Investigation of the Species formed on dissolving Sodium Tetrachloropalladate(II) in Glacial Acetic Acid †

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Spectrophotometric investigation of the species formed when $Na_2[PdCl_4]$ is dissolved in glacial acetic acid has shown that two principal equilibria, (i) and (ii), are set up. At 25 °C, $K_0 = 0.56 \pm 0.02$ and $K' = (2.9 \pm 0.6) \times$

$$2Na_2[PdCl_4] \overset{K_0}{\rightleftharpoons} Na_2[Pd_2Cl_6] + 2NaCl \qquad (i)$$

$$Na_2[Pd_2Cl_6] \overset{K'}{\rightleftharpoons} Na[Pd_2Cl_5(HO_2CMe] + NaCl \qquad (ii)$$

10^{-5} mol dm^{-3}. Some evidence for equilibrium (iii) has been obtained, but the amount of $Na[PdCl_3(HO_2CMe)]$

$$Na_2[PdCl_4] \overset{K''}{\rightleftharpoons} Na[PdCl_3(HO_2CMe)] + NaCl \qquad (iii)$$

present is so small that the standard deviation in the value of K'' is very high [$K'' = (3.5 \pm 3.7) \times 10^{-4}$ mol dm^{-3}].

ALTHOUGH a considerable amount of effort has been devoted to investigating the interaction of chloride ions with palladium(II) species in aqueous solution,[1] very little has been reported for solutions in acetic acid. Since chloropalladium(II) species are extensively used as catalysts in acetic acid,[2-5] a knowledge of the species present in such solutions should be of value in understanding the mechanism of such catalysts. Henry and Marks [6] have investigated the species formed between palladium(II) and lithium chlorides in glacial acetic acid and have shown that $Li_2[PdCl_4]$, $Li_2[Pd_2Cl_6]$, $Li[PdCl_3(HO_2CMe)]$, and $Li_3[Pd_2Cl_7]$ ‡ are formed. Acetic acid has a very low dielectric constant (6.13 at 20 °C) [7] so that its solutions of ionic compounds tend to consist largely of ion pairs. Accordingly it appeared that the equilibrium constants of the various chloropalladium(II) species would be strongly dependent on the cation present and that a study of the interaction between palladium(II) and sodium chlorides would be valuable.

In addition to the fact that $Na_2[PdCl_4]$ has been more widely used than $Li_2[PdCl_4]$ as a source of Pd^{II}, probably due to the more ready availability of the former, sodium salts have a number of advantages over lithium salts in glacial acetic acid solution. (i) The higher polarising ability of lithium as opposed to sodium cations leads to polymerisation. Thus lithium chloride dimerises extensively in acetic acid [8] whereas there is no evidence for any dimerisation of sodium iodide in this solvent.[9] Since chloride ions are less polarisable than iodide it is unlikely that NaCl forms dimers in $MeCO_2H$, a suggestion that is consistent with its low solubility (0.013 mol dm^{-3} at 37.5 °C).[10] (ii) The low solubility of NaCl in $MeCO_2H$ ensured that in the present work all concentrations were kept low [Pd^{II}] *ca.* 1.5×10^{-4}, [NaCl] < 0.013M) § whereas in the earlier $PdCl_2$–LiCl study,[6] in order to obtain an adequate concentration range of monomeric LiCl, it was necessary to vary the total LiCl concentration between 0.046 and 0.85M ([Pd^{II}] $= 1.35 \times 10^{-2}$M). It is virtually impossible to use the constant-high-ionic-strength method [11] to control activity coefficients in $MeCO_2H$, because of the difficulty of finding an electrolyte that dissolves in the acid without either forming ion pairs (as occurs with Li^+ salts) or precipitating either $[Pd_2Cl_6]^{2-}$ or $[PdCl_4]^{2-}$ (as occurs when tetra-alkylammonium salts are used).¶ Accordingly it is essential to ensure that the activity coefficients are maintained as close to unity as possible by working at the minimum concentrations consistent with obtaining accurate data. This condition is more closely attained in the present study with NaCl than in the earlier investigation using LiCl.

