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THE NATURE AND STABILITY OF OLEFIN—PALLADIUM(II)—CHLORIDE COMPLEXES IN ACETIC ACID*

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The formation of palladium(II)—olefin complexes in acetic acid is an essential step in the oxidative acetylation of olefins in the presence of palladium(II) salts [1—3] (1).

$$CH_2{=}CH_2 + CH_3COO^- + Pd^{II} \xrightarrow{CH_3COOH} CH_2{=}CHOCOCH_3 + Pd^0 + H^+ + \text{further acetylated species} \qquad (1)$$

There is very little direct evidence as to the nature [4, 5] and stability of the olefin complexes formed in such solution and it therefore seemed desirable to investigate this and in particular to look at the influence of chain length on the stability of the complexes.

Na_2PdCl_4 was used as the source of palladium(II) because it is readily available commercially and is fairly soluble in acetic acid. The simplest alternative to Na_2PdCl_4 is Li_2PdCl_4 which has several drawbacks. Thus LiCl dimerises in acetic acid [6] whereas NaCl does not; as a consequence of this much smaller amounts of sodium chloride can be used to adjust the chloride concentrations. This has the advantage that the activity coefficients do not vary so much as when larger amounts of lithium chloride are used. It is virtually impossible to compensate for this by controlling the activity coefficients in acetic acid by the inert background electrolyte method [7] since the few electrolytes that dissolve in acetic acid tend to precipitate $[PdCl_4]^{2-}$ and $[Pd_2Cl_6]^{2-}$. A further disadvantage of Li_2PdCl_4 is that it forms a more complex range of species in acetic acid solution [8] than Na_2PdCl_4 does. Accordingly the first stage of the present work involved an investigation of the nature and stability of the species formed when Na_2PdCl_4 is dissolved in glacial acetic acid.

NATURE OF "Na_2PdCl_4" SOLUTIONS

The first stage of the investigation of "Na_2PdCl_4" solutions involved a qualitative study to determine the species present so that in the subsequent quantitative work it would be possible to present the computer with a reasonably precise

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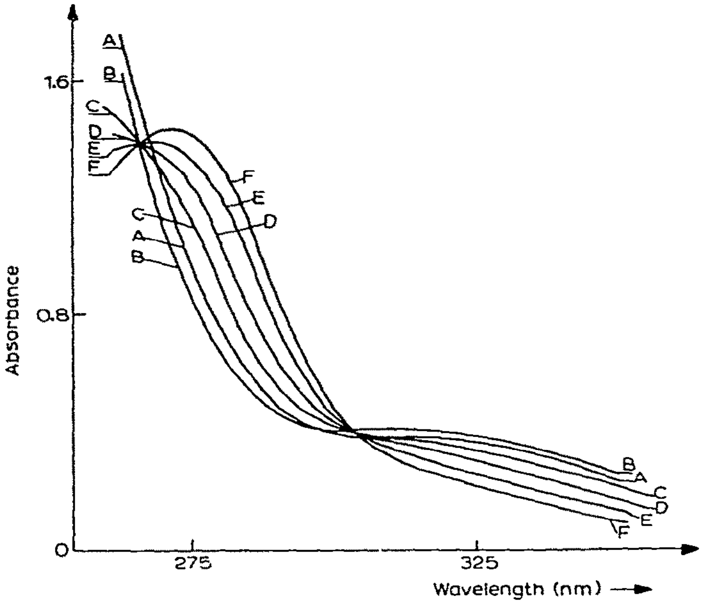

Fig. 1. UV-spectra of chloropalladium species in acetic acid. Total palladium(II) concentration = 1.51 × 10^{-4} *M*; chloride concentrations: A, 5.90 × 10^{-4} *M*; B, 1.98 × 10^{-4} *M*; C, 3.38 × 10^{-3} *M*; D, 6.17 × 10^{-3} *M*; E, 8.96 × 10^{-3} *M*; F, 1.31 × 10^{-2} *M*.

model of the system. This approach to complex equilibrium constant problems seems highly desirable because the more precisely one can describe the species present, the more accurately a computer can determine the equilibrium constants that interrelate those species. The qualitative results may be summarised as follows:

(i) When the UV spectra of a series of solutions all containing the same total palladium concentration and varying amounts of chloride were recorded, all the spectra of solutions containing $[Cl^-]:[Pd^{II}] > 20:1$ passed through two sharp isosbestic points (Fig. 1). Although this is not absolute proof that under these conditions only 2 absorbing species are present [9], it is strongly suggestive of it. At least one more species is present at low chloride concentrations since curve A in Fig. 1 misses both isosbestic points.

