Detection of Reactive Rhodium Containing Intermediates Following Flash Photolysis of a Tris(β-diketonato)rhodium(III) Complex

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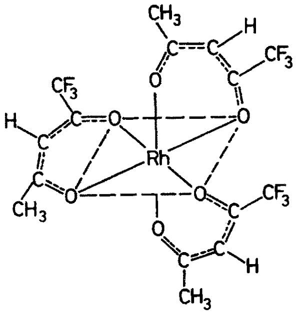
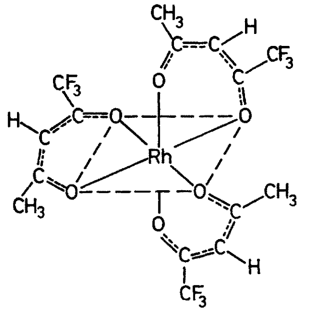
Summary Flash photolysis of *trans*-tris(1,1,1-trifluoropentane-2,4-dionato)rhodium(III) in alcoholic solvents produces a short-lived Rh^{II}-containing species which decays to a longer-lived intermediate tentatively identified as a Rh^{II}-hydride.

Recently we reported[1] that *trans*-$Rh(tfa)_3$ (I) (tfa = 1,1,1-trifluoropentane-2,4-dionato) undergoes two competing photochemical processes: decomposition with release of free H(tfa) ligand and isomerization to the corresponding *cis*-complex (II). The relative importance of either pathway is markedly solvent dependent as evidenced by the sharp rise in the quantum yield ratio, ϕ_{dec}/ϕ_{isom}, from $<0{\cdot}65$ in cyclohexane to >110 in propan-2-ol upon 254 nm irradiation. Values of ϕ_{dec} were found to correlate well with the ease of hydrogen atom abstraction from the solvent, prompting the suggestion that a solvent molecule donates a hydrogen atom to a photogenerated species with considerable radical character. We now report a flash photolysis study of *trans*-$Rh(tfa)_3$, the results of which allow a more precise delineation of several key steps in this photochemical reaction sequence.



(I)



(II)

Sample solutions were prepared by dissolving the pure *trans* complex[2] in solvents which had been previously deaerated by bubbling with argon. Flash irradiations were performed using an apparatus described elsewhere.[3]

No discernible spectral changes occur upon flash photolysing a solution of *trans*-$Rh(tfa)_3$ in pure cyclohexane, whereas comparable irradiation in alcoholic solvents produces a common transient absorption which decays in two successive steps well separated in time. The species, X, responsible for the short-lived stage of the decay displays an absorption maximum at *ca.* 360 nm (Figure). Although small absorbance values and overlap with the spectrum of *trans*-$Rh(tfa)_3$ preclude an accurate spectral characterization of the species, Y, responsible for the long-lived decay, we have established that it has no maximum at wavelengths above 350 nm.

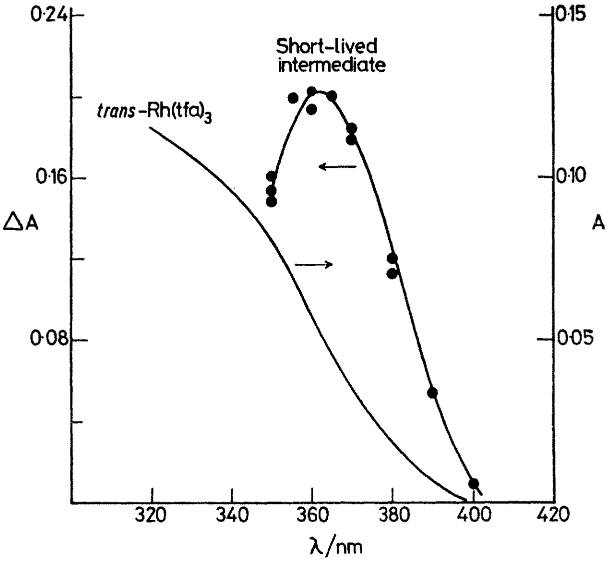


Figure. Absorption spectra in propan-2-ol of the parent complex, *trans*-$Rh(tfa)_3$, and the short-lived transient obtained upon flash photolysis. A is absorbance, while ΔA is the flash-induced change in absorbance extrapolated back to zero time.

The amount of X produced during the *ca.* 30 μs flash lifetime (as measured by the initial absorbance change) increases and eventually attains a limiting value as the mole fraction of alcohol in mixed alcohol–cyclohexane solvents is increased. This initial yield of X depends upon the alcohol employed, being higher for propan-2-ol than for the equivalent mole fraction of ethanol. Furthermore, the initial yield exhibits a linear dependence upon the flash intensity, indicating that X is generated neither in the

