Stability of Palladium(II)–Olefin Complexes in Glacial Acetic Acid †

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Investigation of the species formed when terminal olefins are added to a solution obtained by dissolving $Na_2[PdCl_4]$ in glacial acetic acid has shown that only two olefin complexes, $Na[Pd_2Cl_5(olefin)]$ and $[Pd_2Cl_4(olefin)_2]$, can be detected. The stability constants K_1 and K_2 for the equilibria (i) and (ii) are essentially independent of chain length in the range C_5—C_9.

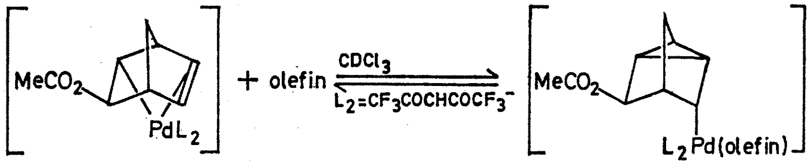
$$Na_2[Pd_2Cl_6] + \text{olefin} \overset{K_1}{\rightleftharpoons} Na[Pd_2Cl_5(\text{olefin})] + NaCl \qquad \text{(i)}$$

$$Na[Pd_2Cl_5(\text{olefin})] + \text{olefin} \overset{K_2}{\rightleftharpoons} [Pd_2Cl_4(\text{olefin})_2] + NaCl \qquad \text{(ii)}$$

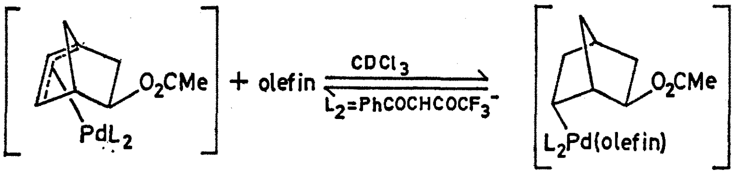
Although the formation of palladium(II)–olefin complexes in solution is a vital first step in many of the important Pd^{II}-catalysed reactions of olefins, there are very few reports describing the exact nature of such complexes in solution and even fewer reports of equilibrium studies on such systems.[1] Most metal–ligand stability-constant studies[2] have been carried out in aqueous solution and of these the majority have involved the use of an inert background electrolyte to maintain constant the ionic strength and activity coefficients of the species present. A few thermodynamic data for reaction (1) in aqueous solution have been reported,[3-9] but

$$[PdCl_4]^{2-} + \text{olefin} \rightleftharpoons [PdCl_3(\text{olefin})]^- + Cl^- \qquad (1)$$

these are subject to considerable error since true equilibrium is not established due to subsequent rapid decomposition of $[PdCl_3(\text{olefin})]^-$ to carbonyl compounds and palladium metal. Accordingly the use of other solvents has been investigated. However, it is often difficult to dissolve sufficient background electrolyte in such solvents and so maintain a constant ionic medium. If no background electrolyte is present it is necessary to work at sufficiently low concentrations of the dissolved species to ensure that the activity coefficients are unity. This in turn requires the use of a sensitive technique for determining concentration and partially accounts for the present use of u.v.–visible spectroscopy which enabled Pd^{II} salt concentrations of the order of 10^{-4}M to be employed.‡ Recent reports of metal–olefin stability constants for reactions (2) and (3) determined by ^1H n.m.r., which is a relatively insensitive method for determining concentration, using solutions as concentrated as 0.82M in metal salt and 0.82M in olefin should be regarded with caution for this reason.[10-12]



(2)



(3)

Following our discovery that Pd^{II} salts reacted with olefins in glacial acetic acid to give palladium(II)–olefin complexes that were stable in the absence of added nucleophiles,[13] we carried out investigations to determine the nature of the species present in solution when a solution of ' $Na_2[PdCl_4]$ ' in glacial $MeCO_2H$ was treated

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† No reprints available.

‡ 1M = 1 mol dm^{-3}.

[1] F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799.

[2] ' Stability Constants of Metal–Ion Complexes,' eds. L. G. Sillén and A. E. Martell, *Special Publ.* Nos. 17 and 25 (1964 and 1971), The Chemical Society, London.

[3] P. M. Henry, *J. Amer. Chem. Soc.*, 1964, **86**, 3246.

[4] I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Doklady Akad. Nauk. S.S.S.R.*, 1963, **152**, 147.

[5] S. V. Pestrikov, I. I. Moiseev, and T. N. Romanova, *Russ. J. Inorg. Chem.*, 1965, **10**, 1199.