The present investigation of the species formed when $Na_2[PdCl_4]$ is dissolved in glacial acetic acid falls into two parts. First a qualitative investigation of the system was carried out in order to attempt to identify how many major species are present and to determine as much as possible about their likely molecular formulae. This information was then used to provide an initial model on which to base the quantitative analysis of the absorbance data. In order to avoid biasing our quantitative results by using an incorrect model, a number of other models that were consistent with the qualitative results were also investigated, the final best-fit model being obtained from a statistical analysis of all the

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† No reprints available.

‡ The formula $Li_3[Pd_2Cl_7]$ was obtained by direct reference to Professor Henry; in the literature [6] a misprint has led to its being written as $Li_2Pd_2Cl_7$.

§ 1M = 1 mol dm^{-3}.

¶ A referee has suggested that a soluble acetate (*e.g.* $Na[O_2CMe]$) might have been used. However, since one of the objectives of this work was to use the data in a study of the interaction of Pd^{II} species with olefins (see following paper), the use of a soluble acetate was precluded since they react with olefins in the presence of Pd^{II} salts.[3]

[1] F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science, London, 1973, ch. 9.

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

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

[4] P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971, vol. 2, pp. 93—105.

[5] P. M. Henry, *Accounts Chem. Res.*, 1973, **6**, 16.

[6] P. M. Henry and O. W. Marks, *Inorg. Chem.*, 1971, **10**, 373.

[7] C. P. Smyth and H. E. Rogers, *J. Amer. Chem. Soc.*, 1930, **52**, 1824.

[8] J. Kenttämaa, *Suomen Kem.*, 1959, **B32**, 9.

[9] W. E. S. Turner and C. C. Bissett, *J.Chem. Soc.*, 1914, 1777.

[10] H. Stephen and T. Stephen, 'Solubilities of Inorganic and Organic Compounds,' Pergamon, New York, 1963, vol. 1, part 1, p. 655.

[11] G. Biedermann and L. G. Sillén, *Arkiv. Kemi*, 1953, **5**, 425.

models. A preliminary account of this work has been reported elsewhere.[12]

EXPERIMENTAL

AnalaR glacial acetic acid (B.D.H.) was used throughout, each fresh sample being checked by Bruckenstein's method [13] to ensure that the water content was less than 0.05%. Stock palladium(II) solutions were analysed for (*i*) palladium using gravimetric methods based on either 2-thiophen-*trans*-aldoxime [14] or PdI_2,[15] and (*ii*) chloride by the Volhard titration [16] using nitrobenzene to inhibit the dissociation of silver(I) chloride near the end-point, after first precipitating the palladium with zinc [17] to prevent the end-point being totally obscured by the colour of Pd^{II}.

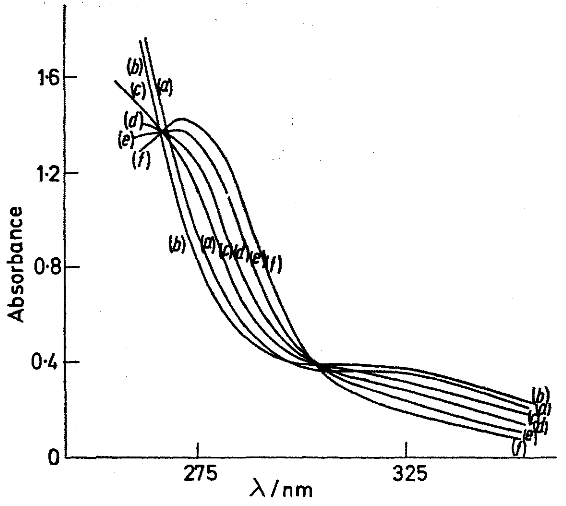

FIGURE 1 U.v. spectra for chloropalladium(II) species in acetic acid: $[Pd^{II}] = 1.51 \times 10^{-4}$M; $[Cl^-] = 5.90 \times 10^{-4}$ (*a*), 1.98×10^{-3} (*b*), 3.38×10^{-3} (*c*), 6.17×10^{-3} (*d*), 8.96×10^{-3} (*e*), and 1.31×10^{-2}M (*f*)

