Transient Photochemistry of (η^5-Cyclopentadienyl)bis(ethene)rhodium

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On laser flash photolysis, using both u.v.–visible and i.r. detection, of $CpRh(C_2H_4)_2$ (Cp = η^5-C_5H_5) in hydrocarbon solutions, two transients are detected, A and B; A is assigned as $CpRh(C_2H_4)$ (probably a triplet state) and decays to products and B *via* first-order kinetics [$k = (1.0 \pm 0.5) \times 10^6\ s^{-1}$]; B [$CpRh(C_2H_4)S$, S = solvent] reacts with incoming ligands *via* second-order saturation kinetics with a strong solvent dependence.

The trio of methods, matrix isolation, product studies in solution, and flash photolysis form a powerful combination for understanding the mechanisms of photosensitive organometallic systems. Combined studies of this type have been confined to a few metal carbonyls and Cp_2MoH_2 (Cp = η^5-C_5H_5).[1,2] We recently reported studies of the photochemistry of $CpRh(C_2H_4)_2$ by product analysis in hydrocarbon and liquid xenon solution, and by matrix isolation, which showed the dominant photoprocess to be dissociation of C_2H_4.[3,4] The reactive intermediate, $CpRh(C_2H_4)$, was detected by i.r. and u.v.–visible spectroscopy, and shown by magnetic circular dichroism to have a diamagnetic (singlet) ground state.[3,5] The resulting vacancy may be filled by another donor ligand (*e.g.* CO) or by oxidative addition (*e.g.* of Et_3SiH). In contrast, ethene dissociation competes with isomerisation to a vinyl hydride for $CpIr(C_2H_4)_2$.[6] We report a mechanistic study of the photochemistry of $CpRh(C_2H_4)_2$ in hydrocarbon solutions using laser flash photolysis with u.v.–visible and i.r. detection.

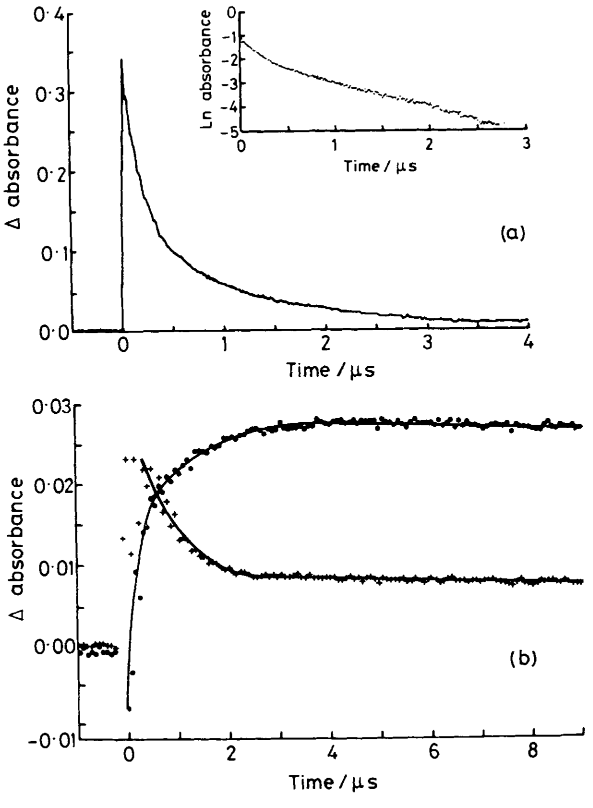

Figure 1. (a) Kinetic trace showing the rise (<50 ns) and decay of transient A monitored at 425 nm, following flash photolysis of (**1**) (5×10^{-3} mol dm^{-3}) in C_6H_{12} under C_2H_4. The inset represents the corresponding first-order plot. The fluorescence of the sample and optics have been subtracted using a full data set of 2000 points. The first-order plot shows slight curvature over the initial 300 ns corresponding to the fluorescence time. (b) Kinetic traces showing the decay of A (+) monitored at 425 nm and the simultaneous rise of B (●) at 360 nm. These plots show data reduced to 250 points without fluorescence subtraction.

Laser flash photolysis† of $CpRh(C_2H_4)_2$ (**1**), in cyclohexane under 1 atm of any of Ar, C_2H_4, CO, N_2, CH_4, CO_2, or H_2, yields a transient absorption monitored at 425 nm, which rises in $\lesssim$ 50 ns and decays in *ca.* 5 µs (Figure 1a). Similar behaviour is observed when cyclohexene and Et_3SiH are the added substrates under an Ar atmosphere. This transient, A, decays *via* good first-order kinetics ($k = 1.0 \pm 0.5 \times 10^6\ s^{-1}$) over *ca.* 4 half lives. The rate constant is independent of added substrate, concentration of (**1**) (10^{-3} to 8×10^{-3} mol dm^{-3}), and solvent (C_6H_{12}, C_6H_6) within the experimental error limits. The decay of A at 425 nm is accompanied by a simultaneous rise in absorption at 360 nm, which occurs at the same rate as the decay of A to within 10% for any given sample (Figure 1b). A point-by-point u.v.–visible spectrum of A obtained 1 µs after the laser flash of (**1**) in C_6H_{12} under CO ($\lambda_{max.}$ 410 ± 10 nm, Figure 2a) is close to that obtained by matrix isolation of $CpRh(C_2H_4)$ (420 nm in Ar, 399 nm in CH_4).‡

