temperature was raised to 170 °C. The absorbance measured at 324 nm differed by less than 4% from the values obtained at 150 and 160 °C.

(19) The low concentration of *trans*-Rh(tfa)$_3$ (typically 4.1×10^{-6} M) employed in the gas-phase photolyses precluded identification of the likely decomposition products (e.g., free H(tfa)). For a discussion of the products formed upon photolyzing the complex in solution, see ref 11.

Table I. Photochemical Quantum Yields[a] for the Decomposition and Isomerization of *trans*-Rh(tfa)$_3$ in the Gas Phase at 150 °C

data set	reaction medium	ϕ_{dec}[b]	ϕ_{isom}[b]
A	vacuum, <1 torr	$(1.3 \pm 0.2) \times 10^{-5}$	$(1.4 \pm 0.2) \times 10^{-5}$
B	1.2×10^3 torr N_2	$(1.7 \pm 0.2) \times 10^{-5}$	$(1.5 \pm 0.2) \times 10^{-5}$
C	1.2×10^3 torr N_2 + 0.05 M benzene vapor	$(1.4 \pm 0.1) \times 10^{-5}$	$(1.3 \pm 0.0) \times 10^{-5}$
D	liquid benzene	$<4.4 \times 10^{-6}$	$<1.1 \times 10^{-6}$
E	liquid mesitylene	$<4.4 \times 10^{-6}$	$<1.1 \times 10^{-6}$
F	1.2×10^3 torr N_2 + 5×10^{-3} M 2-propanol vapor	$(2.6 \pm 0.2) \times 10^{-5}$	$(9.3 \pm 1.1) \times 10^{-6}$
G	1.2×10^3 torr N_2 + 0.025 M 2-propanol vapor	$(4.7 \pm 0.9) \times 10^{-5}$	$(9.0 \pm 0.4) \times 10^{-6}$
H	1.2×10^3 torr N_2 + 0.05 M 2-propanol vapor	$(5.6 \pm 0.2) \times 10^{-5}$	$(1.1 \pm 0.1) \times 10^{-5}$
I	1.2×10^3 torr N_2 + 0.05 M benzene vapor + 10^{-5} M HSn(n-Bu)$_3$ vapor	$(6.2 \pm 0.5) \times 10^{-4}$	$<5 \times 10^{-5}$
J	1.2×10^3 torr N_2 + 0.05 M benzene vapor + 10^{-4} M HSn(n-Bu)$_3$ vapor	$(1.0 \pm 0.1) \times 10^{-2}$	$<10^{-4}$

[a] Irradiations performed at 366 nm. [b] Uncertainties represent deviation from the mean; see ref 20.

benzene.[20] Addition of 2-propanol to the system, on the other hand, causes an increase in ϕ_{dec} but a decrease in ϕ_{isom}. The effects of added HSn(n-Bu)$_3$ are particularly dramatic. Thus even low concentrations of this facile hydrogen-atom donor greatly enhance photodecomposition, while isomerization is no longer observable within our detection limits.

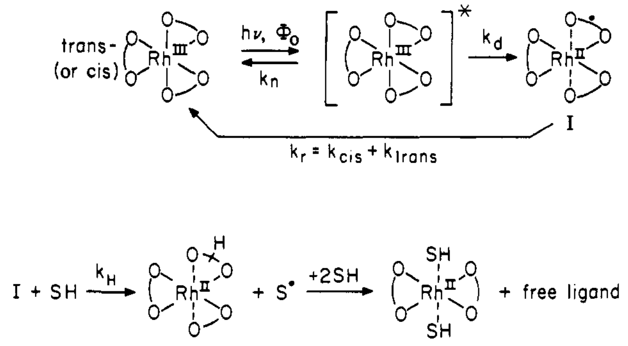
The effect of elevated temperature on the solution photochemistry of *trans*-Rh(tfa)$_3$ was investigated briefly. Benzene or mesitylene solutions of the complex heated to 150 °C were irradiated with 366-nm light. Since no decomposition or isomerization was detected, Table I lists our conservative estimates of the upper limits to the quantum yields of these processes.

