Equilibria and Kinetics of Dissociation of Triphenylphosphine from [*N,N'*-Ethylenebis(salicylideneiminato)]bis(triphenylphosphine)ruthenium(II) in Benzene

Hideo Doine and Hiroshi Fukutomi
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-Okayama, Meguro-ku, Tokyo 152, Japan
Roderick D. Cannon *
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

The reactions (i) and (ii) [H_2salen = *N,N'*-ethylenebis(salicylideneimine)] in benzene solution have been studied by both equilibrium and kinetic spectrophotometric methods. At 25 °C, $k_1 = 1.61 \pm 0.02$

$$[\mathrm{Ru(salen)}] + \mathrm{PPh_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Ru(salen)(PPh_3)}] \qquad \text{(i)}$$

$$[\mathrm{Ru(salen)(PPh_3)}] + \mathrm{PPh_3} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Ru(salen)(PPh_3)_2}] \qquad \text{(ii)}$$

$\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, $k_{-1} = (2.7 \pm 0.4) \times 10^{-4}\,\mathrm{s^{-1}}$, $k_2 = (1.18 \pm 0.05) \times 10^{-1}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, $k_{-2} = (1.20 \pm 0.09) \times 10^{-3}\,\mathrm{s^{-1}}$, $K_1 = (0.60 \pm 0.08) \times 10^4\,\mathrm{dm^3\,mol^{-1}}$, and $K_2 = 98 \pm 6\,\mathrm{dm^3\,mol^{-1}}$.

The complex $[\mathrm{Ru^{II}(salen)(PPh_3)_2}]$ (**1**) [H_2salen = *N,N'*-ethylenebis(salicylideneimine)] was first prepared, independently, by Thornback and Wilkinson,[1] and by Murray *et al.*[2] It was found to be soluble in a variety of organic solvents and easily oxidised to ruthenium(III). A five-cordinate ruthenium(II) derivative, $[\mathrm{Ru(Hsalen)(PPh_3)}]\mathrm{X}$ ($\mathrm{X^-} = \mathrm{BF_4^-}$ or tosylate ion) was also isolated in the solid state.[1] In the course of electrochemical studies[3] on complex (**1**) we observed changes in the absorption spectrum and in the $\mathrm{Ru^{III}}$–$\mathrm{Ru^{II}}$ reduction potential, suggesting replacement of co-ordinated triphenylphosphine by solvent molecules. We have now found that using benzene as solvent the changes can be conveniently monitored, and we present here equilibrium and kinetic evidence for the stepwise complexation reactions (1) and (2).

$$[\mathrm{Ru(salen)}] + \mathrm{PPh_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Ru(salen)(PPh_3)}] \qquad (1)$$

$$[\mathrm{Ru(salen)(PPh_3)}] + \mathrm{PPh_3} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Ru(salen)(PPh_3)_2}] \qquad (2)$$

Results and Discussion

Complex (**1**) was prepared from $[\mathrm{RuCl_2(PPh_3)_3}]$[4] as described previously, and characterised by elemental analysis and absorption spectra. In methanol the spectrum agreed with that reported previously,[3] and in tetrahydrofuran the spectrum was similar. In benzene the spectrum changed slowly with time, and the changes were reversed by addition of triphenylphosphine. The spectra of all these red-brown solutions are characteristic of the ruthenium(II) oxidation state: when air is admitted the colour changes to green, and the spectra of the oxidised products resemble the spectrum reported by Murray *et al.*[2]