The second transient, B, formed from A, is stable over microseconds but decays over milliseconds (Figure 2b). The decay is again first-order in transient and independent of [(**1**)], but is strongly dependent on added substrate (see Scheme 1) and solvent.§ For any given substrate, $k_{obs.}$ is *ca.* 100 times smaller in C_6H_6 than in C_6H_{12}. A point-by-point u.v.–visible absorption spectrum of B was obtained 400 µs after the laser flash of (**1**) in C_6H_{12} under C_2H_4 (Figure 2a, $\lambda_{max.}$ 345 ± 5 nm). When the u.v.–visible spectra of solutions of (**1**) in C_6H_{12} were monitored before and after *ca.* 250 flashes, we found the system to be reversible under C_2H_4, but new products were formed with other substrates.

Closer examination of the effect of substrate (L = Et_3SiH, C_6H_{10}) on the decay rate of B shows it to be linear in [L] at low [L] but saturating to a limiting rate at higher [L] (Figure 3).¶

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† For u.v. detection (in York) the laser flash at 308 nm (EMG-50 Excimer laser) lasted *ca.* 25 ns. Pulse energy was reduced to *ca.* 5 mJ per pulse with neutral density filters. The transients were detected *via* an Applied Photophysics laser kinetic spectrophotometer and a Gould 4500 digital oscilloscope. The minimum detectable risetime is *ca.* 50 ns. Transient signals were averaged over 16 flashes. The apparatus for flash photolysis with i.r. detection (in Nottingham) is described in ref. 7, but the flash lamp was replaced by a laser (also 308 nm).

‡ We have remeasured the matrix u.v. spectra. These values are revised from ref. 3.

§ Transient B was unaffected by H_2O. The rate of decay in the presence of C_2H_4 changed by only 2.5% between dried solvent and solvent containing 0.1 M H_2O. The rate of reaction under CH_4 was very similar to that under Ar, indicating the absence of C–H oxidative addition.

¶ Since we are limited to 1 atm pressure for gaseous L, this effect was only observed for L = Et_3SiH or C_6H_{10}.