Discussion

Before the gas-phase photobehavior of *trans*-Rh(tfa)$_3$ is considered, it will be helpful to summarize our earlier investigation[11] of its solution photochemistry. Ultraviolet (particularly 254-nm) irradiation of the complex results in two competing processes: redox decomposition with release of free H(tfa) and trans to cis isomerization. While the latter pathway is of minor importance ($\phi_{\text{isom}} < 10^{-4}$) in all solvents studied, the quantum efficiency of decomposition rises from $<6 \times 10^{-5}$ in cyclohexane to 0.13 in cyclohexane containing HSn(n-Bu)$_3$. The strong correlation between ϕ_{dec} and the hydrogen atom donor ability of the solvent led us to postulate that a key step in the decomposition process is the donation of a hydrogen atom from a solvent molecule to a photogenerated species possessing considerable radical character. Thus, in addition to its normal role as a reaction medium, solvent functions as a *direct* chemical participant in the photodecomposition of the complex. Several lines of evidence point to the existence of two photoreactive excited states in *trans*-Rh(tfa)$_3$. The higher energy state A is characterized by a competition between decomposition and isomerization, while the second state B strongly favors decomposition. On the basis of its reactivity characteristics, we suggested that A possesses appreciable ligand to metal charge-transfer character. As depicted in Scheme I,[21] the immediate consequence of populating this state would be the production of a short-lived rhodium(II)–ligand radical intermediate I. Thereafter, I can undergo either of two processes: (i) back-electron transfer to the ligand with regeneration of the original trans complex or (if rearrangement precedes electron transfer) its cis isomer; (ii) hydrogen atom abstraction from the solvent to yield, ultimately, a solvated Rh(II) complex and free H(tfa). Possible assignments of B are a second ligand to metal charge-transfer state or a ligand-localized n–π* state arising from transfer of a nonbonding electron on oxygen to a π* molecular orbital.

On a qualitative level, the photochemical behavior of *trans*-Rh(tfa)$_3$ in the gas phase parallels that described above. Both isomerization and decomposition result from ultraviolet irradiation, and the relative importance of these pathways depends upon the nature of the surrounding medium. In the absence of a good hydrogen atom donor (e.g., vacuum, N_2 atmosphere), the two processes occur with small and comparable quantum yields.[22] Addition of 2-propanol or HSn(n-Bu)$_3$ to the system, however, greatly facilitates decomposition. We infer from these results that many, if not all, of the processes depicted in Scheme I occur in the vapor phase as well as in solution. In particular, it seems clear that intermolecular hydrogen atom abstraction by a photogenerated species constitutes an important step in the photodecomposition of *trans*-Rh(tfa)$_3$ in both environments. Moreover, the observation that the gas-phase value of ϕ_{dec} experiences a greater change than does ϕ_{isom} upon addition of 2-propanol (compare data sets A and H in Table I) is consistent with the presence of two photoreactive excited states in the complex (vide supra).

Scheme I



The analogy between the solution and gas-phase photochemistries of *trans*-Rh(tfa)$_3$ is less satisfactory on a quantitative level. Thus a strict comparison of quantum yields measured under identical conditions of irradiation wavelength and temperature reveals some significant differences. As seen in Table I, the complex is photoinert within our detection limits in benzene or mesitylene solution at 150 °C,[23] while in the gas phase at the same temperature decomposition and isomerization occur with small but measurable efficiencies (compare data sets C and D in Table I).

