Kinetics and Mechanism of Vinylation of *ortho*-Palladated *NN*-Dialkylbenzylamines by para-Substituted Styrenes †

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The kinetics of vinylation of *ortho*-palladated *NN*-dialkylbenzylamines (1a—g) by $CH_2=CHC_6H_4R^3$-*p* (R^3 = H, Cl, Br, Me, and MeO) to form the respective 2-dialkylaminomethylstilbenes (2) has been studied mainly at 30 °C in acetic acid solvent. The reaction follows second-order kinetics: $d[(2)]/dt = k_2[(1)][\text{styrene}]$. The rate constants k_2 increase markedly in the presence of both alkali-metal perchlorates ($MClO_4$) and small concentrations of perchloric acid, k_2 being directly proportional to $[HClO_4]$. It is shown that the salt effect originates from the solvolytic reaction $MClO_4 + HOAc \rightleftharpoons MOAc + HClO_4$. Conversion of dimer (1a) into the respective monomer (3) stops the reaction, but the latter species readily forms π-complexes with styrenes. The stability constants of 1 : 1 π-complexes have been determined and their Hammett correlation with a slope of −1.87 is established. For a series of substituted styrenes $\lg k_2$ is the linear function of Hammett σ_p values with a slope of *ca.* −1. For a series of ring-substituted complexes (1) $\lg k_2$ correlates with the pK_a of the parent benzylamines with a slope of 0.98. The results are interpreted in terms of a mechanism involving intermediate protonation of (1), π-co-ordination of alkene, and subsequent rate-determining intramolecular insertion of styrene into a Pd–C bond through a four-centred transition state.

Cyclometallation and reactions of cyclometallated compounds have recently received considerable attention.[1] Complexes with palladocycles are of unique importance, since they appear to be valuable intermediates for regioselective carbonylation,[2] vinylation,[3] alkylation,[4,5] halogenation,[6] and phosphination[7] of organic moieties. In all these reports attention has been focused on the synthetic aspects of the reactions. Little if any effort has been expended on the systematic investigation of the reaction mechanisms on the basis of kinetic data. In this paper we report the first results of a kinetic study of the vinylation of *ortho*-palladated *NN*-dialkylbenzylamines by *para*-substituted styrenes in acetic acid solvent [reaction (1)]. Reaction (1) is of interest not only as an example of the conversion of cyclopalladated complex. It may also serve as a good model for arylation of olefins both by arenes and organometallic compounds in the presence of palladium salts,[8] since it is known[9] that the rate-determining step in these reactions is the formation of unstable arylpalladium intermediates. The subsequent interaction of arylpalladium species with alkenes is fast and it is impossible to study this step by direct kinetic methods. The presence of the stable Pd–C bond in (1) provides a good opportunity to investigate not only olefin insertion processes, but also other fast steps of various palladium-catalysed reactions.[10]

Results

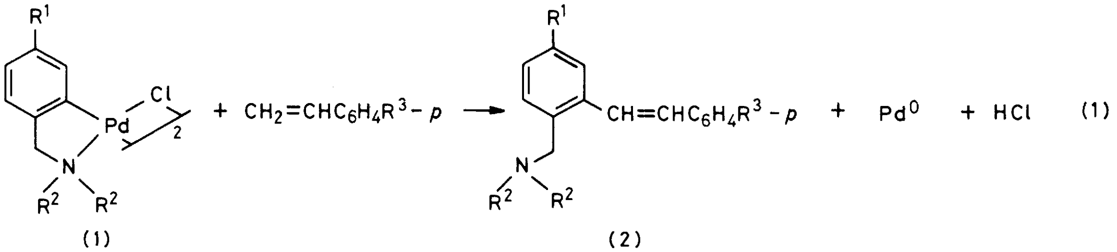
The Rate Law.—It has been demonstrated in the preceding paper[11] that under the synthetic conditions used the interaction between (1a) and styrene under argon in the presence of 0.1M-$NaClO_4$ gives 2-dimethylaminomethylstilbene in a 57% yield. Under kinetic conditions, *e.g.* at low concentrations of (1a) (10^{-6}—10^{-4}M) and at least a 20-fold excess of styrene (10^{-4}—10^{-1}M) in pure acetic acid under argon, the yield of (2) usually exceeds 80%, providing a convenient system for kinetic study.