[6] S. V. Pestrikov, I. I. Moiseev, and B. A. Tsvilikhovskaya, *Russ. J. Inorg. Chem.*, 1966, **11**, 931.

[7] S. V. Pestrikov, I. I. Moiseev, and L. M. Sverzh, *Russ. J. Inorg. Chem.*, 1966, **11**, 1113.

[8] S. V. Pestrikov and I. I. Moiseev, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1965, 349.

[9] A. M. Osipov and V. A. Likholobov, *Izvest. Vyssh. Ucheb. Zaved., Khim. Tekhnol.*, 1972, **15**, 1166 (*Chem. Abs.*, 1972, **77**, 144457).

[10] R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1972, **34**, C51.

[11] E. M. Ban, R. P. Hughes, and J. Powell, *J.C.S. Chem. Comm.*, 1973, 591.

[12] E. M. Ban, R. P. Hughes, and J. Powell, *J. Organometallic Chem.*, 1974, **69**, 455.

[13] F. R. Hartley and J. L. Wagner, *J.C.S. Dalton*, 1972, 2282.

with a terminal olefin. Preliminary work[14] suggested that at least five species were present: $\mathrm{Na_2[PdCl_4]}$; $\mathrm{Na_2[Pd_2Cl_6]}$; $\mathrm{Na[Pd_2Cl_5(HO_2CMe)]}$; $\mathrm{Na[Pd_2Cl_5(olefin)]}$; and $\mathrm{[Pd_2Cl_4(olefin)_2]}$. In the previous paper[15] we reported on the nature of solutions of '$\mathrm{Na_2[PdCl_4]}$' in glacial $\mathrm{MeCO_2H}$ in the absence of olefin, and here we report on the nature and stability of the species formed in such solutions when terminal olefins are added. Although obviously of relevance to the general problem of thermodynamic stability of palladium(II)–olefin complexes, this work is of particular relevance to the oxidative acetylation of olefins in $\mathrm{MeCO_2H}$ in the presence of $\mathrm{Pd^{II}}$ salts which is used commercially to convert ethylene into vinyl acetate.[16] A preliminary account of this work has been reported elsewhere.[17]

EXPERIMENTAL

AnalaR glacial acetic acid (B.D.H.) was used throughout, each fresh sample being checked by Bruckenstein's method[18] to ensure that the water content was less than 0.05%. The olefins were redistilled before use and their purity shown by g.l.c. to be greater than 99%. None of the olefins absorbs in the spectral region of interest (270—335 nm). Standard solutions of the olefins in $\mathrm{MeCO_2H}$ were prepared by weight. Stock palladium(II) and sodium chloride solutions were standardised before use, using the methods described previously.[15]

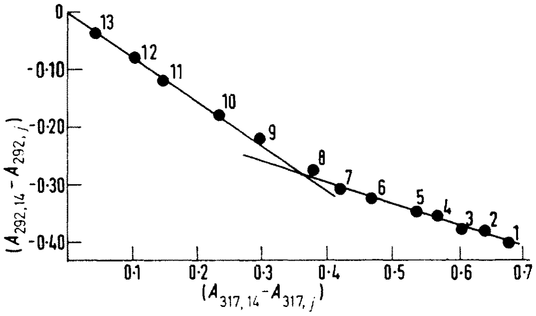

FIGURE 1 Coleman *et al.*[19] two-species test for palladium(II)–pent-1-ene: (absorbance at 292 nm for solution 14) — (absorbance at 292 nm for solution *j*) ($j = 1$—13) plotted against (absorbance at 317 nm for solution 14) — (absorbance at 317 nm for solution *j*). The pent-1-ene concentration increases successively as *j* increases

Determination of the Number of Species Present.—A series of solutions in glacial acetic acid each containing $3.71 \times 10^{-4}\mathrm{M}$-$\mathrm{Pd^{II}}$, $1.20 \times 10^{-2}\mathrm{M}$-$\mathrm{Cl^-}$, and olefin concentrations between 0 and 0.03M were prepared and their absorbance spectra recorded on a Unicam SP 800 spectrophotometer between 270 and 355 nm against a reference containing glacial $\mathrm{MeCO_2H}$. Coleman plots (*e.g.* Figure 1), testing for the presence of two, three, and four species, were prepared.[19] Only the two-species test gave a positive result. The form of the plot (Figure 1) suggested that at low total [olefin] : $[\mathrm{Pd^{II}}]$ ratios two species exist over a definite [olefin] : $[\mathrm{Pd^{II}}]$ range (each successive point on the plot represents a solution with a higher total [olefin] : $[\mathrm{Pd^{II}}]$ ratio) and thereafter a further species forms while one of the species originally present becomes of minor importance. In earlier work[14] we noted that when a series of palladium(II)–olefin solutions such as the present ones were prepared those with a low total [olefin] : $[\mathrm{Pd^{II}}]$ ratio exhibited an isosbestic point at 293 nm, but on increasing the ratio this isosbestic point shifted to 297 nm. It is significant that the point of intersection of the present plots occurs in the same [olefin] : $[\mathrm{Pd^{II}}]$ range as that observed previously for the shift of isosbestic point. This is consistent with the inference, based on Raman studies and the method of continuous variations,[14] that equations (4) and (5) represent the major palladium(II)–olefin equilibria present in solution.