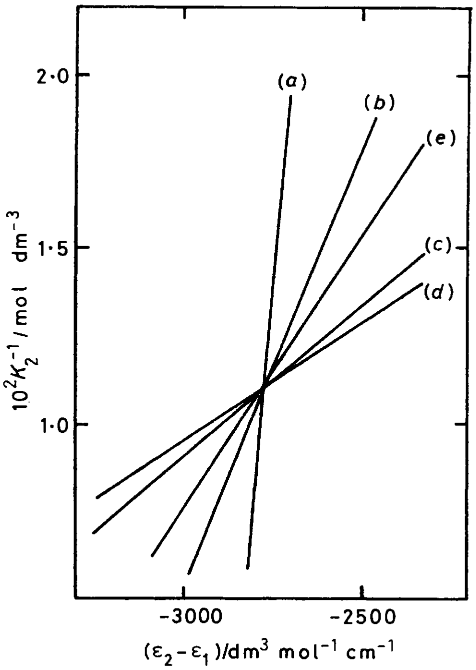

Figure 1. Rose–Drago plots for equilibrium (1). $[\mathrm{PPh_3}]$ = (*a*) 1.57×10^{-3}, (*b*) 3.15×10^{-3}, (*c*) 4.72×10^{-3}, (*d*) 6.29×10^{-3}, (*e*) 9.43×10^{-3} mol dm^{-3}; $[\mathrm{Ru^{II}}] = 5.41 \times 10^{-4}$ mol dm^{-3}. λ = 790 nm. T = 25 °C

Spectral changes in the triphenylphosphine concentration range 1.6—9.4 mmol dm^{-3} added were consistent with a single equilibrium, reaction (2), and values of absorbance, A, at $\lambda_{\max.}$ = 790 nm were used to determine K_2 by two different calculation procedures. (*i*) In a variant of the method of Rose and Drago,[5] equation (3) was used, where ε_1 and ε_2 are the molar absorption

$$K_2^{-1} = (A - \varepsilon_1\, l[\mathrm{M}]_\mathrm{T})/(\varepsilon_2 - \varepsilon_1)l - [\mathrm{M}]_\mathrm{T} - [\mathrm{L}]_\mathrm{T} + (\varepsilon_2 - \varepsilon_1)l[\mathrm{M}]_\mathrm{T}[\mathrm{L}]_\mathrm{T}/(A - \varepsilon_1\, l[\mathrm{M}]_\mathrm{T}) \qquad (3)$$

coefficients of complexes $[\mathrm{ML}_i]$ [M = Ru(salen), L = $\mathrm{PPh_3}$, i = 1 or 2], $[\mathrm{M}]_\mathrm{T}$ and $[\mathrm{L}]_\mathrm{T}$ are total concentrations, and l is the path length. The value $\varepsilon_2 = 800 \pm 20$ dm^3 mol^{-1} cm^{-1} was obtained from the limiting spectrum at high $[\mathrm{L}]_\mathrm{T}$. For each pair of data (A, $[\mathrm{L}]_\mathrm{T}$), values of K_2^{-1} were calculated with a series of arbitrary values of ε_1, and plotted against $(\varepsilon_2 - \varepsilon_1)$ as shown in Figure 1. The intersection point gives the true values of K_2^{-1} and ε_1. (*ii*) Following James and Markham,[6] a trial value of ε_1 was used to calculate [ML] and $[\mathrm{ML_2}]$, and the ratio $[\mathrm{ML}]/[\mathrm{ML_2}]$ was plotted against $[\mathrm{L}]^{-1}$ so that

Table. Rate and equilibrium data for reactions (1) and (2)[a]

	T/°C					
	15	21	25	30	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
$10^1\ k_1$/dm^3 mol^{-1} s^{-1}	7.3 ± 0.8	10.9 ± 1.4	16.1 ± 0.2	22.0 ± 0.7	52 ± 5	−66 ± 9
$10^4\ k_{-1}$/s^{-1}	*b*	*b*	2.7 ± 0.4	18.3 ± 4.6	—	—
$10^{-3}\ K_1$/dm^3 mol^{-1} [c]	—	—	6.0 ± 0.8	1.2 ± 0.2	—	—
$10^2\ k_2$/dm^3 mol^{-1} s^{-1}	7.0 ± 0.4	9.6 ± 0.2	11.8 ± 0.5	13.5 ± 0.5	30 ± 2	−160 ± 13
$10^4\ k_{-2}$/s^{-1}	3.9 ± 0.4	7.7 ± 0.4	12.0 ± 0.9	18.3 ± 0.8	74 ± 3	−55 ± 8
$10^{-1}\ K_2$/dm^3 mol^{-1} [c]	18 ± 1.5	12.5 ± 0.5	9.8 ± 0.6	7.4 ± 0.3	—	—
$10^{-1}\ K_2$/dm^3 mol^{-1} [d]			9.1 ± 0.6			