(ii) The rank of the matrix of the absorbance data [10, 11] for a series of solutions containing "Na_2PdCl_4" and NaCl indicated that for solutions containing $[Cl^-]:[Pd^{II}] > 20:1$ only two absorbing species were present.

(iii) Use of Coleman, Mastin and Varga's graphical method [12] to determine the number of species present suggested that there were two absorbing species present at all except the lowest chloride concentrations, since the 2-species test gave a straight line plot except at the lowest chloride concentrations (Fig. 2a), whereas other *n*-species tests gave randomly scattered points (e.g., the 3-species test in Fig. 2b).

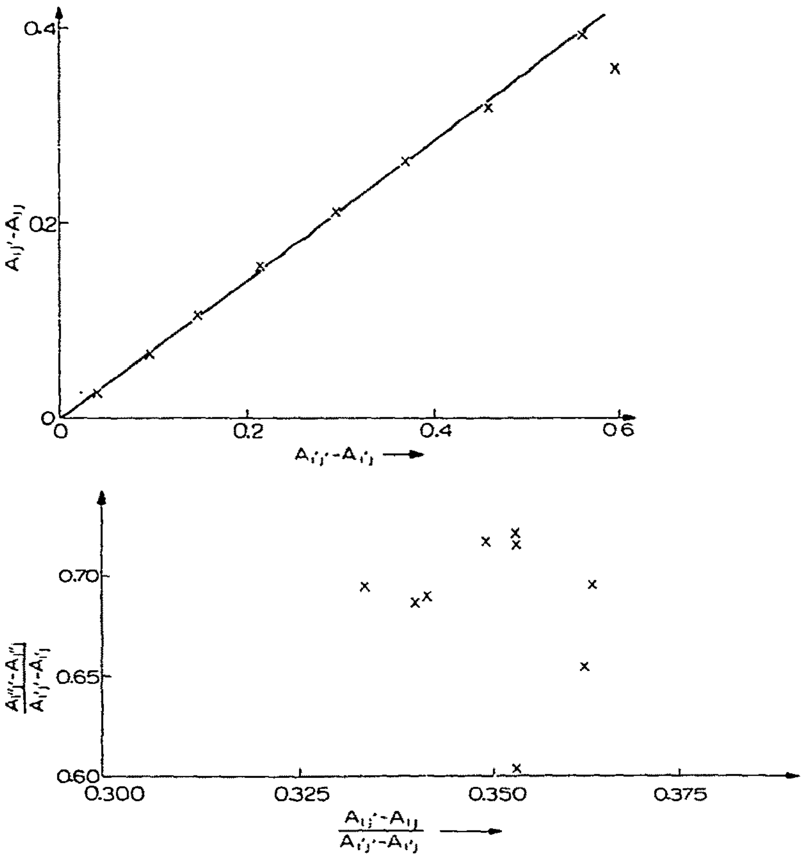

Fig. 2. Plots obtained using Coleman, Varga and Mastin's graphical method (ref. 10). (a) 2-species test (b) 3-species test. A_{ij} = absorbance of solution j at wavelength i.

Reference to the known chemistry of chloropalladium(II) species in organic solvents [13—15] suggests that the two main absorbing species are Na_2PdCl_4 and $Na_2Pd_2Cl_6$ and that the third species is probably a solvo-species which may be $Na[Pd_2Cl_5(CH_3COOH)]$ or $Na[PdCl_3(CH_3COOH)]$. Accordingly, a model involving all 4 of these species was used to analyse the absorbance data obtained at 10 wavelengths for 59 solutions whose chloride:palladium(II) concentrations varied between 2.7:1 and 87:1. Reasonable estimates of both the equilibrium constants and the molar absorptivities of each of the species present were requried by the program, which then used these to calculate the absorbance. This calculated absorbance was compared to the observed absorbance and the equilibrium constants and molar absorptivities were successively refined until the best fit between the observed and calculated absorbances was obtained. The resultant equilibrium constants are shown in eqns. 2—4.

