

AN INVESTIGATION OF THE EQUILIBRIA FORMED BETWEEN PALLADIUM(II) CHLORIDE COMPLEXES AND TERMINAL OLEFINS IN ACETIC ACID SOLUTION

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SUMMARY

An investigation of the equilibria formed between the terminal olefins 1-hexene and 1-octene and $\text{Na}_2\text{Pd}_2\text{Cl}_6$ in glacial acetic acid, using preparative, Raman, and ultra-violet and visible spectroscopic methods has shown that the principal olefin complexes formed are $\text{Na}[\text{Pd}_2\text{Cl}_5(\text{Olefin})]$, at low olefin concentrations, and $[\text{Pd}_2\text{Cl}_4(\text{Olefin})_2]$, at high olefin concentrations. The value is emphasised of using the Method of Continuous Variations (Job's Method) at as wide a range of wavelengths as possible for studying systems in which more than one metal-ligand complex is formed.

INTRODUCTION

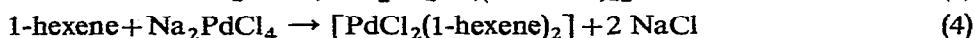
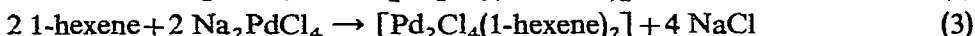
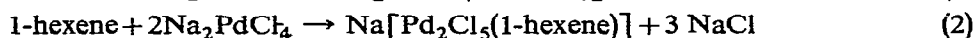
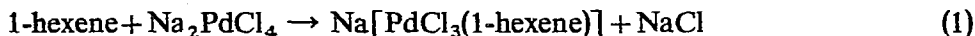
Although a number of olefin complexes of palladium(II) with multidentate ligands containing at least one olefinic functional group have been reported, relatively few stable palladium(II) complexes of monoolefins have been reported¹. Since monoolefins are potentially more interesting than the multidentate ligands, because of their direct relevance to an understanding of the role of palladium(II) in catalysing reactions such as the oxidative hydrolysis, acetylation, carbonylation, and isomerisation of simple olefins, we are currently investigating their complexes with palladium(II). In a previous paper the preparation and properties of allylammonium complexes of palladium(II) such as $[\text{Pd}(\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_3)\text{Cl}_3]$ were described². These complexes, probably because of their zwitterionic character, were stable in the absence of moisture, and could be isolated as crystalline products. The present paper extends this work to complexes of simple terminal olefins containing no additional functional groups. Since simple olefins are insoluble in water and palladium(II)-olefin complexes are only stable in aqueous solution in the presence of very high acid concentrations², glacial acetic acid was used as the reaction medium. During the course of the present work somewhat similar studies using allylbenzene were reported³. However, there are significant differences between our present conclusions and those drawn from the earlier work which we feel do not arise from the slight differences in the olefins used.

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EXPERIMENTAL

1. *Quantitative analysis of the reaction of Na₂PdCl₄ with 1-hexene*

An accurately weighed amount of Na₂PdCl₄ was dissolved in 1-hexene by shaking at room temperature for 6 h. The residual white deposit of sodium chloride was filtered off on a previously weighed sinter, washed with 1-hexene and dried by heating to constant weight. The ratios of the weight of Na₂PdCl₄ to weight of NaCl observed were 2.43, 2.50 and 2.43 in three successive determinations. The ratios calculated for reactions (1)–(4) were 5.02, 3.36, 2.51 and 2.51 respectively, indicating that either [Pd₂Cl₄(1-hexene)₂] or [PdCl₂(1-hexene)₂] was formed.

2. *Isosbestic points*

A series of 17 solutions were prepared each containing 0.513×10^{-3} M Na₂Pd₂Cl₆ in glacial acetic acid saturated with sodium chloride and different 1-octene concentrations in the range $0\text{--}50 \times 10^{-3}$ M. The spectra were recorded on separate sheets of chart paper as this enabled them to be examined in more detail subsequently than if they had all been recorded on the same paper. The latter technique, which was used initially, obscured the small differences around the 293 nm isosbestic point as the olefin concentration was increased above 9.25×10^{-3} M because of the concentration of the lines around the isosbestic points.