$$\mathrm{Na_2[Pd_2Cl_6]} + \text{olefin} \overset{K_1}{\rightleftharpoons} \mathrm{Na[Pd_2Cl_5(olefin)]} + \mathrm{NaCl} \tag{4}$$

$$\mathrm{Na[Pd_2Cl_5(olefin)]} + \text{olefin} \overset{K_2}{\rightleftharpoons} \mathrm{[Pd_2Cl_4(olefin)_2]} + \mathrm{NaCl} \tag{5}$$

In the course of the present work a particular advantage of the graphical plots of Coleman *et al.*[19] over the computer-based matrix-rank approach[20,21] to the determination of the number of species present was observed. This arises when at low ligand : metal ratios two absorbing species, (A) and (B), are well defined and at high ligand : metal ratios one of these together with a further absorbing species, (B) and (C), are well defined. The matrix-rank computer approach shows three species present if all the solutions are treated together, but because of the scrambling of the solutions during the computation it requires a great deal of computer time to show that only two are well defined at low ligand : metal ratios and two at high ligand : metal ratios. Such a result can be obtained much more readily by the graphical approach.

A complication that might arise when a terminal olefin is added to a solution of $\mathrm{Pd^{II}}$ salt is isomerisation of that olefin, since $\mathrm{Pd^{II}}$ salts are known to be catalysts for the migration of olefinic double bonds.[1] However, on addition of the olefin the u.v. absorbance of the $\mathrm{Pd^{II}}$ solutions showed an initial rapid change that was complete within the time of mixing. Thereafter the absorbance changed only very slowly. This latter change was ascribed to slow isomerisation, in agreement with previous workers,[22] rather than oxidative hydrolysis of the olefin since no palladium metal was deposited on leaving the solutions to stand.[14]

Measurement of Stability Constants.—For each olefin a series of solutions (*ca.* 12), each containing the same total $\mathrm{Pd^{II}}$ and sodium chloride concentrations but varying concentrations of olefin, were prepared. The $\mathrm{Pd^{II}}$ was added immediately before recording the spectra over the range 270—335 nm in cuvettes thermostatted at 25.00 ± 0.01 °C. Absorbances at about nine equally spaced wavelengths were determined giving a total of *ca.* 100 absorbance values per olefin. Data for each olefin were determined at two different $\mathrm{Pd^{II}}$ concentrations; at the lower concentration 10 mm

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[14] F. R. Hartley and J. L. Wagner, *J. Organometallic Chem.*, 1973, **55**, 395.

[15] R. M. Alcock, F. R. Hartley, D. E. Rogers, and J. L. Wagner, preceding paper.

[16] A. Aguiló, *Adv. Organometallic Chem.*, 1967, **5**, 321.

[17] R. M. Alcock, F. R. Hartley, D. E. Rogers, and J. L. Wagner, *Co-ordination Chem. Rev.*, 1975, **16**, 59.

[18] S. Bruckenstein, *Analyt. Chem.*, 1956, **28**, 1920.

[19] J. S. Coleman, L. P. Varga, and S. H. Mastin, *Inorg. Chem.*, 1970, **9**, 1015.

[20] R. M. Wallace and S. M. Katz, *J. Phys. Chem.*, 1964, **68**, 3890.

[21] L. P. Varga and F. C. Veatch, *Analyt. Chem.*, 1967, **39**, 1101.

[22] G. M. Panchenkov, G. V. Demidovich, I. N. Kartsivadze, and Yu M. Zhorov, *Neftekhimiya*, 1973, **13**, 650.

cuvettes were used, whereas 5 mm cuvettes were used at the higher concentration. A complete description of the experiments carried out is given in Table 1.