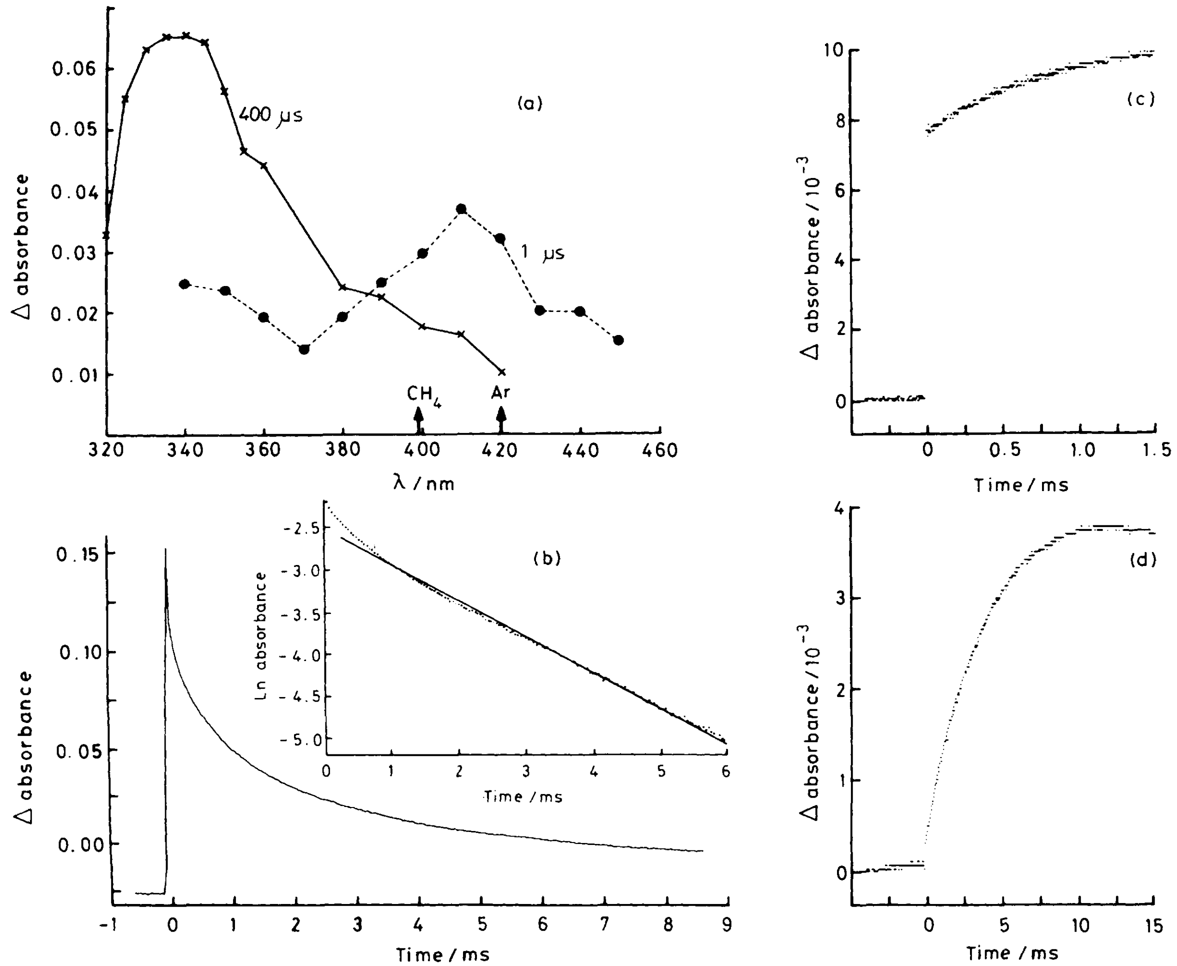


Figure 2. (a) Point-by-point u.v.–visible difference spectra obtained 1 (●) and 400 (×) μs after the laser flash of (**1**) in C_6H_{12}. The spectrum after 1 μs is chiefly of A with some contribution from B below 370 nm. The spectrum after 400 μs is due to B. The arrows mark the absorption maxima of $CpRh(C_2H_4)$ in CH_4 and Ar matrices. (b) Kinetic trace and first-order plot for the decay of transient B in C_6H_{12} under 1 atm C_2H_4. (c), (d) Kinetic traces with i.r. detection showing the two-stage formation of $CpRh(C_2H_4)CO$ in n-heptane under (c) 1.5 atm CO, (d) a reduced pressure of CO ($\nu_{mon.}$ 1990 cm^{-1}), note change of timescale.

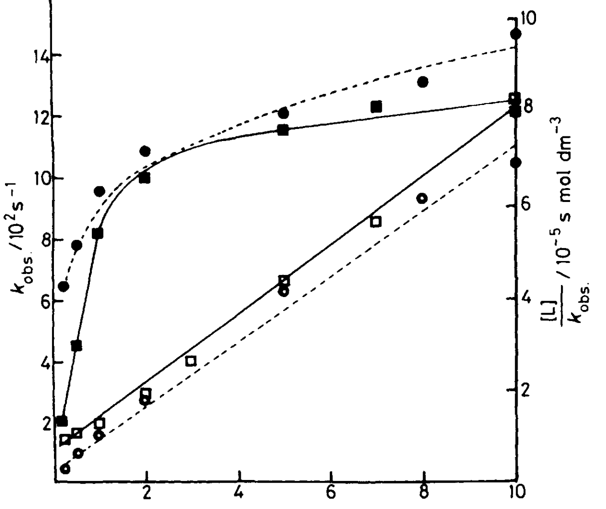


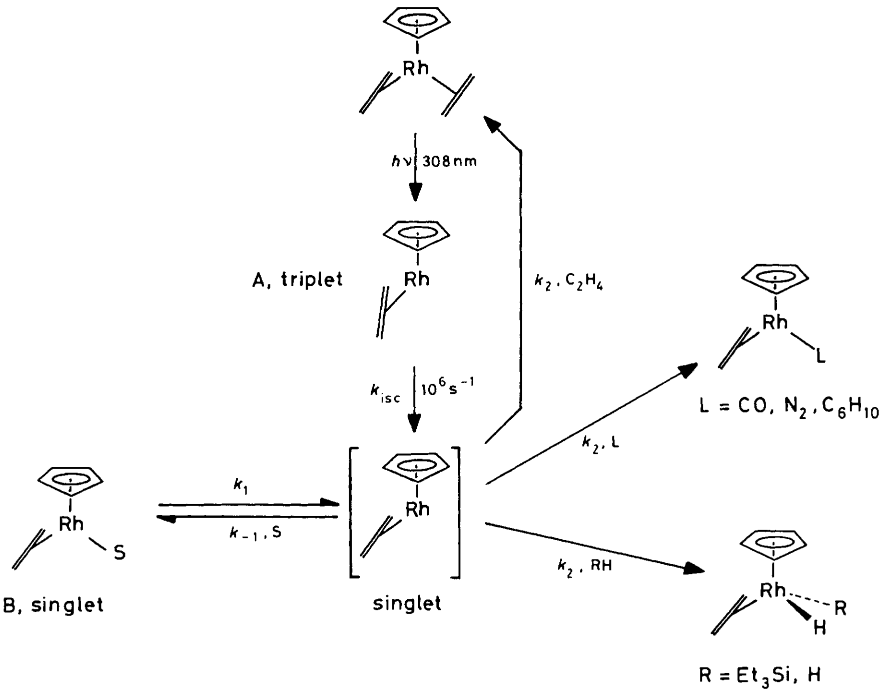
Figure 3. Curved plots (left hand ordinate axis): dependence of the observed first-order decay of transient B, $k_{obs.}$, on concentration of added substrate [L] (■ for Et_3SiH and ● for C_6H_{10} respectively). Linear plots (right hand ordinate axis): dependence of $[L]/k_{obs.}$ on [L] [see equation (2), Et_3SiH □, C_6H_{10} ○].