The dimeric compounds (1) do not dissociate to form monomeric complexes in the chosen concentration range, as is evident from the constancy of the extinction coefficients of the former.[12] The reaction was found to be first order in (1), and the observed pseudo-first-order rate constants were linear functions of alkene concentration [equation (2)]. Thus

$$k_{obs.} = k_2[\text{styrene}] \qquad (2)$$

$$d[(2)]/dt = k_2[(1)]\,[\text{styrene}] \qquad (3)$$

the complete rate expression can be written as (3). The k_2 values obtained under various conditions together with the



(1)

(2)

(1)

a; R^1 = H, R^2 = Me
b; R^1 = H, R^2 = Et
c; R^1 = Me, R^2 = Et
d; R^1 = OMe, R^2 = Et
e; R^1 = 4, 5-$(OMe)_2$, R^2 = Et
f; R^1 = Cl, R^2 = Et
g; R^1 = H, R^2 = Pr^n

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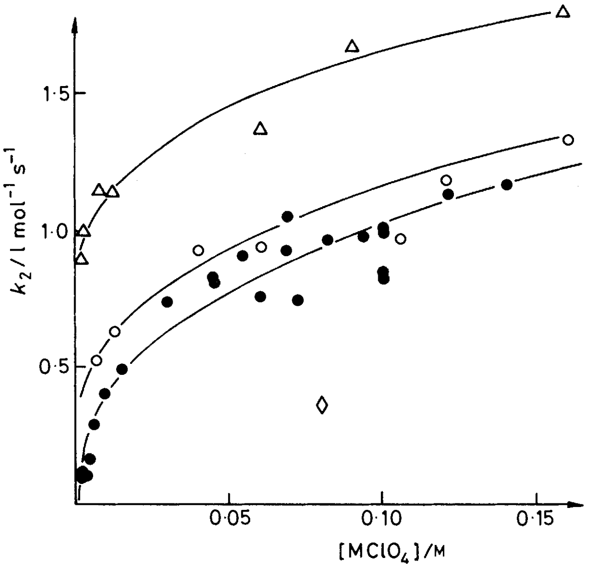


Figure 1. A plot of k_2 *versus* salt concentration for the reaction of (1a) with styrene at 30 °C: ○, $LiClO_4$; ●, $NaClO_4$; △, $Mg(ClO_4)_2$; and ◇ $[Bu^n_4N]ClO_4$

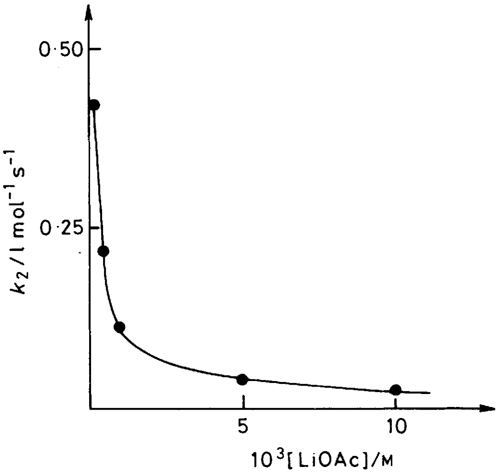


Figure 2. A plot of k_2 *versus* [LiOAc] at a fixed concentration of $LiClO_4$ (0.01M) for the reaction of (1a) with styrene at 30 °C

respective activation parameters ($\Delta H^\ddagger$, $\Delta S^\ddagger$) are collected in Table 1.

The Effects of Salts and Acid.—It has been found previously[11] that addition of alkali-metal perchlorates strongly reduces the reaction time. Figure 1 shows the dependence of k_2 on salt concentration. The considerable rate enhancement reaching two orders of magnitude is evident. The effect of salt depends on the nature of the cation, Mg^{2+} being the most effective and $Bu^n_4N^+$ the least. The strong salt effect exists, however, only in acetic acid solvent. The reaction is not accelerated by $LiClO_4$ (up to 0.175M) or $[Bu^n_4N]ClO_4$ in aprotic dioxane or protic, but less acidic than acetic acid, methanol. In both solvents the reaction rate is extremely low even in the presence of salts or at elevated temperatures and cannot be measured reliably.