Determination of the Number of Species Present.—A series of solutions in glacial acetic acid each containing 1.51×10^{-4}M-Pd^{II} and having chloride concentrations between 5.89×10^{-4} and 1.28×10^{-2}M were prepared, and their absorption spectra recorded between 260 and 375 nm against a reference containing glacial $MeCO_2H$. Two sharp isosbestic points were observed at 268.5 and 305.5 nm for all solutions containing $[Cl^-] : [Pd^{II}]$ ratios in excess of 20 : 1 (Figure 1). Although the observation of an isosbestic point cannot be taken as absolute proof of the presence of only two absorbing species,[18,19] the present observation of two such points strongly suggests that at $[Cl^-] : [Pd^{II}]$ ratios in excess of 20 : 1 only two absorbing species are present.

In addition the absorption spectra were analysed by the matrix-rank method [20,21] which indicated that at $[Cl^-] : [Pd^{II}]$ ratios in excess of 20 : 1 only two absorbing species are present. In the course of using this matrix-rank approach we found a disadvantage that, to our knowledge, has not been previously reported. Thus because of 'scrambling' of the order of the solutions that occurs during the determination of the rank of the absorbance matrix, only by expenditure of a considerable amount of computer time is it possible to determine whether some of the solutions contain more species than others.

Further analysis of the absorption spectra was carried out using the graphical method of Coleman *et al.*[22] in which functions of absorbance are plotted. The specific functions used depend on the number of species present, but the important feature of the plot is that it is readily possible to identify the original solutions that contribute to each point. Plots obtained on analysing the present data for both two and three absorbing species are shown in Figure 2.

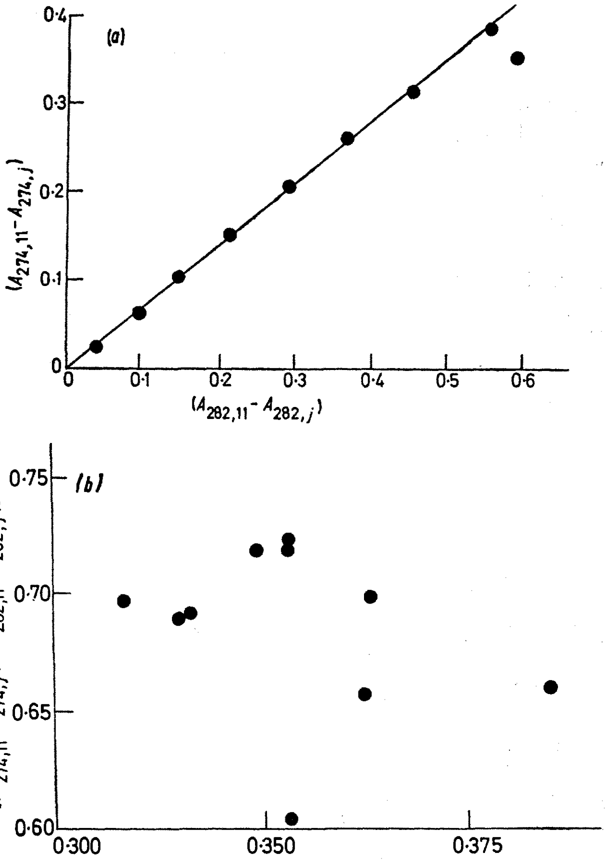

FIGURE 2 Plots obtained using the method of Coleman *et al.*[22]: (*a*) two-species test, (*b*) three-species test. $A_{297,j}$ = Absorbance of solution *j* at 297 nm

From these it can be seen that the three-species analysis gave randomly scattered points whereas the two-species analysis gave a straight line passing through the origin,

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

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

[14] F. R. Hartley and J. L. Wagner, *J. Organometallic Chem.*, 1972, **42**, 477.

[15] F. E. Beamish and J. Dale, *Ind. and Eng. Chem.* (*Analyt. Edn.*), 1938, **10**, 697.

[16] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961, p. 266.

[17] W. W. Scott, ' Standard Methods of Chemical Analysis,' 6th edn., Van Nostrand, Princeton, New Jersey, 1962, vol. 1, p. 883.

[18] Ch. Chylewski, *Angew. Chem. Internat. Edn.*, 1971, **10**, 195 and refs. therein.

[19] T. Nowicka-Jankowska, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2043 and refs. therein.