$$2\,Na_2PdCl_4 \xrightleftharpoons{K_1 = 0.56 \pm 0.02\ M} Na_2Pd_2Cl_6 + 2\,NaCl \tag{2}$$

$$Na_2Pd_2Cl_6 \xrightleftharpoons{K_2 = (2.9 \pm 0.6) \times 10^{-5}\ M} Na[Pd_2Cl_5(CH_3COOH)] + NaCl \tag{3}$$

$$Na_2PdCl_4 \xrightleftharpoons{K_3 = (3.5 \pm 3.7) \times 10^{-4}\ M} Na[PdCl_3(CH_3COOH)] + NaCl \tag{4}$$

It is apparent that the standard deviation of K_3 is rather high. This is because this species is never present to an extent greater than 3.35% (see Fig. 3).

In addition to determining the equilibrium constants the molar absorptivities of each of the species present were also calculated and these could then be compared with the estimated spectra. For $Na_2Pd_2Cl_6$ and Na_2PdCl_4 the fits were within 1% and 5% respectively, and moreover the predicted isosbestic points agreed closely with those observed experimentally. This high degree of agreement between the estimated and computer calculated spectra gives a considerable degree of confidence in the chosen model. When a rather complex system, such as the present one, is being studied by presenting a series of reasonable models to the computer and analysing the data in terms of each, then absorbance data is more useful than potentiometric data. This is because, although potentiometric measurements are generally more precise than UV—visible absorbance measurements, they lack an intensive parameter corresponding to the molar absorptivity by which each species can make its own unique contribution to the observable. Furthermore, in UV—visible spectroscopy the relative contributions of each of the species to the observable (absorbance) can be altered by altering the wavelength at which the system is studied since

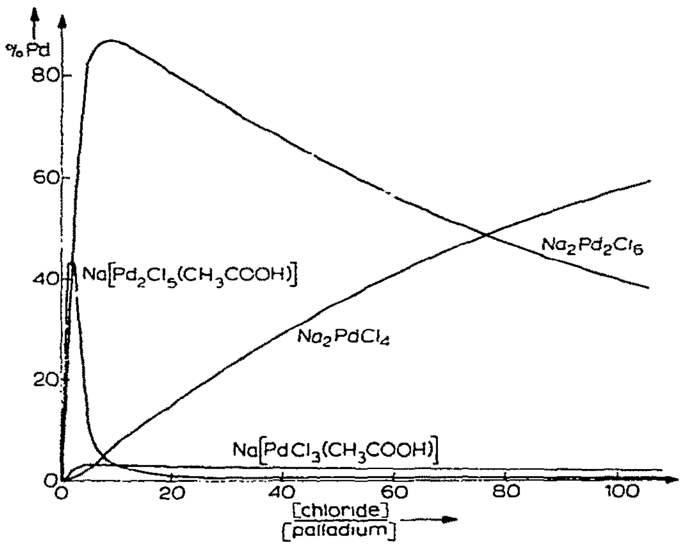

Fig. 3. Percentage of palladium(II) present in each form as a function of the ratio of the concentrations of chloride and palladium(II).

the molar absorptivities are wavelength dependent. Thus for very complicated systems UV—visible spectroscopy will often give a more reliable indication of the species present because it also gives rise to molar absorptivities which can be checked to see if they are reasonable (e.g., they must always be zero or positive in value and give rise to fairly smooth curves when joined up to form a spectrum). However, once the correct model has been chosen potentiometric data will give rise to more precise equilibrium constants than absorbance data because of the overlap of the broad bands present in UV—visible spectra, which leads to correlation between the calculated equilibrium constants and molar absorptivities. Clearly, the ideal approach is to combine absorbance and potentiometric data.