Lithium acetate exhibits very little effect on the reaction rate in the absence of $LiClO_4$. However, addition of LiOAc to a 0.1M solution of $LiClO_4$ decreases the rate (Figure 2), k_2 being inversely proportional to the LiOAc concentration.

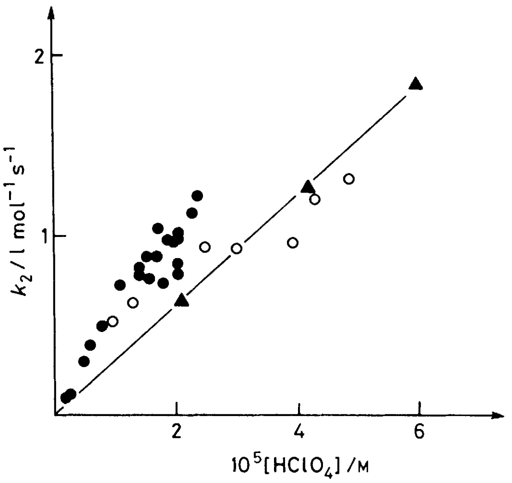


Figure 3. The dependence of k_2 on the concentration of added $HClO_4$ (△) and the data of Figure 1 recalculated to plot k_2 against $[HClO_4]$, the latter liberated in solvolytic reaction (4), for the reaction of (1a) with styrene: ○, $LiClO_4$; ●, $NaClO_4$

Taking into account these observations we assume that the salt effect results from the solvolysis of metal perchlorates ($MClO_4$) in acetic acid to form strong perchloric acid, the latter being responsible for the catalytic effect [equation (4)].

$$MClO_4 + HOAc \rightleftharpoons HClO_4 + MOAc\ (K_M) \quad (4)$$

$$M = Li, Na;\ K_M = [HClO_4][MOAc]/[MClO_4]$$

In order to verify this assumption we have studied the effect of small concentrations of $HClO_4$ on the rate of reaction (1). The second-order rate constant k_2 was found to be directly proportional to the concentration of $HClO_4$ according to equation (5) (Figure 3) where $k_3 = k_2$ in the absence of salt

$$k_2 = k_3 + k_4[HClO_4] \quad (5)$$

or $HClO_4$ and $k_4 = 2.9 \times 10^4$ l^2 mol^{-2} s^{-1} at 30 °C. Perchloric acid catalyses the reaction not only in HOAc, but in those solvents where the reaction is unmeasurably slow in the absence of acid, *e.g.* in dioxane and methanol. In these two solvents the reaction rate follows equation (5) with k_4 equal to 39.7 and 1.79 l^2 mol^{-2} s^{-1} at 30 °C, respectively, but k_3 is close to zero in both solvents.

Some other salts have also been tested, but none of them catalyses the reaction as metal perchlorates do. For instance, lithium chloride inhibits the reaction completely due to the cleavage of chloro-bridges of (1a) to form the unreactive anionic complex (3).[13] It is interesting to note that (1a) does not react with LiCl in methanol. However, addition of catalytic quantities of $HClO_4$ leads to the cleavage of chloro-bridges to give (3). In the presence of $LiNO_3$ a process similar to that in the case of LiCl proceeds, but since it does not result in the enhancement of the rate of reaction (1) we have not studied this interaction in detail.