The absorbance data were analysed using a number of chemical models. Initially three were used [models (1)—(3), Table 2]. Model (1) is that suggested as most likely on the basis of the preliminary work on neutral olefins reported previously [14] and above. Model (2) contains species analogous to those isolated previously [13] with charged olefins (*e.g.* $CH_2{=}CHCH_2NH_3^+$) and model (3) contains species whose existence under extreme conditions has been postulated.[23] The major problem encountered in this work was our inability to isolate the palladium(II)–olefin complexes and determine their molar absorption coefficients directly. Accordingly the constants for the palladium(II)–olefin equilibria in each of these models were determined using a damped non-linear least-squares computer program.[24] The values of the equilibrium constants, K_1' and K_2', and molar absorption coefficients $\varepsilon\{Na[Pd_2Cl_5(olefin)]\}$ and $\varepsilon\{[Pd_2Cl_4(olefin)_2]\}$ were adjusted simultaneously to minimise the variance between the observed and calculated absorbances. Adjustments were continued until the maximum change in each of the parameters had been reduced to less than 1% between two cycles. Initially K_0, $\varepsilon(Na_2[PdCl_4])$, and $\varepsilon(Na_2[Pd_2Cl_6])$ were held constant at their previously determined values.[15] In the case of the most probable model, (1), values of K_1', K_2', $\varepsilon\{Na[Pd_2Cl_5(olefin)]\}$ and $\varepsilon\{[Pd_2Cl_4(olefin)_2]\}$ were determined for each olefin (see Table 3 and Figure 2). In each case the absorption coefficient profiles intersected close to 295 nm in agree-

TABLE 1

Description of the data used to evaluate palladium(II)–olefin stability constants at 25 °C

Olefin	Experiment series *	$10^4[Pd^{II}]_T/M$	$[Cl^-]_T : [Pd^{II}]_T$	Number of experiments, *m*	Number of wavelengths, *n*	$[olefin]_T : [Pd^{II}]_T$
Pent-1-ene	*a*	5.72	26.0	12	9	0.62—62.0
	b	3.71	32.3	13	8	0.96—96.0
Hex-1-ene	*a*	5.72	26.0	11	9	0.50—30.0
	b	3.71	32.3	12	8	1.66—82.8
Hept-1-ene	*a*	6.09	19.1	12	9	0.52—52.0
	b	2.93	30.5	12	10	1.07—107.0
Oct-1-ene	*a*	6.12	19.0	12	9	0.40—48.4
	b	2.93	30.6	13	9	0.84—84.0
Non-1-ene	*a*	6.10	19.1	11	9	0.37—44.6
	b	3.06	29.2	13	13	0.73—73.0

* This letter is referred to in the other Tables and text.

TABLE 2

Possible chemical models for the equilibria between ' $Na_2[PdCl_4]$ ' and olefins in acetic acid

Model	Equilibria	Equilibrium number
(1)	$2Na_2[PdCl_4] \overset{K_0}{\rightleftharpoons} Na_2[Pd_2Cl_6] + 2NaCl$	(6)
	$Na_2[Pd_2Cl_6] + \text{olefin} \overset{K_1'}{\rightleftharpoons} Na[Pd_2Cl_5(\text{olefin})] + NaCl$	(4)
	$Na[Pd_2Cl_5(\text{olefin})] + \text{olefin} \overset{K_2'}{\rightleftharpoons} [Pd_2Cl_4(\text{olefin})_2] + NaCl$	(5)
(2)	$2Na_2[PdCl_4] \overset{K_0}{\rightleftharpoons} Na_2[Pd_2Cl_6] + 2NaCl$	(6)
	$Na_2[PdCl_4] + \text{olefin} \overset{K_3''}{\rightleftharpoons} Na[PdCl_3(\text{olefin})] + NaCl$	(7)
	$Na_2[Pd_2Cl_6] + \text{olefin} \overset{K_1''}{\rightleftharpoons} Na[Pd_2Cl_5(\text{olefin})] + NaCl$	(4)
(3)	$2Na_2[PdCl_4] \overset{K_0}{\rightleftharpoons} Na_2[Pd_2Cl_6] + 2NaCl$	(6)
	$Na_2[PdCl_4] + \text{olefin} \overset{K_3'''}{\rightleftharpoons} Na[PdCl_3(\text{olefin})] + NaCl$	(7)
	$Na[PdCl_3(\text{olefin})] + \text{olefin} \overset{K_4'''}{\rightleftharpoons} [PdCl_2(\text{olefin})_2] + NaCl$	(8)
(4)	$Na_2[Pd_2Cl_6] + \text{olefin} \overset{K_1''''}{\rightleftharpoons} Na[Pd_2Cl_5(\text{olefin})] + NaCl$	(4)
	$Na[Pd_2Cl_5(\text{olefin})] + \text{olefin} \overset{K_2''''}{\rightleftharpoons} [Pd_2Cl_4(\text{olefin})_2] + NaCl$	(5)
(5)	$2Na_2[PdCl_4] \overset{K_0}{\rightleftharpoons} Na_2[Pd_2Cl_6] + 2NaCl$	(6)
	$Na_2[Pd_2Cl_6] + \text{olefin} \overset{K_1'''''}{\rightleftharpoons} Na[Pd_2Cl_5(\text{olefin})] + NaCl$	(5)
(6)	$2Na_2[PdCl_4] \overset{K_0}{\rightleftharpoons} Na_2[Pd_2Cl_6] + 2NaCl$	(6)
	$Na_2[Pd_2Cl_6] \overset{K_5'''''}{\rightleftharpoons} [Pd_2Cl_4(\text{olefin})_2] + 2NaCl$	(9)