3. *Method of Continuous Variations (Job's Method)*

A standard solution of Na₂Pd₂Cl₆, prepared by dissolving Na₂PdCl₄ in glacial acetic acid saturated with sodium chloride and filtering off the precipitated sodium chloride, was analysed for palladium using a gravimetric procedure based on *trans*-2-thiophene-aldoxime⁴. A standard solution of 1-octene in sodium chloride-saturated glacial acetic acid was prepared by directly weighing freshly redistilled 1-octene (b.p. 120°; lit.⁵ 120.1°). A series of solutions (7 for the study between 265 and 320 nm and 11 for the study between 370 and 410 nm) each containing *x*% palladium(II) and (100–*x*)% 1-octene were prepared and their absorbance values determined shortly after they were made up. Since the differences in the extinction coefficients of Na₂Pd₂Cl₆ and the palladium(II)–olefin complexes were small (see Figs. 1 and 2) it was essential to achieve the highest possible accuracy in determining the absorbances. Accordingly the absorbances due to Na₂Pd₂Cl₆ and 1-octene were not calculated, as is usual in determining Job plots, but measured for each solution by preparing solutions containing *x*% of palladium(II) in the absence of olefin, and (100–*x*)% of 1-octene in the absence of palladium(II). At some wavelengths plots of the absorbance of palladium(II) in the absence of olefin against the palladium(II) concentration were virtually linear, as required by Beer's Law, but at others slight curvature, either convex or concave was observed. This curvature is expected since although the bulk of the palladium(II) is present as Na₂Pd₂Cl₆, a small proportion will be present as Na₂PdCl₄⁶.

4. Spectra

Raman spectra were recorded on a Cary 81 spectrometer using the 17600 cm^{-1} exciting line of a Coherent Radiation model 52 krypton/argon laser. The solutions were held in very thin-walled flat-bottomed capillary tubes prepared and mounted as described in the literature.⁷ NMR spectra were recorded in CDCl_3 on a Perkin-Elmer R12 spectrometer using the CHCl_3 peak for calibration because the introduction of tetramethylsilane caused decomposition of the palladium(II)-olefin complexes. Isosbestic point studies were carried out on a Unicam SP800 recording spectrophotometer and Job plot studies were made using a Unicam SP500 manual spectrophotometer.

RESULTS

1. Attempts to isolate palladium(II)-olefin complexes

Since both 1-hexene and 1-octene react rapidly with a solution of $\text{Na}_2\text{Pd}_2\text{Cl}_6$ in glacial acetic acid to form palladium(II)-olefin complexes which are indefinitely stable towards decomposition to palladium metal, attempts were made to isolate the complexes. In the first attempt the acetic acid was removed by evaporation at room temperature under vacuum (2 mmHg). This yielded PdCl_2 , indicating that the olefins had been removed during the evacuation. A second attempt, involving reducing the volume of acetic acid and then adding low boiling petroleum ether, yielded a dark red oil. On treatment with dichloromethane, a sample of this oil immediately yielded a dark red precipitate of PdCl_2 . The bulk of the red oil was left under the glacial acetic acid/petroleum ether mother liquor, which still contained some free olefin, and after four days it crystallised to yield yellow crystals which had black spots of metallic palladium in them. The infrared spectrum of the yellow crystals exhibited a band at 1520 cm^{-1} , consistent with the presence of a palladium(II)-olefin complex⁸. The crystals decomposed fairly rapidly on removal of the solvent and this precluded analysis. On redissolving a few of them in glacial acetic acid saturated with sodium chloride, a solution of $\text{Na}_2\text{Pd}_2\text{Cl}_6$ was obtained, indicating that the olefin complex is only stable in the presence of an excess of the olefin.