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

indicating that only two absorbing species are present. Furthermore, one point, for the solution with the lowest ratio of [Cl^-] : [Pd^{II}], lay well off the straight line indicating that this solution contains more than two absorbing species.

Probable Molecular Nature of Species Present.—Analysis of the absorbance data suggested that there are two main Pd^{II} species present except at very low chloride concentrations when a further species is formed. Preparative results, which show that $[(H_5C_3)H_3N]_2[PdCl_4]$ and $[Pr^nH_3N]_2[PdCl_4]$ can be precipitated from NaCl-saturated $MeCO_2H$ solutions of ' $Na_2[PdCl_4]$ ' on addition of allyl- and n-propyl-ammonium chorides respectively,[23] suggest that $Na_2[PdCl_4]$ is one of these species. The isolation of $Na[Pd_2Cl_5(CH_2{=}CHCH_2NH_3Cl)]$ on treating a solution of ' $Na_2[PdCl_4]$ ' in $MeCO_2H$ with allylammonium perchlorate[23] suggests that $Na_2[Pd_2Cl_6]$ is also present. At low chloride concentrations displacement of chloride by the solvent is expected by analogy with displacement of chloride by water when $Na_2[PdCl_4]$ is dissolved in that solvent.[24,25] Thus the qualitative results are consistent with two equilibria, (1) and (2), being set up when ' $Na_2[PdCl_4]$ ' is dissolved in $MeCO_2H$. These equilibria are consistent with the known

$$2Na_2[PdCl_4] \overset{K_0}{\rightleftharpoons} Na_2[Pd_2Cl_6] + 2NaCl \qquad (1)$$

$$Na_2[Pd_2Cl_6] \overset{K'}{\rightleftharpoons} Na[Pd_2Cl_5(HO_2CMe)] + NaCl \qquad (2)$$

chemistry of chloropalladium(II) species in non-aqueous solvents.[1,26,27] It is impossible to decide on the qualitative evidence whether or not $Na[PdCl_3(HO_2CMe)]$ is also present since it contains the same amount of chloride relative to Pd^{II} as $Na_2[Pd_2Cl_6]$ and thus cannot of itself account for the deviations observed at very low [Cl^-] : [Pd^{II}] concentrations.

Measurement of the equilibrium constants (mol dm^{-3})

Data set *	Number of wave-lengths studied, n	Number of solutions prepared, m	$10^4[Pd^{II}]_T$/M	[Cl^-] : [Pd^{II}]	K_0	σ_{K_0}	K'	$\sigma_{K'}$	R †	R_{limit} ‡
a	14	9	1.51	3.9—87.2	0.542	0.064	3.16×10^{-5}	2.27×10^{-5}	0.002 83	0.0307
b	9	11	1.51	3.9—87.2	0.572	0.029	2.49×10^{-5}	6.39×10^{-6}	0 003 16	0.0322
c	9	11	1.50	3.9—87.2	0.531	0.038	7.61×10^{-5}	3.55×10^{-5}	0.003 82	0.0325
d	9	11	1.48	3.9—87.2	0.595	0.053	7.25×10^{-5}	2.99×10^{-5}	0.003 82	0.0321
e	13	7	3.13	3.7—23.6	0.440	0.960	7.68×10^{-6}	3.32×10^{-6}	0.008 58	0.0261
f	8	10	8.03	2.7—17.7	0.499	0.332	3.67×10^{-4}	2.84×10^{-4}	0.005 48	0.0517

* Data sets *a*—*e* were obtained using a Unicam SP 800 spectrophotometer; *f* was obtained using a Unicam SP 500 spectrophotometer. † $R = \left\{\left[\sum_{i=1}^{nm}(A_i^{calc.} - A_i^{obs.})^2\right]\Big/\left[\sum_{i=1}^{nm}(A_i^{obs.})^2\right]\right\}^{\frac{1}{2}}$, where A = absorbance. ‡ $R_{limit} = \left\{\sum_{i=1}^{nm}\varepsilon_i^2\Big/\left[\sum_{i=1}^{nm}(A_i^{obs.})^2\right]\right\}^{\frac{1}{2}}$, where 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%.