Scheme 1 takes account of the kinetic saturation, the u.v.–visible spectra of A and B, the identification of stable products,[3,4] and the solvent effect. According to Scheme 1, $k_{obs.}$ is given by equation (1), which may be rearranged to equation (2). From a plot of $[L]/k_{obs.}$ *vs.* [L] for C_6H_{12} solutions, k_1 is determined to be 1330 ± 30 (Et_3SiH) and 1450 ± 100 s^{-1} (cyclohexene) showing excellent agreement between ligands as Scheme 1 requires (Figure 3). In contrast, for solutions in benzene, k_1 was found to be 4.1 ± 0.1 s^{-1} (L = Et_3SiH). Transient B is therefore assigned as $CpRh(C_2H_4)S$ (S = solvent). From the intercepts of these plots the ratio k_{-1}/k_2 is found to be $(6 \pm 4) \times 10^{-4}$ and $(9 \pm 3) \times 10^{-4}$ for C_6H_{10} and Et_3SiH respectively, showing a surprisingly large preference for ligand attack over solvation by $CpRh(C_2H_4)$. Confirmation of the stability of $CpRh(C_2H_4)$ (η^2-arene) complexes is obtained by photolysing (**1**) in toluene at −60 °C. A stable pink colour develops with $\lambda_{max.}$ 339 and 507 nm (relative intensities 28 : 1) which disappears slowly on warming.

$$k_{obs.} = k_2k_1[L]/(k_2[L] + k_{-1}[S]) \qquad (1)$$

$$[L]/k_{obs.} = [L]/k_1 + k_{-1}[S]/k_1k_2 \qquad (2)$$

Time-resolved i.r. spectroscopy[7] has been used to monitor the formation of $CpRh(C_2H_4)CO$ ($\nu_{mon.}$ 1990 cm^{-1}) by



Scheme 1. Transient photochemistry of $CpRh(C_2H_4)_2$.

photolysis of (**1**) in n-heptane when CO is the added substrate. $CpRh(C_2H_4)CO$ is formed by two processes under 1.5 atm of CO: 80% of the product is formed rapidly (≤ 1 μs) while 20% is formed slowly (~4 ms, Figure 2c). The fast process corresponds to direct product formation from unsolvated $CpRh(C_2H_4)$; the slow process involves prior formation of B (Scheme 1). From the proportion of product formed rapidly and the concentrations of CO (1.6×10^{-2} mol dm^{-3}) and solvent (6.8 mol dm^{-3}), k_{-1}/k_2 is determined to be 5×10^{-4} in agreement with the results above. The i.r. kinetic traces under lower CO pressure are consistent with this model: (i) the proportion of product formed rapidly is greatly reduced, (ii) the rate of the slow process is decreased by a factor of ~5 (Figure 2d).

We propose that A is $CpRh(C_2H_4)$, probably in a triplet state, and that A reacts to form either B [$CpRh(C_2H_4)S$] or other products *via* a very short-lived singlet state (Scheme 1). This three-intermediate scheme has been confirmed by kinetic modelling. Calculations carried out on the analogous CpRhCO fragment suggest that the singlet and triplet states have similar energies, but different Cp–M–CO angles.[8] Matrix isolated $CpRh(C_2H_4)$ may correspond to intermediate A or the undetected singlet $CpRh(C_2H_4)$, but the m.c.d. evidence supports the latter identification.

These experiments provide detailed *kinetic* characterisation of an unsaturated non-carbonyl organometallic. The application of the powerful combination of flash photolysis with both u.v. and i.r. detection reveals: (i) two intermediates, both intimately involved in product formation and (ii) the importance of specific solvation for one. of the intermediates [compare $M(CO)_5S$, M = Cr,Mo,W].[1]

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