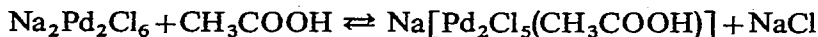
This failure to isolate stable palladium(II) complexes of higher terminal olefins is consistent with previous results⁹. However, the relatively high stability of the palladium(II)-olefin complexes in the presence of an excess of olefin was exploited in identifying them. Thus when Na_2PdCl_4 was dissolved in an excess of 1-hexene, both molecules of sodium chloride were precipitated, indicating that the product formed was either $[\text{PdCl}_2(1\text{-hexene})_2]$ or $[\text{Pd}_2\text{Cl}_4(1\text{-hexene})_2]$, and eliminating the possibility that it was either $\text{Na}[\text{PdCl}_3(1\text{-hexene})]$ or $\text{Na}[\text{Pd}_2\text{Cl}_5(1\text{-hexene})]$, both of which are analogous to the two complexes isolated by reaction of $\text{Na}_2\text{Pd}_2\text{Cl}_6$ in acetic acid with allylammonium chloride². When the 1-hexene was removed by evaporation under vacuum at room temperature, a light brown solid, which decomposed slowly in air, was formed. This product exhibited an infrared absorption band at 1520 cm^{-1} , and olefinic protons at lower field than in free 1-hexene in the NMR spectrum, both of which are consistent⁸ with the presence of an olefin coordinated to palladium(II).

Raman spectroscopy was used to distinguish between the two possible olefin complexes formed, namely $[\text{PdCl}_2(\text{Olefin})_2]$ and $[\text{Pd}_2\text{Cl}_4(\text{Olefin})_2]$. Thus the Raman spectrum of the solution obtained by dissolving Na_2PdCl_4 in an excess of 1-octene

exhibited three strong bands in the palladium–chlorine stretching region at 361, 303 and 286 cm^{-1} . These are consistent with the olefin complex being $[\text{Pd}_2\text{Cl}_4(1\text{-octene})_2]$, since $[\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2]$ is reported¹⁰ to exhibit bands at 355, 302 and 271 cm^{-1} in the infrared, and for complexes of C_{2h} symmetry the infrared and Raman active palladium–chlorine stretching modes should be identical. $[\text{PdCl}_2(1,5\text{-cyclooctadiene})]$ can be regarded as a model complex for $[\text{PdCl}_2(1\text{-octene})_2]$, since this latter compound, if formed, would undoubtedly exist in the *cis*-form, as studies with bis-olefin platinum(II) complexes show the *cis*-isomer to be more stable¹¹, and since palladium(II) complexes undergo isomerisation to the thermodynamically more stable isomer¹². Since $[\text{PdCl}_2(1,5\text{-cyclooctadiene})]$ exhibits three infrared bands in a very different frequency pattern (335, 325 and 296 cm^{-1})¹³ from the present 1-octene complex, it is apparent that this 1-octene complex is indeed $[\text{Pd}_2\text{Cl}_4(1\text{-octene})_2]$.

2. Isosbestic points

Although, as has been emphasised on a number of occasions, the interpretation of isosbestic points requires great care^{14–16}, they can be used to give a considerable insight into the number of species present. Accordingly a series of solutions were prepared containing $0.5 \times 10^{-3} \text{ M}$ $\text{Na}_2\text{Pd}_2\text{Cl}_6$ in glacial acetic acid and varying concentrations of 1-octene in the range 0–0.1 *M*. The equilibria were established within the time of mixing, and thereafter the spectra changed only very slowly on standing as a result of isomerisation of the olefin. Very poor isosbestic points were obtained between 420 and 430 nm and between 285 and 295 nm. This is similar to previous results with allylbenzene³. However, when the glacial acetic acid was first saturated with sodium chloride, very sharp isosbestic points were obtained, almost certainly because the equilibrium



is driven to the left. One sharp isosbestic point was found at 441 nm for 1-octene concentrations between 0 and 0.12 *M* (Fig. 1). A second sharp isosbestic point was observed at 293 nm for the solutions containing between 0 and $9.25 \times 10^{-3} \text{ M}$ 1-octene (Fig. 2a). For solutions containing between 9.25×10^{-3} and $20.78 \times 10^{-3} \text{ M}$