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[23] A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, 1967, **6**, 657.

[24] R. M. Alcock, F. R. Hartley, and D. E. Rogers, unpublished work.

ment with our earlier isosbestic data.[14] The consistently higher standard deviation in K_1' than in K_2' is due to the high correlation between K_1' and $\varepsilon\{Na[Pd_2Cl_5(olefin)]\}$ where

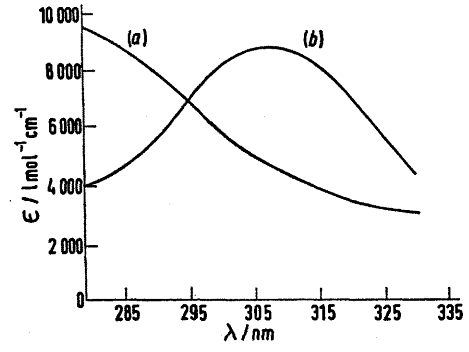

FIGURE 2 Final molar absorption coefficient profiles calculated for (*a*) $Na[Pd_2Cl_5(pent\text{-}1\text{-}ene)]$ and (*b*) $[Pd_2Cl_4(pent\text{-}1\text{-}ene)_2]$

the correlation coefficient exceeds 0.90. This also accounts for the fact that the standard deviation in $\varepsilon\{Na[Pd_2Cl_5(olefin)]\}$ (between 3 and 9%) is generally about four times that in $\varepsilon\{[Pd_2Cl_4(olefin)_2]\}$ (between 1 and 2%).

TABLE 3

Equilibrium constants K_1' and K_2' evaluated for model (1) at 25 °C

Olefin	Experiment series	$10^4[Pd^{II}]_T/M$	K_1'	K_2' *	R †
Pent-1-ene	*a*	5.72	5.2(4.0)	4.4(1.8)	0.0207
	b	3.71	5.6(2.1)	4.1(0.7)	0.0117
Hex-1-ene	*a*	5.72	14.8(5.4)	3.3(0.5)	0.0109
	b	3.71	8.3(2.8)	3.5(0.4)	0.0097
Hept-1-ene	*a*	6.09	12.2(6.3)	1.9(0.2)	0.0164
	b	2.93	6.9(1.7)	2.1(0.3)	0.0098
Oct-1-ene	*a*	6.12	4.9(3.2)	2.8(0.5)	0.0146
	b	2.93	6.2(0.7)	2.7(0.1)	0.0044
Non-1-ene	*a*	6.10	7.4(2.7)	2.4(0.2)	0.0087
	b	3.06	12.7(5.0)	2.4(0.2)	0.0131

* Standard deviations are given in parentheses. † $R = \left\{\left[\sum_{i=1}^{nm} (A_i^{calc.} - A_i^{obs.})^2\right] \Big/ \left[\sum_{i=1}^{nm} (A_i^{obs.})^2\right]\right\}^{\frac{1}{2}}$ where A = absorbance.

TABLE 4

Comparison of the results obtained for pent-1-ene (*b*) and oct-1-ene (*b*) using models (1)—(3)

Model	Olefin	K_1 *	K_2 *	K_3 *	K_4 *	R	Variance †
(1)	Pent-1-ene (*b*)	5.6(2.1)	4.1(0.7)			0.0117	0.0195
	Oct-1-ene (*b*)	6.2(0.7)	2.7(0.1)			0.0044	0.0024
(2)	Pent-1-ene (*b*)	4.1(2.0)		11.2(0.5)		0.012	0.021
	Oct-1-ene (*b*)	0.6(0.2)		7.5(0.6)		0.0041	0.0021
(3)	Pent-1-ene (*b*)			7.9(1.5)	1.6(0.2)	0.015	0.033
	Oct-1-ene (*b*)			9.1(0.4)	0.6(0.1)	0.044	0.0036

* Standard deviations are given in parentheses. † Variance $\Sigma(A^{obs.} - A^{calc.})^2$.