Quantitative Investigation of the Chloropalladium(II) *Species present in Acetic Acid Solution.*—A series of solutions each containing the same total palladium concentration and varying chloride concentrations were prepared and their absorption spectra recorded over the range 260—375 nm. Absorbances at *ca.* 10 approximately equally spaced wavelengths were determined for each solution. The experiment was repeated six times and each set of data (see Table) analysed according to equations (1) and (2) using a damped non-linear least-squares computer program.[28] If the molar absorption coefficients of each species present had been known K_0 and K' could readily have been calculated from the measured absorbances and the mass-balance equations for each solution. In practice, accurate values of the absorption coefficients were not available because of the impossibility of preparing $MeCO_2H$ solutions containing only a single chloropalladium(II) species. Accordingly, it was necessary to use the computer program to determine not only K_0 and K' but also the absorption coefficients of the species present. The coefficients were then compared with those of $Na_2[Pd_2Cl_6]$ and $Na_2[PdCl_4]$ which were estimated at a number of wavelengths by the techniques outlined below and which were accurately known at the isosbestic wavelengths shown in Figure 1.

The absorption coefficient of $Na_2[Pd_2Cl_6]$ was estimated by plotting absorbances of a series of solutions of constant [Pd^{II}] and decreasing [Cl^-] and extrapolating to obtain the absorbance at a [Cl^-] : [Pd^{II}] ratio of 3 : 1. From such plots (see Figure 3) it was apparent that at high chloride concentrations the absorbances fell on a smooth curve. As expected from the model, the observed absorbances deviated from this curve at low [Cl^-] due to the presence of $Na[Pd_2Cl_5(HO_2CMe)]$. When the molar absorption coefficients obtained in this way, together with those obtained at the isosbestic wavelengths, were plotted against wavelength a smooth spectrum resulted [Figure 4(*a*)]; abrupt changes in the estimated coefficients near the 'fixed' isosbestic wavelengths would have indicated that the approximations inherent in these estimations were invalid.

The absorption coefficient of $Na_2[PdCl_4]$ could not be estimated from the data in Figure 3 because even at the highest chloride concentrations attainable using NaCl only *ca.* 65% of the Pd^{II} was present as $Na_2[PdCl_4]$. However, by using $PdCl_2$ and LiCl, solutions with [Cl^-] : [Pd^{II}] ratios in excess of 10^3 could be obtained and the spectra of these solutions were virtually independent of [Cl^-] suggesting $Li_2[PdCl_4]$ was virtually the only Pd^{II} species present.

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

[24] H. A. Droll, B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, 1957, **61**, 1000.

[25] A. A. Biryukov and V. I. Shlenskaya, *Russ. J. Inorg. Chem.*, 1964, **9**, 450.

[26] N. R. Davies, *Austral. J. Chem.*, 1964, **17**, 212.

[27] I. I. Volchenskova and K. B. Yatsimirskii, *Russ. J. Inorg. Chem.*, 1973, **18**, 990.

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

From such solutions, assuming that $Li_2[PdCl_4]$ and $Na_2[PdCl_4]$ have similar spectra, the spectrum in Figure 4(*b*) was obtained. Again the lack of any discontinuity at the isosbestic wavelength suggests that the approximations and assumptions in this analysis are valid. In addition the peak at 277 nm (ε 11 250 l mol^{-1} cm^{-1}) is very close to that observed previously[29] for $K_2[PdCl_4]$ in aqueous solution (278 nm; ε 12 000 l mol^{-1} cm^{-1}).

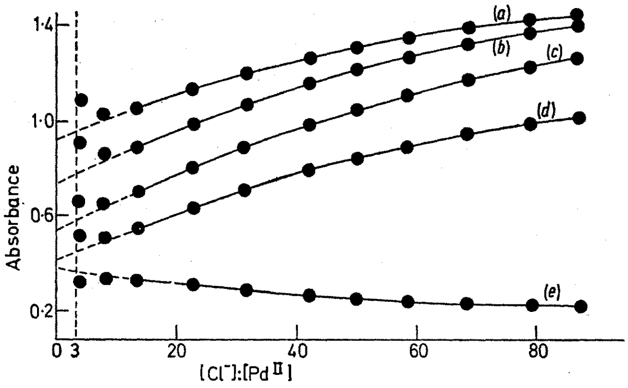

FIGURE 3 Plots of absorbance against $[Cl^-] : [Pd^{II}]$ mol ratio at 274 (*a*), 277 (*b*), 282 (*c*), 287 (*d*), and 322 nm (*e*)