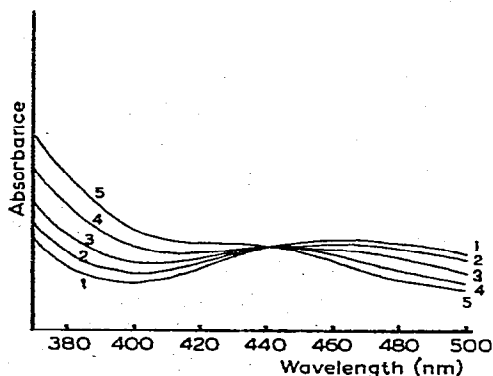


Fig. 1. Isosbestic point at 441 nm in solutions of $\text{Na}_2\text{Pd}_2\text{Cl}_6$ ($0.513 \times 10^{-3} \text{ M}$) in sodium chloride-saturated glacial acetic acid containing 1-octene. 1-Octene concentrations: curve (1), 0 *M*; curve (2), $1.35 \times 10^{-3} \text{ M}$; curve (3), $4.05 \times 10^{-3} \text{ M}$; curve (4), $9.01 \times 10^{-3} \text{ M}$; curve (5), 0.119 *M*.

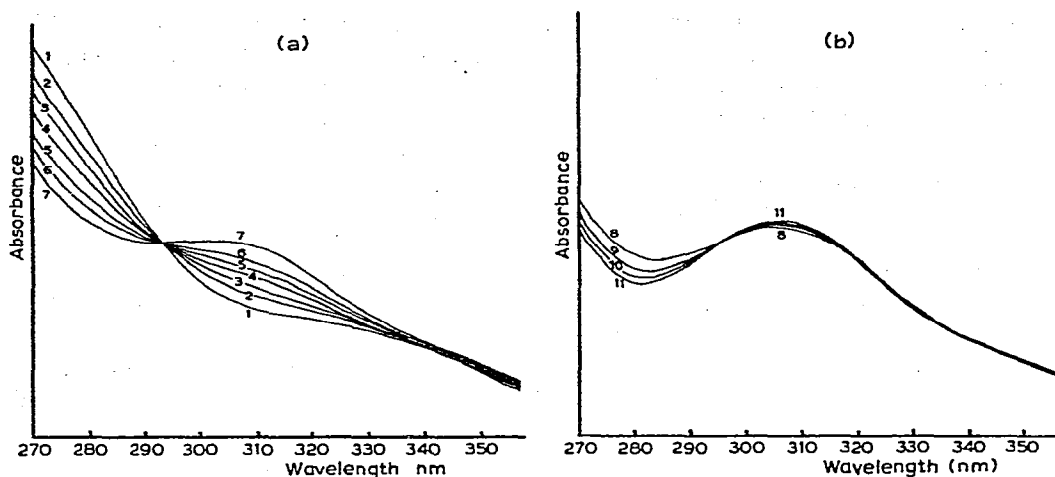


Fig. 2. Isosbestic points at 293 nm (Fig. 2a) and 297 nm (Fig. 2b) in solutions of $\text{Na}_2\text{Pd}_2\text{Cl}_6$ ($0.513 \times 10^{-3} M$) in sodium chloride-saturated glacial acetic acid containing 1-octene. 1-Octene concentrations: curve (1), $0 M$; curve (2), $1.03 \times 10^{-3} M$; curve (3), $2.06 \times 10^{-3} M$; curve (4), $3.08 \times 10^{-3} M$; curve (5), $5.14 \times 10^{-3} M$; curve (6), $6.16 \times 10^{-3} M$; curve (7), $9.25 \times 10^{-3} M$; curve (8), $2.08 \times 10^{-2} M$; curve (9), $3.11 \times 10^{-2} M$; curve (10), $4.15 \times 10^{-2} M$; curve (11), $5.19 \times 10^{-2} M$.

1-octene this isosbestic point shifted gradually to 297 nm. Solutions containing between 20.8×10^{-3} and $51.9 \times 10^{-3} M$ 1-octene all exhibited a sharp isosbestic point at 297 nm (Fig. 2b).