Table. Rate constants for decay of the intermediates produced in flash irradiations of *trans*-$Rh(tfa)_3$.[a]

k_{obs}/s^{-1} [b]	Conditions	
Short-lived intermediate (X)		
$(5{\cdot}3 \pm 0{\cdot}5) \times 10^3$	100%	Ethanol
$(2{\cdot}0 \pm 0{\cdot}6) \times 10^3$	90%	Propan-2-ol in cyclohexane
$(8{\cdot}3 \pm 0{\cdot}3) \times 10^2$	100%	t-Butyl alcohol
$(8{\cdot}8 \pm 0{\cdot}5) \times 10^2$	100%	t-Butyl alcohol, 5×10^{-3} M $HClO_4$
Long-lived intermediate (Y)		
$(2{\cdot}0 \pm 0{\cdot}3)$	100%	t-Butyl alcohol
(90 ± 5)	100%	t-Butyl alcohol, 2×10^{-2} M $HClO_4$[c]

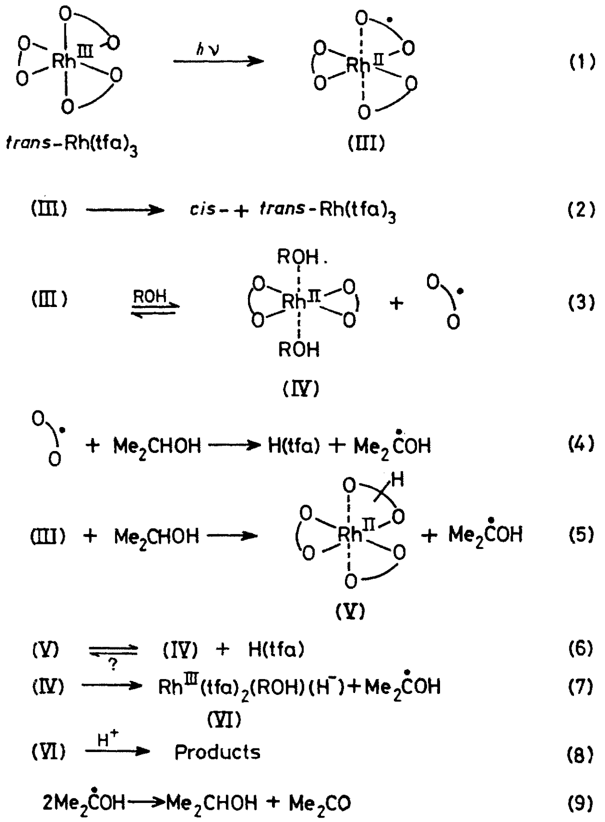
[a] Flash energies of 250 J per pulse were employed; the transient decay was monitored at 360 nm. [b] Average of 4—10 determinations. [c] Obtained by dilution of 70% $HClO_4$ with t-butyl alcohol.

disproportionation nor the dimerization of a precursor species. The disappearance of X obeys a first order rate law whose rate constant, k_{obs} depends upon the identity but not the concentration of the alcohol component in mixed solvent systems; moreover, this rate constant is unaffected by the addition of acid (Table). In contrast, k_{obs} for the disappearance of Y exhibits an approximate linear dependence upon the concentration of added hydrogen ion.

To determine whether the two species observed in the flash photolysis of *trans*-Rh(tfa)$_3$ are characteristic of β-diketone compounds in general, we flash photolysed alcoholic solutions of free H(tfa) and *trans*-Co(tfa)$_3$. Neither system displays transient behaviour which resembles that reported above. Consequently, it seems reasonable to identify both X and Y as Rh containing species.

The sequence of reactions shown in equations (1)—(9) accommodates all of the present observations as well as the continuous photolysis results reported previously.[1] We propose that the initial consequence of light absorption is production of a short-lived ($< 1\,\mu s^4$) Rh$^{\text{II}}$–ligand radical species (III) (equation 1). Within the lifetime of the flash, (III) may regenerate the parent complex (equation 2), rearrange to the corresponding *cis*-isomer (equation 2), or undergo reactions which result in redox decomposition (equations 3—6). The key role of solvent in regulating the photochemical behaviour of *trans*-Rh(tfa)$_3$ resides in its ability to react with and solvate the various intermediates produced. Thus a good hydrogen atom donating solvent (*e.g.*, propan-2-ol) can intercept the tfa radical (equation 4) and prevent its recombination with (IV) (equation 3); alternatively, (III) may abstract a hydrogen atom directly from a solvent molecule to produce (V) (equation 5), which subsequently eliminates free H(tfa) and forms (IV) (equation 6). In either case, however, the extent of decomposition is predicted to depend upon the hydrogen atom donor ability of the solvent as required by the continuous photolysis results.[1]

We assign (IV) as the short-lived intermediate, X, produced in flash photolysis. This assignment is consonant with the observation that the initial yields of X produced during the flash depend upon the identity of the alcohol in mixed solvent systems, being higher for propan-2-ol than for ethanol (a poorer hydrogen atom donor). Subsequent intramolecular reaction of (IV) produces the long-lived intermediate Y, which we tentatively identify as a Rh$^{\text{III}}$-hydride species (VI) (equation 7). While additional evidence is needed to verify this latter assignment, it is consistent with the observed acid-dependent decay of Y (equation 8)[5] and the reported behaviour of some Rh$^{\text{III}}$-hydride complexes.[6]



A portion of the research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. C. K. wishes to thank Matthey Bishop, Inc. for a generous loan of rhodium trichloride.

(*Received*, 26*th July* 1978; *Com.* 810.)

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