Substituent Effects.—Figure 4 shows the plot lgk_2 *versus* Hammett constants σ_p for the reaction of (1a) with *para*-substituted styrenes at $[NaClO_4]$ 0.1M. A satisfactory linear plot is observed with slope ρ^{R^3} −1.06. In the absence of salt,

Table 1. The second-order rate constants k_2 and the activation parameters of reaction (1) in the absence and in the presence of salt (0.1M) in acetic acid solvent [a]

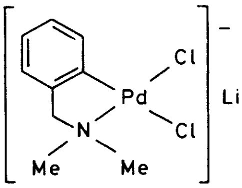
Complex	$CH_2CHC_6H_4R^3$-*p* R^3	*T*/K	Salt	k_2/l mol^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
(1a)	H	298		1.1×10^{-2}		
		303		1.3×10^{-2}		
		308		1.8×10^{-2}	26.8	−192
		318		2.3×10^{-2}		
		293	$NaClO_4$	0.32		
		298	$NaClO_4$	0.62	16.1	−190
		303	$NaClO_4$	0.84		
		308	$NaClO_4$	1.3		
		303	$LiClO_4$	0.91		
		303	$Mg(ClO_4)_2$	1.7		
		303	Bu_4NClO_4 [b]	0.35		
	Br	303		9.3×10^{-3}		
		293	$NaClO_4$	0.51		
		303	$NaClO_4$	0.62	37.0	−124
		308	$NaClO_4$	1.1		
		318	$NaClO_4$	1.7		
	Cl	303		7.7×10^{-3}		
		293	$NaClO_4$	0.53		
		303	$NaClO_4$	0.75	31.8	−141
		313	$NaClO_4$	1.3		
	Me	303		2.9×10^{-2}		
		293	$NaClO_4$	1.2		
		298	$NaClO_4$	1.3	27.8	−148
		303	$NaClO_4$	1.9		
		318	$NaClO_4$	2.2		
	OMe	298		5.0×10^{-2}		
		303		6.9×10^{-2}	37.8	−143
		313		1.1×10^{-1}		
		293	$NaClO_4$	1.9		
		298	$NaClO_4$	2.1	9.8	−206
		303	$NaClO_4$	2.2		
(1b)	H	303	$NaClO_4$	0.18		
	Br	303	$NaClO_4$	0.09		
	Cl	303	$NaClO_4$	0.09		
	Me	303	$NaClO_4$	0.19		
	OMe	303	$NaClO_4$	0.25		
(1c)	H	303	$NaClO_4$	0.27		
(1d)	H	303	$NaClO_4$	0.28		
(1e)	H	303	$NaClO_4$	0.19		
(1f)	H	303	$NaClO_4$	0.11		
(1g)	H	303	$NaClO_4$	0.16		

[a] Errors in k_2 and $\Delta H^‡$ are 5—10%, in $\Delta S^‡$ 10—20%. [b] 0.08M.

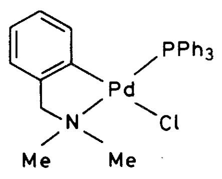
when the reaction rate is much lower, the slope is more negative (ρ^{R^3} −1.26). The analogous plot is observed for the reaction of (1b); at $[NaClO_4]$ 0.1M the slope is equal to −0.86. The lengthening of the alkyl chain at the nitrogen donor atom of (1) retards the reaction rate slightly (Table 1). However, the unambiguous discrimination between electronic and steric effects might be misleading in the light of recent work.[14]

The variation of ring substituents in complexes (1b—f) results in little change in k_2. No straightforward correlation has been found when lgk_2 values are plotted against σ_m Hammett constants, but in general, electron-donating ring substituents favour the reaction. A clear correlation exists between lgk_2 and the basicity of substituted benzylamines (Figure 5) with a slope of +0.98.

Kinetic Isotope Effects.—The ratios $k_2^{PhCHCH_2}/k_2^{PhCHCD_2}$ have been measured at three different $NaClO_4$ concentrations, 0.00, 0.015, and 0.0744M. The respective values are 1.15, 1.01,



(3)



(4)