NATURE AND STABILITY OF PALLADIUM(II)—OLEFIN COMPLEXES

Having determined the composition of an "Na_2PdCl_4" solution it was possible to investigate the species formed when an olefin was added. In order to reduce the number of species present all the solutions were treated with sodium chloride, thus minimising the formation of solvo-complexes (see Fig. 3). Again qualitative investigations of these chloro—palladium(II)—olefin solutions were carried out [5] using preparative techniques, Raman spectroscopy and analysis of the UV—visible spectra by the Method of Continuous Variations together with the matrix rank and graphical methods used previously. These investigations suggested that eqns. 5 and 6 represent the olefin complex equilibria.

$$Na_2Pd_2Cl_6 + \text{olefin} \overset{K_4}{\rightleftharpoons} Na[Pd_2Cl_5(\text{olefin})] + NaCl \qquad (5)$$

$$Na[Pd_2Cl_5(\text{olefin})] + \text{olefin} \overset{K_5}{\rightleftharpoons} [Pd_2Cl_4(\text{olefin})_2] + NaCl \qquad (6)$$

Quantitative absorbance data was then obtained for a series of terminal olefins by preparing a number of solutions (about 12) each containing the same total palladium(II) and sodium chloride concentrations but varying concentrations of the olefin (see Table 1). The palladium(II) was added immediately before recording the spectra over the range 270—335 nm. Absorbances at about 9 equally spaced wavelengths were determined giving a total of about 110 absorbance values per olefin. Data for each olefin was determined at two different palladium(II) concentrations. A non-linear least-squares computer program was used to analyse the absorbance data in terms of a model based on eqns. 2, 5 and 6. Again the computer program generated the spectra of the absorbing species and for this particular model predicted spectra which suggested that an isosbestic point should be observed near to 295 nm, in close agreement with our earlier observation [5] of such a point at 293 nm at low olefin concentrations and 297 nm at high olefin concentrations. We tried a number of other models but none gave as good agreement, as determined by the Hamilton R-factor, together with satisfactory spectra for the absorbing species. The resultant equilibrium constants are shown in Table 1. An R_{limit} value of 0.033

TABLE 1

Equilibrium constant data for palladium(II)—olefin complexes at 25°C.

Olefin	Experiment series	$[Pd]_T$ × 10^4 [a]	$[Cl]_T$/ $[Pd]_T$ [b]	Range of $[ol]_T/[Pd]_T$ [c]	Number of experiments	Number of solutions	K_4 [d]	K_5 [d]	R-factor [e]
1-pentene	a	5.72	26.0	0.62–62.0	12	9	5.2 (4.0)	4.4 (1.8)	0.0207
	b	3.71	32.3	0.96–96.0	13	8	5.6 (2.1)	4.1 (0.7)	0.0117
1-hexene	a	5.72	26.0	0.50–30.0	11	9	14.8 (5.4)	3.3 (0.5)	0.0109
	b	3.71	32.3	1.66–82.8	12	8	8.3 (2.8)	3.5 (0.4)	0.0097
1-heptene	a	6.09	19.1	0.52–52.0	12	9	12.2 (6.3)	1.9 (0.2)	0.0164
	b	2.93	30.5	1.07–107.0	12	10	6.9 (1.7)	2.1 (0.3)	0.0098
1-octene	a	6.12	19.0	0.40–48.4	12	9	4.9 (3.2)	2.8 (0.5)	0.0146
	b	2.93	30.6	0.84–84.0	13	9	6.2 (0.7)	2.7 (0.1)	0.0044
1-nonene	a	6.10	19.1	0.37–44.6	11	9	7.4 (2.7)	2.4 (0.2)	0.0087
	b	3.06	29.2	0.73–73.0	13	13	12.7 (5.0)	2.4 (0.2)	0.0131

[a] $[Pd]_T$ = total palladium(II) concentration.

[b] $[Cl]_T/[Pd]_T$ = ratio of total chloride to total palladium(II) concentration.

[c] $[ol]_T/[Pd]_T$ = ratio of total olefin to total palladium(II) concentration.

[d] Standard deviations are given in parentheses.