This interesting trend toward higher quantum yields in the gas phase cannot be attributed to reaction from vibrationally "hot" (i.e., nonequilibrated)[24] electronic excited states of *trans*-Rh(tfa)$_3$, since ϕ_{dec} and ϕ_{isom} are invariant to a 10^4 increase in the total pressure in the system (Table I, data sets A and B). While a complete explanation of the observed behavior is not possible at this time, two possibilities merit serious consideration. (1) Reaction occurs from the same vibrationally equilibrated excited states of

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[20] The fraction of light absorbed by vaporized *trans*-Rh(tfa)$_3$ (typically 5.3%) was calculated by using Beer's law and a value of $(2.87 \pm 0.06) \times 10^3$ M^{-1} cm^{-1} (four determinations) for the extinction coefficient at 366 nm. We have assumed that all of the incident light lies at this wavelength. Since the filter combination used in the study has a half-width of 21 nm, this assumption introduces some error in the reported quantum yields. On the basis of sample calculations, however, we judge the error to be no larger than 10%.

[21] In Scheme I, SH is a hydrogen-containing solvent molecule, ϕ_0 is the efficiency of forming the reactive excited state, and the k's represent rate constants for the indicated processes.

[22] The small amount of decomposition observed in vacuum or under a N_2 atmosphere may reflect bimolecular hydrogen atom transfer from ground-state *trans*-Rh(tfa)$_3$ to the photoexcited complex.

[23] The complex is also photoinert when irradiated at 366 nm in room-temperature cyclohexane, ethanol, or 2-propanol.[11]

[24] In condensed media, molecules in excited vibronic states rapidly dissipate their excess vibrational energy to the surroundings via collisionally induced energy transfer. Since this process occurs more slowly in the gas phase at low pressures, other deactivation pathways (e.g., chemical reactions) could conceivably compete. See: Rynbrand, J. D.; Rabinovitch, B. S. *J. Chem. Phys.* **1971**, *54*, 2275.

the complex in solution and the gas phase, but at least one of the processes that populate or depopulate these states (refer to Scheme I) is sensitive to the nature of the environment.[25] Precedent for this type of behavior comes from the recent observation[26] that the emissive excited state of $W(CO)_5L$ (L is 4-acetylpyridine or 4-cyanopyridine) is longer lived in the gas phase than in hydrocarbon solution. (2) The encapsulation effect of the solvent cage hinders those molecular motions of the photogenerated intermediate I that lead to decomposition and isomerization.[6,7] As a result, back-electron transfer with no net chemical change is more likely to occur in solution than in the vapor phase.

A final aspect of the present study concerns the observation of bimolecular photochemistry between *trans*-Rh(tfa)$_3$ and good hydrogen atom donor substrates in the gas phase. According to Scheme I, these substrates facilitate photodecomposition of the complex by intercepting the reactive intermediate I. The kinetics of this process can be analyzed in terms of simple gas-phase collision theory[27] to provide an estimate of the lifetime of this rhodium(II)–ligand species. As a first step, we need to calculate the number of collisions per second between I and a given concentration, n, of the hydrogen atom donor. The requisite relationship is given by eq 1, where Z_1 is the collision number, σ is

$$Z_1 = (2)^{1/2}\pi\sigma^2\bar{c}n \qquad (1)$$

the collision diameter, and $\bar{c}$ is the velocity of the colliding particles. With $\sigma = 1 \times 10^{-7}$ cm, $\bar{c} = 1.5 \times 10^4$ cm/s, and a HSn(n-Bu)$_3$ concentration of 1×10^{-5} M ($n = 6 \times 10^{15}$ molecules/cm^3), we obtain $Z_1 = 4 \times 10^6$ collisions/s.[28]