Although model (1) appeared to give a very satisfactory interpretation of the experimental data, it seemed prudent to consider the other two models, (2) and (3). When the pent-1-ene (*b*) * and oct-1-ene (*b*) * data were interpreted in terms of models (2) and (3) (Table 4) model (3) gave much higher Hamilton R factors than (1) and was accordingly dismissed. Model (2) can be rejected on the basis of the fact that for the pent-1-ene (*b*) data it yielded negative values of $\varepsilon\{Na[Pd_2Cl_5(olefin)]\}$ which are unacceptable, and for the oct-1-ene (*b*) data it gave absorption coefficient profiles that crossed at two points (301 and 324 nm) which is in contradiction to the experimental observation of only a single isosbestic point (at 297 nm).

Since a computer fit of any experimental absorbance data can always be obtained if sufficient variables are ' adjusted ', an attempt was made to reduce the number of ' adjustable parameters ' by trying to fit the data obtained for the oct-1-ene (*a*) and pent-1-ene (*b*) systems to each of three two-equilibria models [models (4)—(6), Table 2]. Since in each case K_0, $\varepsilon(Na_2[PdCl_4])$, and $\varepsilon(Na_2[Pd_2Cl_6])$ were held constant, model (4) has fewer degrees of freedom than (5) and (6). The results (Table 5) demonstrate that none of the models (4)—(6) is as good as (1), suggesting that all four species $Na_2[PdCl_4]$, $Na_2[Pd_2Cl_6]$, $Na[Pd_2Cl_5(olefin)]$, and $[Pd_2Cl_4(olefin)_2]$ are well defined over a significant region of the concentration range used (see Figure 3). It is noteworthy that, although model (4) was less effective than (1) over the whole concentration range, further computation showed that at total [olefin] : $[Pd^{II}]$ ratios in excess of 7.6 : 1 it was as effective as (1). This provides support for model (1) in that it implies that, whilst equilibria (4) and (5) are the most important at higher [olefin] : $[Pd^{II}]$ ratios, equilibrium (6) is also present to a lesser extent.

Further computational tests were carried out on the oct-1-ene (*b*) and non-1-ene (*a*) data, which are the two sets in Table 3 that give the lowest Hamilton R factors. First K_0 was allowed to vary and the results (Table 6) indicate that no great constraint was imposed on the system by fixing K_0 since none of the values changed dramatically. Clearly, in addition to being an argument in support of model (1), these results also offer support for the value of K_0 determined in the absence of olefin. Further similar evidence for the oct-1-ene (*b*) data was obtained by allowing $\varepsilon(Na_2[Pd_2Cl_6])$ and $\varepsilon(Na_2[PdCl_4])$ to vary. The absorption coefficient profiles for the species $Na_2[PdCl_4]$ and $Na_2[Pd_2Cl_6]$ obtained from results 5—7 of Table 6 were, within the limits of their standard deviations, identical to those

* The letter *b* corresponds to the experiment series in Table 1.

obtained previously in the absence of olefin.[15] The results in Table 6 illustrate that, when the number of variable parameters was increased so that the number of degrees of freedom was decreased, the standard deviations of the parameters determined increased, although, of course, the overall agreement between experimental and calculated absorbances, as determined by the Hamilton R factor, improved. Thus if, as in the present case, some of the parameters $\{K_0$, $\varepsilon(Na_2[PdCl_4])$, and $\varepsilon(Na_2[Pd_2Cl_6])\}$ are known to within a reasonable accuracy and if the number of parameters is large relative to the number of experimental absorbances, the solution is best approached by holding the known parameters constant in order to maximise the number of degrees of freedom. Results 6 and 7 in Table 6 show that when the condition for a minimum was such that all corrections to the parameters had been reduced to less than 0.5% as opposed to 1% an improved fit arose in which the standard deviations in the parameter variables were significantly better. However, unless the errors in the data are small, as in the case of oct-1-ene (b), it is not practicable to use this condition since the cost of computing result 7 was about four times that for 6.