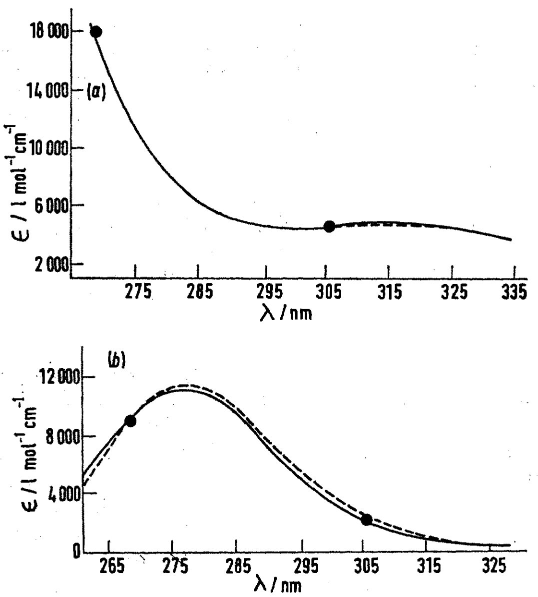

FIGURE 4 Estimated (——) and computed (— — —) spectra of (*a*) $Na_2[Pd_2Cl_6]$ and (*b*) $Na_2[PdCl_4]$. The estimated spectrum of $Na_2[PdCl_4]$ was obtained by assuming it to be the same as that of $Li_2[PdCl_4]$ (see text); (●) molar absorption coefficients at the isosbestic wavelengths

Since our earlier work,[30] together with that reported here, suggested that only equilibrium (1) was significant at high $[Cl^-]$, it was possible to use the estimated absorption coefficients for $Na_2[PdCl_4]$ and $Na_2[Pd_2Cl_6]$ together with total $[Pd^{II}]$ and $[Cl^-]$ to estimate K_0 for the solutions that had $[Cl^-] : [Pd^{II}]$ ratios in excess of 20 : 1. These first estimates of K_0 and the absorption coefficients were then refined by adjusting the values of all three variables simultaneously in order to minimise the variance between the observed and calculated absorbances in solutions that had a $[Cl^-] : [Pd^{II}]$ ratio in excess of 20 : 1. When minimisation had been achieved, solutions containing lower chloride contents were introduced, together with estimated values for K' and the absorption coefficient of $Na[Pd_2Cl_5(HO_2CMe)]$. In this way, values of 0.56 and 2.9×10^{-5} mol dm^{-3} with standard deviations of 0.02 and 0.6×10^{-5} mol dm^{-3} were obtained for K_0 and K' respectively. The calculated absorption coefficient profiles of $Na_2[Pd_2Cl_6]$ and $Na_2[PdCl_4]$ [Figures 4(*a*) and 4(*b*)] agreed within 1 and 5% respectively with those estimated previously.

Sillén[31-34] showed that systematic errors in a set of data should be treated as extra parameters that may be determined during the computer analysis. This is an important technique in building up a chemical ' model ' because often a better fit to the data can be obtained by adjusting these extra parameters than by assuming the presence of extra species. If, however, the adjustments to these parameters are larger than their expected experimental error, or if they vary systematically in an implausible way, then the ' model ' is probably incorrect and further species exist.[34] Accordingly the ' model ' obtained so far was rerun on the computer to allow the program to adjust the systematic errors in the total chloride and Pd^{II} concentrations. It was immediately apparent that the computer was attempting to improve the fit by assuming unreasonable errors in the chloride concentrations (>20%), especially at low $[Cl^-] : [Pd^{II}]$ ratios. Accordingly, further chloropalladium(II) species in addition to those in equilibria (1) and (2) were added to the ' model ' and the variance between the observed and calculated absorbances reminimised. Of the species tried only $Na[PdCl_3(HO_2CMe)]$ led to a slightly improved fit, but it was significant that with this species the computer then adjusted for much smaller systematic errors in the total chloride concentrations (<3%). The standard deviation of K'' [equation (3)] was of the same order of magnitude as the