The observation of a shift in the position of the isosbestic point with increasing concentration of olefin indicates that at least two metal-olefin complexes are formed. These could be $\text{Na}[\text{Pd}_2\text{Cl}_5(1\text{-octene})]$, formed at low olefin concentration, and $[\text{Pd}_2\text{Cl}_4(1\text{-octene})_2]$, formed at higher olefin concentration. This would be consistent with the formation of $[\text{Pd}_2\text{Cl}_4(1\text{-octene})_2]$ at very high olefin concentrations, as shown above by Raman spectroscopy.

3. Application of the Method of Continuous Variations (Job's Method)

The Method of Continuous Variations^{17,18} (Job's Method¹⁹) has rarely been applied to the study of organometallic species in solution. Although, as has been emphasised on a number of occasions, the method is generally unsuitable for the determination of equilibrium constants, it is a powerful technique for identifying the species present in systems in which more than one metal-ligand complex is suspected. Basically the method consists of preparing a series of solutions in which the mole fraction of the metal (x) is varied between 0 and 1 whilst the mole fraction of the ligand is adjusted to a value of $(1-x)$. A plot of the difference between the absorbance calculated from the mole fractions of the metal and ligand added initially assuming no interaction and that actually observed (ΔA) will show a maximum or a minimum. If only one complex is formed the position of this maximum or minimum corresponds to the molar ratio of the metal and ligand concentrations in the complex. If, however, the metal and the ligand react to form more than one complex the interpretation of the resulting Job plot is more complex, but also potentially more informative, since the position of the maximum or minimum depends on both the relative concentrations

of all the absorbing species and on their extinction coefficients²⁰. This latter dependence can, in ideal cases, result in Job plots in different regions of the spectrum exhibiting maxima or minima at different molar ratios of metal and ligand and hence giving information about the metal-ligand complexes formed.

Job plots were prepared for the system $\text{Na}_2\text{Pd}_2\text{Cl}_6/1\text{-octene}$ in glacial acetic acid saturated with sodium chloride in three main regions of the spectrum in which the palladium(II)-olefin complexes gave significantly different absorption spectra from the chloropalladium(II) complexes (see Figs. 1 and 2), namely, between 265 and 285 nm, 300 and 320 nm (see Fig. 3), and 370 and 410 nm (Fig. 4). Between 265 and 320 nm the plots show a maximum (or minimum) at palladium(II) to 1-octene ratios of about 2/1, indicating that species such as $\text{Na}[\text{Pd}_2\text{Cl}_5(1\text{-octene})]$ are present. However, between 370 and 410 nm the plots show maxima at palladium(II) to 1-octene ratios of about 2/3. At first sight this might seem to indicate the presence of species containing a 1/1 ratio of palladium(II) to 1-octene such as $[\text{Pd}_2\text{Cl}_4(1\text{-octene})_2]$