TABLE 5

Comparison of minima for models (1), (4), (5), and (6)

Olefin	Model	K_1 *	K_2 *	R	Variance	N †
Oct-1-ene ‡	(1)	6.2(0.7)	2.7(0.1)	0.0044	0.0024	97
	(4)		No fit could be obtained §			97
	(5)	3.1(0.1)		0.0178	0.0379	107
	(6)		141.4(39.2)	0.1534	2.922	107
Pent-1-ene †	(1)	5.6(2.1)	4.1(0.7)	0.0117	0.0195	86
	(4)		No fit could be obtained §			86
	(5)	2.4(0.2)		0.0259	0.0957	95
	(6)		17.9(1.0)	0.0218	0.0677	95

* Standard deviations are given in parentheses. † N = Number of degrees of freedom = (total number of readings) − (total number of parameters determined from the readings). ‡ Data from series b experiments in Table 1. § Corrections to the variable parameters could not be reduced to less than 1% of the parameter values with a simultaneous decrease in the variance.

TABLE 6

Minima located using model (1) when additional parameters were varied

Olefin	Result no.	Parameters varied *	K_0 †	K_1' †	K_2' †	R	N
Non-1-ene (a)	1		0.56 ‡	7.4(2.7)	2.4(0.2)	0.008 69	79
	2	K_0	0.685(0.039)	9.7(2.6)	2.6(0.3)	0.007 18	78
Oct-1-ene (b)	3		056 ‡	6.2(0.7)	2.7(0.1)	0.004 43	97
	4	K_0	0.542(0.029)	6.2(0.9)	2.6(0.2)	0.004 33	96
	5	$K_0,\varepsilon(Na_2[Pd_2Cl_6])$	0.55(1.10)	5.4(0.9)	2.6(0.9)	0.003 04	87
	6	$K_0,\varepsilon(Na_2[Pd_2Cl_6])$, $\varepsilon(Na_2[PdCl_4])$	0.55(4.63)	5.4(8.8)	2.6(2.2)	0.003 03	78
	7 §	$K_0,\varepsilon(Na_2[Pd_2Cl_6])$, $\varepsilon(Na_2[PdCl_4])$	0.56(0.46)	5.1(3.0)	2.6(2.1)	0.002 95	78

* In addition to K_1', K_2', $\varepsilon\{Na[Pd_2Cl_5(olefin)]\}$, and $\varepsilon\{[Pd_2Cl_4(olefin)_2]\}$ which were always varied. † Standard deviations are given in parentheses. ‡ K_0 was held constant. § The condition for a minimum was that all the corrections to the parameters were less than 0.5% as opposed to 1% used in all other cases.

The results were tested for systematic error by plotting the absorbance errors at a number of wavelengths against the [olefin] : [Pd^{II}] ratio. The resulting plots showed that the errors were randomly scattered about a horizontal mean and that no further palladium species were present in significant amount. An R_{limit} value of 0.033 was calculated from equation (6). (The symbols have the same meanings

$$R_{\text{limit}} = \left\{ \sum_{i=1}^{nm} \varepsilon_i^2 \Big/ \left[\sum_{i=1}^{nm} (A_i^{\text{obs.}})^2 \right] \right\}^{\frac{1}{2}} \qquad (6)$$

as in Tables 1 and 3 and ε_i is the residual in the ith equation calculated from pessimistic estimates of the errors in all the experimental quantities using the usual rules for the propagation of error.) The following pessimistic estimates of the errors in the data were used: absorbance ±2%; total chloride concentration ±1%; total palladium concentration ±1%; and total olefin concentration ±1.5%. This R_{limit} value suggests that model (1) (Table 3) gives a statistically acceptable representation of the system since $R < R_{\text{limit}}$.[25]

Final ' best ' values of the stability constants for each olefin (Table 7) were obtained by taking a weighted mean of the two values in Table 3. A typical plot of the percentage of the total palladium that is present in the form of each species at various [olefin] : [Pd^{II}] ratios is shown in Figure 3. It is apparent that whilst the two chloropalladium species and $Na[Pd_2Cl_5(olefin)]$ are more important at low [olefin] : [Pd^{II}] ratios, the olefin complexes $Na[Pd_2Cl_5(olefin)]$ and $[Pd_2Cl_4(olefin)_2]$ are more important at higher ratios. This is consistent with the results obtained from a study of the isosbestic points [14] and the graphical method of Coleman *et al.*[19] described above.