$$Na_2[PdCl_4] \overset{K''}{\rightleftharpoons} Na[PdCl_3(HO_2CMe)] + NaCl \quad (3)$$

value of K'' itself [$(3.5 \pm 3.7) \times 10^{-4}$ mol dm^{-3}]. This is expected because when the final values of K_0, K', and K'' were used to determine the percentage of Pd^{II} present in the form of each species as a function of the $[Cl^-] : [Pd^{II}]$ ratio it was found that no more than 3.35% of the Pd^{II} was present as $Na[PdCl_3(HO_2CMe)]$ (Figure 5).

The final *R* factors (see Table) obtained for a model based on equilibria (1) and (2) only are significantly less than the limiting value of *R* calculated from pessimistic errors in the experimental observables, indicating that this ' model ' gives a statistically acceptable representation of the system.[35] However, it is possible, as pointed out by a referee, that equilibria (1) and (2), which were suggested on the basis of the qualitative studies of the system, are incorrect. Accordingly a large number of other models

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

[31] L. G. Sillén, *Acta Chem. Scand.*, 1962, **16**, 159.

[32] L. G. Sillén, *Acta Chem. Scand.*, 1964, **18**, 1085.

[33] P. Brauner, L. G. Sillén, and R. Whiteker, *Arkiv. Kemi*, 1969, **31**, 365.

[34] L. G. Sillén in ' Coordination Chemistry,' ed. A. E. Martell, Amer. Chem. Soc. Monograph 168, 1971, vol. 1, p. 520.

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

involving the species $[Pd_2Cl_4(HO_2CMe)_2]$, $[PdCl_2(HO_2CMe)_2]$, $Na_3[Pd_2Cl_7]$, $Na_3[PdCl_5]$, and species with coordinated acetate ions were investigated. Few of these gave a minimum in the variance between the observed and calculated absorbances, and the few that did gave final R factors well in excess of the limiting value as well as ' unreasonable ' spectra for the species present. (An ' unreasonable ' spectrum is either one with negative molar absorption coefficients or one which is not a smooth curve typical of the electronic spectra of transition-metal complexes.)

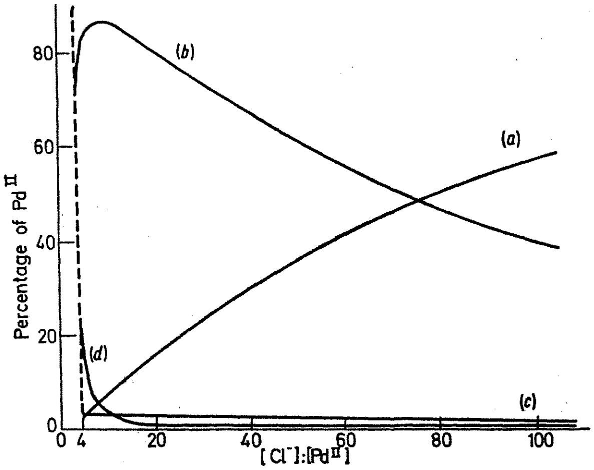

FIGURE 5 Percentage of Pd^{II} present in each form as a function of the ratio of the concentrations of chloride and palladium(II): (*a*) $Na_2[PdCl_4]$; (*b*) $Na_2[Pd_2Cl_6]$; (*c*) $Na[PdCl_3(HO_2CMe)]$; and (*d*) $Na[Pd_2Cl_5(HO_2CMe)]$

The final values of the equilibrium constants (K) and their standard deviations (σ) were obtained using equations (4) and (5),[36] where subscripts *a*, *b*, and *c* refer to data sets *a*, *b*,

$$K(\text{weighted mean}) = \frac{1}{(\sigma_a^{-2} + \sigma_b^{-2} + \sigma_c^{-2}, etc.} \cdot \left(\frac{K_a}{\sigma_a^2} + \frac{K_b}{\sigma_b^2} + \frac{K_c}{\sigma_c^2} +, etc.\right) \quad (4)$$

$$\sigma^{-2}\ (\text{weighted mean}) = \sigma_a^{-2} + \sigma_b^{-2} + \sigma_c^{-2} +, etc. \quad (5)$$

and *c* in the Table. The values were $K_0 = 0.56$, $\sigma_{K_0} = 0.02$, $K' = 2.9 \times 10^{-5}$, $\sigma_{K'} = 0.6 \times 10^{-5}$, $K'' = 3.5 \times 10^{-4}$, and $\sigma_{K''} = 3.7 \times 10^{-4}$ mol dm^{-3}.