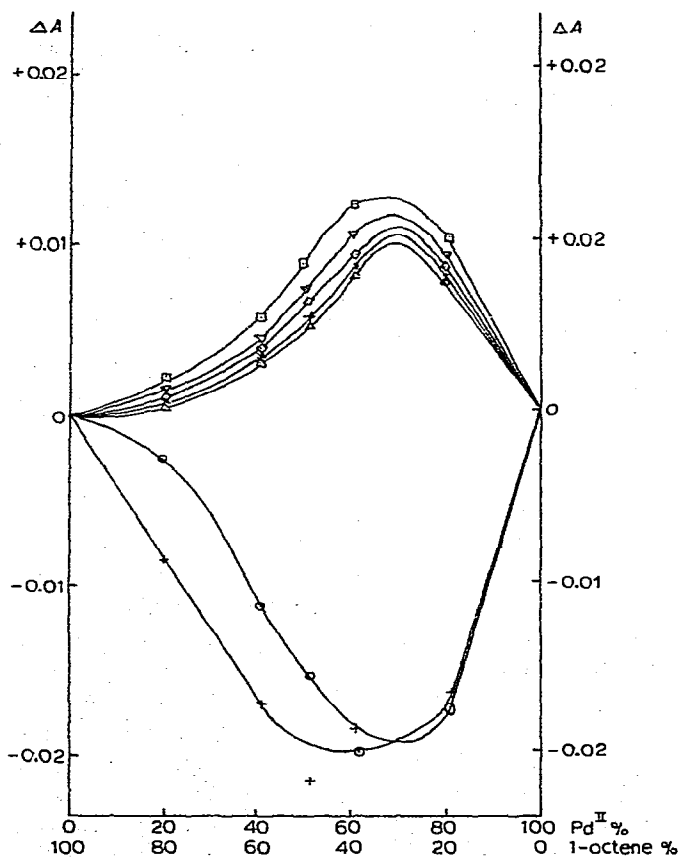


Fig. 3. Job plots for the system 1-octene/palladium(II) in sodium chloride-saturated glacial acetic acid at 265 (+), 285 (⊙), 300 (□), 305 (Δ), 310 (◇), 315 (×) and 320 (∇). ΔA = difference between the absorbance calculated from the sums of the absorbances of the palladium(II) and 1-octene solutions determined separately and the absorbance determined for a solution in which both palladium(II) and 1-octene are present simultaneously.

and $\text{Na}[\text{PdCl}_3(1\text{-octene})]$ together with species containing a 1/2 molar ratio of palladium(II) to 1-octene such as $[\text{PdCl}_2(1\text{-octene})_2]$. However, the presence of a maximum below a 1/1 molar ratio of palladium(II) to 1-octene is not necessarily indicative of the presence of 1/2 species, since it has been shown previously^{21,22}, that when two complexes such as ML_n and ML_{n+1} are present, the first may well reach its maximum concentration at a reagent ratio below the formal value of n and the second at a reagent ratio above the formal value of $n+1$. Thus the two Job plots confirm the presence of 2/1 and 1/1 palladium(II)/1-octene complexes, but to postulate the presence of a 1/2 complex would require independent experimental evidence. This is lacking, since the preparative and Raman results discussed earlier give no support for the presence of significant amounts of 1/2 palladium(II)-olefin complexes.

DISCUSSION

Previous workers^{6,23} have shown that a solution prepared by dissolving sodium tetrachloropalladate(II) in glacial acetic acid contains principally $\text{Na}_2\text{Pd}_2\text{Cl}_6$. However, by analogy with $\text{Li}_2\text{Pd}_2\text{Cl}_6$, a small amount of Na_2PdCl_4 should also be present⁶. The present work, together with further work to be published shortly, suggests that in the absence of added sodium chloride a small amount of $\text{Na}[\text{Pd}_2\text{Cl}_5(\text{CH}_3\text{COOH})]$ is also present, but that this can be eliminated by the addition of sodium chloride. The results of the isosbestic points experiments suggest the presence of at least two palladium(II)-olefin complexes, one formed at low olefin concentra-