TABLE 7

Weighted-mean stability constants * at 25 °C

Olefin	K_1 †	K_2 †
Pent-1-ene	5.5(1.9)	4.2(0.6)
Hex-1-ene	9.7(2.5)	3.4(0.3)
Hept-1-ene	7.3(1.6)	2.0(0.2)
Oct-1-ene	6.1(0.7)	2.7(0.1)
Non-1-ene	9.7(2.4)	2.4(0.2)

* The weighted mean (w.m.) of two values A and B is given by w.m. $= [(A/\sigma_A^2) + (B/\sigma_B^2)](\sigma_A^2\sigma_B^2)/(\sigma_A^2 + \sigma_B^2)$ where σ = standard deviation. † The constants K_1 and K_2 are defined by equations (4) and (5). The standard deviation, given in parentheses, was obtained from the formula $\sigma_{\text{w.m.}} = [\sigma_A^2\sigma_B^2/(\sigma_A^2 + \sigma_B^2)]^{\frac{1}{2}}$ (N. C. Barford, ' Experimental Measurements: Precision, Error, and Truth,' Addison–Wesley, London, 1967, pp. 63—64).

Gas–Liquid Chromatography.—Gas–liquid chromatograms were obtained on a Perkin-Elmer model 452 fitted with a

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[25] A. Vacca, A. Sabatini, and M. A. Gristina, *Co-ordination Chem. Rev.*, 1972, **8**, 45.

flame-ionisation detector, using a 2m column packed with diatomite coated with poly(propylene glycol) adipate (15% w/w).

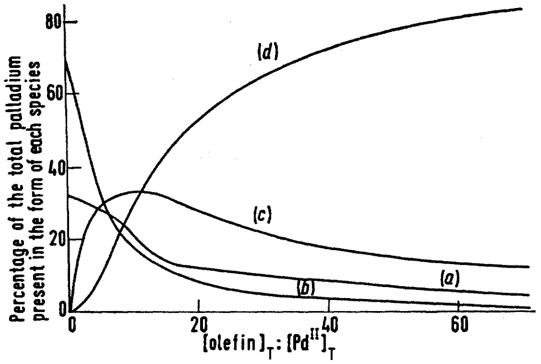

FIGURE 3 Dependence of the concentrations of the species present on the olefin concentration for the chloropalladium(II)–oct-1-ene system: (*a*) $Na_2[PdCl_4]$; (*b*) $Na_2[Pd_2Cl_6]$; (*c*) $Na[Pd_2Cl_5$(oct-1-ene)]; and (*d*) $[Pd_2Cl_4$(oct-1-ene)$_2]$

DISCUSSION

Since the accuracy of any stability-constant calculation is dependent on how precisely the natures of the species present in solution are known, considerable effort has been expended on qualitative experiments to determine both the number of species present in significant amount and their chemical formulae. The subsequent quantitative work has confirmed the conclusions of the qualitative experiments in showing that only two palladium(II)–olefin complexes are formed in significant amount in glacial acetic acid, namely $Na[Pd_2Cl_5$(olefin)] and $[Pd_2Cl_4$(olefin)$_2]$. We cannot readily explain the absence of the mononuclear complex $Na[PdCl_3$(olefin)] particularly in view of the presence of $Na_2[PdCl_4]$, although it is consistent with the qualitative observations of many workers.

The results summarised in Table 7 indicate that chain length over the range C_5—C_9 has little influence on the stability of palladium(II)–olefin complexes in $MeCO_2H$. Because of the complexity of the system and the consequent relatively high standard deviations of these stability constants, no attempt was made to determine their temperature dependence and hence obtain enthalpy and entropy values. Thus it is uncertain whether the enthalpy and entropy changes are similarly independent of chain length or whether some mutual compensation occurs.

For all five olefins studied K_1 is greater than K_2 as expected. Although, as a consequence of the high standard deviations in the individual values, K_1/K_2 varies considerably, its mean value (2.6) is very close to that expected statistically if the second olefin can replace any of the three terminal chloride ligands in $Na[Pd_2Cl_5$(olefin)] (2.66), and is significantly less than that expected (8) if the second olefin is limited solely to the position *trans* to the first (which corresponds to the geometry found in $[M_2Cl_4$(olefin)$_2]$ complexes that have been isolated[26,27]). Since many factors play a part in determining the observed ratio of successive stability constants we refrain from commenting on any significance that the present value may have.

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[26] J. N. Dempsey and N. C. Baenziger, *J. Amer. Chem. Soc.*, 1955, **77**, 4984.

[27] J. R. Holden and N. C. Baenziger, *J. Amer. Chem. Soc.*, 1955, **77**, 4987.