[e] $R = [\{\Sigma_{i=1}^{n \times m}(A_i^{calc} - A_i^{obs})^2\}/\{\Sigma_{i=1}^{n \times m}(A_i^{obs})^2\}]^{1/2}$ where n = number of wavelengths studied, m = number of solutions used and A = absorbance.

was calculated from eqn. 7

$$R_{\text{limit}} = \left[\left\{ \sum_{i=1}^{nxm} \epsilon_i^2 \right\} \Big/ \left\{ \sum_{i=1}^{nxm} (A_i^{\text{obs}})^2 \right\} \right]^{1/2} \tag{7}$$

where A_i^{obs} = observed absorbance and ϵ_i the residual in *i*th equation calculated from pessimistic estimates of the errors in all the experimental quantities (absorbance ± 2%, total chloride concentration ± 1.5%, total olefin concentration ± 1.5%) using the usual rules for the propagation of errors. Since in all cases $R < R_{\text{limit}}$, the results in Table 1 are a statistically acceptable interpretation of the data [16].

For most of the work the value of K_1 as well as the molar absorptivities of Na_2PdCl_4 and $Na_2Pd_2Cl_6$ were fixed at those found in the absence of olefin. However, for one set of data these were allowed to vary (Table 2) and it was gratifying to find that the calculated equilibrium constants changed very little when this was done although, of course, the standard deviations went up significantly. Normally the condition for a minimum was that all the corrections to the parameters were less than 1%; however in the last result in Table 2 refinement was continued until all the corrections were less than 0.5%. It is apparent that this causes a marked decrease in the standard deviations but little change in the actual numerical values of the equilibrium constants. Since this last calculation took four times as much computer time we did not analyse all our results to this degree of precision.

The final equilibrium constants (Table 3) confirm our earlier suggestion [5] that only 2 palladium(II)—olefin species are formed in significant amount and that they are both chloride-bridged palladium(II) complexes. The reason for the absence of monomeric Na[PdCl$_3$(olefin)] is not clear, although its absence is entirely consistent with the qualitative observations of many workers. The results indicate that the chain length over the range C_5—C_9 has little in-

TABLE 2

Equilibrium constants obtained for the 1-octene (b) data when parameters in addition to K_4, K_5 and the molar absorptivities of Na[Pd$_2$Cl$_5$(1-octene)] and [Pd$_2$Cl$_4$(1-octene)$_2$] were varied [a].

Extra parameters varied [b]	K_1	K_4	K_5
None	0.56	6.2 (0.7)	2.7 (0.1)
K_1	0.54 (0.03)	6.2 (0.9)	2.6 (0.2)
K_1, $\epsilon_{Na_2Pd_2Cl_6}$	0.55 (1.10)	5.4 (0.9)	2.6 (0.9)
K_1, $\epsilon_{Na_2Pd_2Cl_6}$, $\epsilon_{Na_2PdCl_4}$	0.55 (4.63)	5.4 (8.8)	2.6 (2.2)
K_1, $\epsilon_{Na_2Pd_2Cl_6}$, $\epsilon_{Na_2PdCl_4}$	0.56 (0.46) [c]	5.1 (3.0) [c]	2.6 (2.1) [c]

[a] Standard deviations are given in parentheses.

[b] ϵ = molar absorptivity.

[c] The condition for a minimum in this case was that all the corrections to the parameters were less than 0.5% as opposed to 1% used in all other results.

TABLE 3

Weighted mean equilibrium constants at 25°C.

Olefin	K_4 [a]	K_5 [a]
1-pentene	5.5 (1.9)	4.2 (0.6)
1-hexene	9.7 (2.5)	3.4 (0.3)
1-heptene	7.3 (1.6)	2.0 (0.2)
1-octene	6.1 (0.7)	2.7 (0.1)
1-nonene	9.7 (2.4)	2.4 (0.2)

[a] The weighted mean of two equilibrium constants K^a and K^b is given by $\{K^a/\sigma_a^2 + K^b/\sigma_b^2\}\cdot\{\sigma_a^2\sigma_b^2\}/\{\sigma_a^2 + \sigma_b^2\}$ where σ = standard deviation. The standard deviation, given in parentheses, is given by $\{(\sigma_a^2\sigma_b^2)/(\sigma_a^2 + \sigma_b^2)\}^{1/2}$ (ref. 17).

fluence on the stability of palladium(II)—olefin complexes in acetic acid, a result that should be of interest to anyone wishing to use longer chain olefins as starting materials for chemical reactions.

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