The quantum yield for decomposition of *trans*-Rh(tfa)$_3$ in the presence of HSn(n-Bu)$_3$ is given by eq 2, where the symbols refer

$$\phi_{\text{dec}} = \phi_0\left(\frac{k_d}{k_n + k_d}\right)\left(\frac{k_H[SH]}{k_r + k_H[SH]}\right) \qquad (2)$$

to processes depicted in Scheme I.[19] Let us consider the limiting case in which (i) I is formed with unit efficiency (i.e., $\phi_0(k_d/k_n + k_d) = 1$), and (ii) each collision of I with HSn(n-Bu)$_3$ results in decomposition (i.e., $k_H[SH] = 4 \times 10^6$ s^{-1}).[29] With the experimentally determined value of $\phi_{\text{dec}} = 6.2 \times 10^{-4}$, we calculate $k_r = 6.5 \times 10^9$ s^{-1}. The lifetime of I in the absence of HSn(n-Bu)$_3$ is simply k_r^{-1} or 1.5×10^{-10} s.[30] It should be noted that this calculated value represents a lower limit to the actual lifetime. Thus I could be considerably longer lived if either or both of the above assumptions regarding its behavior is faulty.[31]

Concluding Remarks

Only a few previous studies of transition-metal photochemistry in the gas phase have been reported, and these were concerned with organometallic complexes containing metals in low ($\leq$+1) formal oxidation states.[32] In the present investigation we have taken advantage of the volatility imparted by fluorinated β-diketonate ligands to examine the vapor-phase photobehavior of trivalent rhodium in *trans*-Rh(tfa)$_3$. We find that the photoreactions of the complex in the gas phase bear a qualitative resemblance to those observed in solution but, quite interestingly, the quantum efficiencies are consistently higher in the former environment. While the full implications of this behavior must await further studies, it seems clear that the role of solvent cannot be ignored in discussions of photoreactivity in solution. The observation of bimolecular photochemistry in the gas phase is noteworthy, since it suggests the possibility of obtaining kinetic information (e.g., reaction order, rate constants) about excited-state reactions in the absence of solvent–solute interactions. Such information will be of obvious value in assigning the mechanisms of photochemical processes, particularly if it is augmented by vapor-phase luminescence measurements.

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Registry No. *trans*-Rh(tFa)$_3$, 67145-51-1; *cis*-Rh(tFa)$_3$, 65309-05-9; HSn(n-Bu)$_3$, 688-73-3; benzene, 71-43-2; 2-propanol, 67-63-0; mesitylene, 108-67-8.

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[25] For example, a larger value of k_d (see Scheme I) in the gas phase than in solution would accommodate the observed trend in quantum yields.

[26] Brooks, K.; Adamson, A. W. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, Mar 1982; American Chemical Society: Washington, DC, 1982; INOR 207. Additional studies of transition-metal luminescence in the vapor phase are clearly needed. In this regard, the recent observation of gas-phase emission from a chromium(III) β-diketonate complex is a promising development (private communication from W. F. Coleman).

[27] Barrow, G. M. "Physical Chemistry"; McGraw-Hill: New York, 1961; Chapter 2.

[28] Equation 1 is applicable to collisions between identical molecules. Since *trans*-Rh(tfa)$_3$ and HSn(n-Bu)$_3$ possess different velocities and collision diameters, we employ average values for these quantities. The diameters of the molecules were estimated from X-ray data and molecular models. See: Morrow, J. C.; Parker, E. B. *Acta Crystallogr., Sect. B* **1973**, *B29*, 1145. Gordon, M. S.; Koob, R. D. *J. Am. Chem. Soc.* **1973**, *95*, 5863.

[29] A more detailed analysis requires knowledge of the values of ϕ_0, k_d, k_n, and k_H.

[30] Repeating the calculation for a HSn(n-Bu)$_3$ concentration of 10^{-4} M yields a lifetime of 2.5×10^{-10} s.

[31] For example, assumption ii probably overestimates the value of k_H, since only that fraction of the total collisions that bring the H–Sn bond into close proximity to intermediate I should result in hydrogen atom transfer.

[32] For interesting recent studies, see: Evans, W.; Zink, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 2635. Tumas, W.; Gitlin, B.; Rosan, A. M.; Yardley, J. T. *Ibid.* **1981**, *103*, 55.