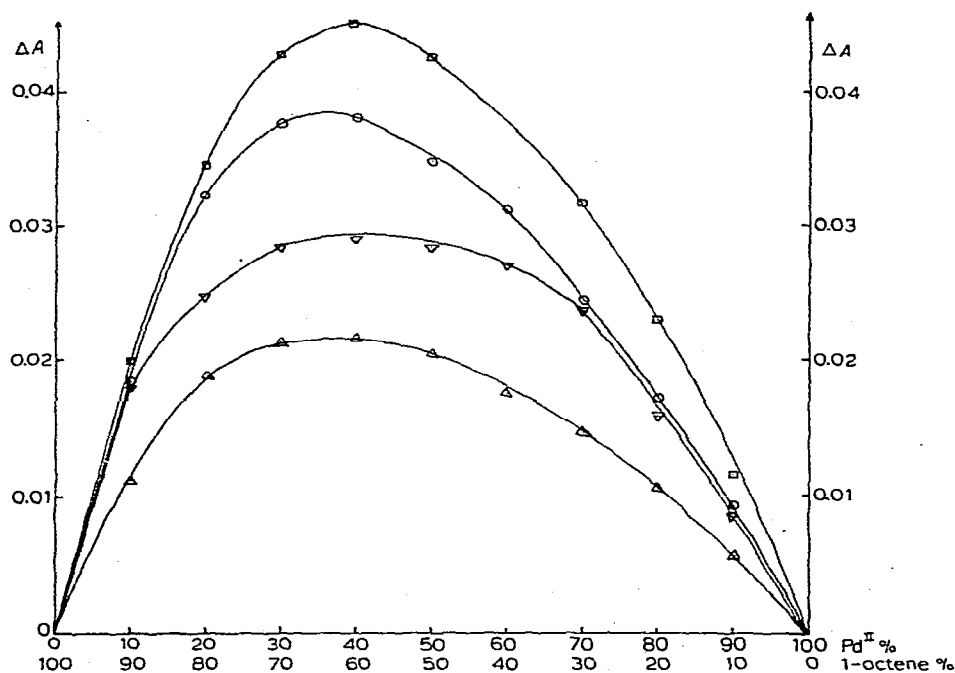
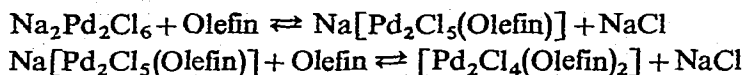


Fig. 4. Job plots for the system 1-octene/palladium(II) in sodium chloride-saturated glacial acetic acid at 380 (\square), 390 (\circ), 400 (∇) and 410 (\triangle). ΔA has the same meaning as in Fig. 3.

tions and the other at higher olefin concentrations. Quantitative determinations show that when Na_2PdCl_4 is dissolved in an excess of olefin all the sodium chloride is precipitated, so that the highest complex is either $[\text{Pd}_2\text{Cl}_4(\text{Olefin})_2]$ or $[\text{PdCl}_2(\text{Olefin})_2]$. The Raman spectrum of the solution indicates that only the former is present in sufficient quantity to be detected. The Job plots are consistent with the formation of 2/1 and 1/1 palladium(II)-olefin complexes. These results together indicate that when terminal olefins such as 1-octene react with $\text{Na}_2\text{Pd}_2\text{Cl}_6$ in glacial acetic acid the principal equilibria present are:



Na_2PdCl_4 , which is present in low concentration, would also be expected to react to yield a small amount of $\text{Na}[\text{PdCl}_3(\text{Olefin})]$, but the amount formed was below the limits of detection of the present work. This is not, perhaps, surprising in view of Moiseev's observation²⁴ that in aqueous solution $\text{Pd}_2\text{Cl}_6^{2-}$ is more reactive towards olefins than PdCl_4^{2-} .

During the course of the present work a similar, less complete, study on the interaction of allylbenzene with chloropalladium(II) complexes in glacial acetic acid was published³. Since all three olefins may be written as $\text{RCH}_2\text{CH}=\text{CH}_2$, it was of interest to compare the present results with aliphatic R groups with those obtained for an aromatic R group. As expected, the two studies are in broad agreement in that both observe $\text{Na}[\text{Pd}_2\text{Cl}_5(\text{Olefin})]$ and $[\text{Pd}_2\text{Cl}_4(\text{Olefin})_2]$ as the principal species present. However, Cruikshank and Davies³, because they did not use sodium chloride-saturated glacial acetic acid, were forced to postulate the minor formation of a third olefin complex $[\text{PdCl}_2(\text{allylbenzene})_2]$ in order to account for the lack of a sharp isosbestic point around 400 nm, whereas our results suggest that this was probably due to the presence of small amounts of $\text{Na}[\text{Pd}_2\text{Cl}_5(\text{CH}_3\text{COOH})]$ rather than to a third olefin complex. Furthermore, their suggestion that at very high olefin concentration $[\text{PdCl}_2(\text{allylbenzene})_2]$ is the main species present does not apply to the aliphatic terminal olefins, as shown by Raman spectroscopy.

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