U.v.–Visible Spectra.—U.v.–visible spectra were recorded on a Unicam SP 800 spectrophotometer (data sets *a*—*e*) and on a Unicam SP 500 spectrophotometer (data set *f*). The spectrophotometers were fitted with a water-filled constant-temperature cell housing maintained at 25.00 ± 0.01 °C using a Grant Instruments SB3X water-bath. The temperature of the cell compartment was measured using a copper-advance thermocouple which was standardised against an N.P.L. calibrated thermometer. The spectrophotometers were calibrated for wavelength using a holmium filter and for absorbance using standard absorbance filters; absorbances were correct to within 1%.

Potentiometric Experiments.—Two attempts were made to determine the chloride concentrations potentiometrically since this would have yielded further data, and hence enabled the equilibrium constants to be determined more precisely. However, a series of silver–silver(I) chloride electrodes, prepared according to Brown,[37] were found not to be reversible to $[Cl^-]$ in glacial $MeCO_2H$. A Phillips IS 550–Cl solid-state chloride-ion-selective electrode combined with a mercury–mercury(I) sulphate reference electrode was reversible to chloride ion in glacial $MeCO_2H$ but unfortunately Pd^{II} interfered strongly with this electrode preventing its being used in the present work.

DISCUSSION

The present results, summarised in Figure 5, clearly demand comparison with the $PdCl_2$–LiCl results reported earlier.[6] In the present work $Na_2[PdCl_4]$ and $Na_2[Pd_2Cl_6]$ are the main species present at all except the lowest chloride concentrations, whereas in the lithium system $Li_2[PdCl_4]$ and $Li[PdCl_3(HO_2CMe)]$ are the principal species present below a $[Cl^-] : [Pd^{II}]$ ratio of 100 : 1. Furthermore, the present value of 0.56 mol dm^{-3} for K_0 when sodium is present contrasts with the value of 10 mol dm^{-3} observed with lithium. Although some difference between lithium and sodium is expected, due to the high tendency for ion pairs to be formed in $MeCO_2H$, a factor of 20 was larger than we anticipated, although it should be pointed out that the difference only amounts to 6.36 kJ mol^{-1}. Further differences between the two systems are apparent in the species observed. Thus in the presence of sodium $Na_2[PdCl_4]$, $Na_2[Pd_2Cl_6]$, $Na[PdCl_3(HO_2CMe)]$, and $Na[Pd_2Cl_5(HO_2CMe)]$ were found, whereas in the presence of lithium $Li_2[PdCl_4]$, $Li_2[Pd_2Cl_6]$, $Li[PdCl_3(HO_2CMe)]$, and $Li_3[Pd_2Cl_7]$ were observed.

Although many of the differences between the sodium and lithium systems are probably genuine, we feel that the earlier lithium results should be approached with caution for two reasons. (i) As mentioned in the introduction the wide variations used in the LiCl concentrations (between 0.046 and 0.85M) in a given series of solutions may, in the absence of any material added to maintain the ionic strength constant, have led to variations in the activity coefficients of the species present and hence to errors in the equilibrium constants which were calculated on the basis of concentrations rather than activities. In the present work all the concentrations were much lower, thus minimising variations in the activity coefficients of the species present. (ii) The previous authors failure to obtain constant values for two of their three equilibrium constants [6] may have been due to neglect of activity coefficients or to an incorrect ' model '.

We thank Dr. R. Baker for allowing us to use the Unicam SP 800 spectrophotometer, Johnson, Matthey and Co. Ltd. for their generous loan of the palladium salts, and the S.R.C. for the award of studentships (to R. M. A. and J. L. W.).

[4/1930 *Received, 20th September,* 1974]

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