[a] Solutions in benzene; $[\mathrm{Ru}]_T = 0.2$ mmol dm^{-3}. [b] Intercepts of plots according to equation (4) were within the standard deviation of the points. [c] Calculated from kinetic parameters. [d] From spectrophotometric measurements. Absorption coefficients $\varepsilon_1 = 3\,400 \pm 300$ and $\varepsilon_2 = 800 \pm 20$ dm^3 mol^{-1} cm^{-1}; $\lambda = 790$ nm.

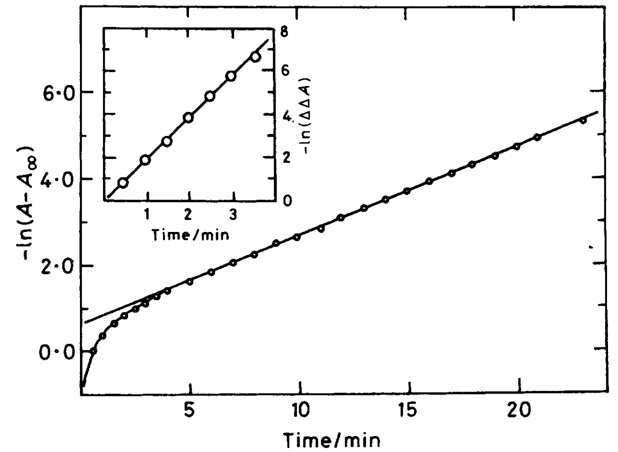

Figure 2. Plot of $-\ln(A - A_\infty)$ *vs.* time. $[\mathrm{Ru^{II}}] = 2.10 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{PPh_3}] = 0.0199$ mol dm^{-3}; 25 °C. The inset shows $-\ln(\Delta\Delta A)$ *vs.* time, where $\Delta\Delta A = A - A'$ and A' is the value of A read from the extrapolated linear part of the main curve

the slope of the line gave a first approximation to K_2^{-1}. From this a second approximation to ε_1 was calculated, and so on until the values converged. The two methods gave $K_2^{-1} = (11.0 \pm 0.7) \times 10^{-3}$ and $(10.2 \pm 0.9) \times 10^{-3}$ mol dm^{-3}, respectively, at 25 °C. The spectra do not show isosbestic points, but the good coincidence of the lines in Figure 1 supports the assumption that only two species absorb significantly in the concentration range used, and the final values of K_1 and K_2, compared below, confirm this.

Equilibrated dilute solutions ($[\mathrm{M}]_T = 0.2$ mol dm^{-3}) prepared from complex (**1**) treated with excess triphenylphosphine showed a monotonic decrease in absorbance. Plots of $\ln(A - A_\infty)$ against time indicated two phases, both pseudo-first order. Rate constants k' and k'' were obtained by the usual method[7] as shown in Figure 2. Plots of k' and k'' against [L] in the range [L] = 7—30 mol dm^{-3} gave the linear expressions (4) and (5) and least-squares fitting gave the values of k_1, k_{-1}, k_2, and k_{-2} listed in the Table. The values calculated for K_2 agree well with the values obtained from the equilibrium measurements.

$$k' = k_1[\mathrm{L}] + k_{-1} \qquad (4)$$

$$k'' = k_2[\mathrm{L}] + k_{-2} \qquad (5)$$

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