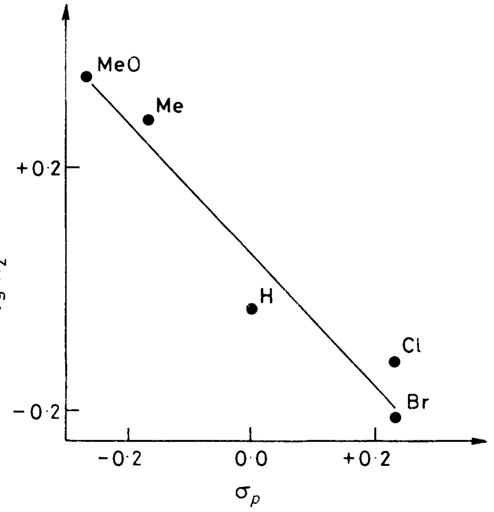


Figure 4. A Hammett plot of lgk_2 *versus* σ_p for the reaction of (1a) with *para*-substituted styrenes at [NaClO$_4$] 0.1M and 30 °C. The data are from Table 1

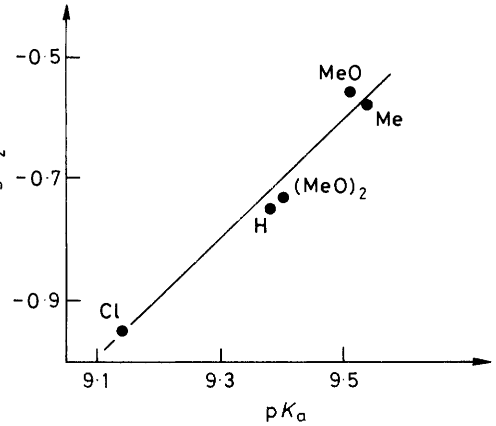


Figure 5. The effect of substituents in (1). The correlation of lgk_2 with pK_a of ring-substituted benzylamines, taken from ref. 39

and 1.06. These quantities show that the cleavage of the C–H bond of alkene is not involved in the rate-determining step.

π-Complex Formation of Styrenes with Mononuclear Species (3).—As mentioned above the monomeric complex (3) could not be converted into (2). However, addition of styrene (10^{-3}—10^{-1}M) to a solution of (3) in HOAc (10^{-4}—10^{-5}M) results in a change of spectrum (Figure 6) due to π-complex formation. The change of absorbance, ΔA, as a function of alkene concentration has been fitted to equation (6) for 1 : 1 complex formation. In equation (6) $\Delta\varepsilon = \varepsilon_\pi - \varepsilon$; ε_π and ε are the extinction coefficients of the π-complex and of the starting

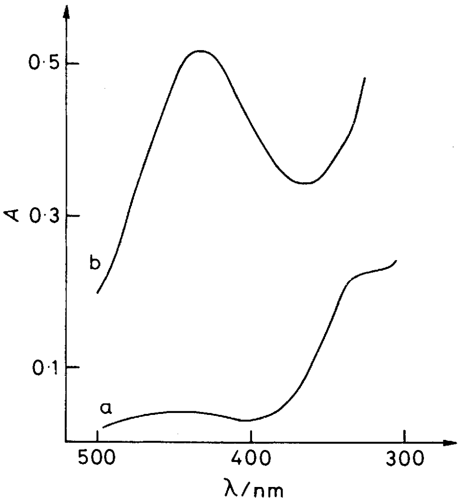


Figure 6. The spectral changes on addition of *p*-methoxystyrene to the solution of (3) in HOAc: (a) the spectrum of (3) in HOAc; (b) the spectrum of (3) in the presence of 6.3 × 10^{-3}M of *p*-methoxystyrene: 30 °C, [(3)] 2.85 × 10^{-4}M

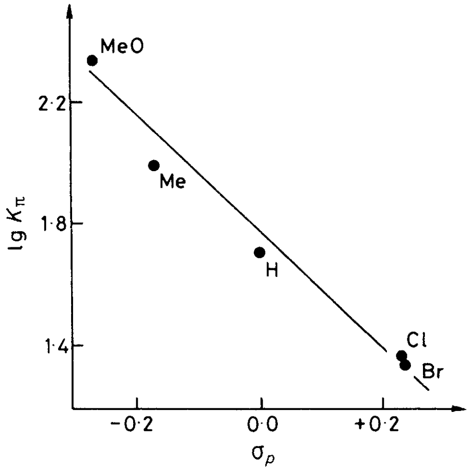


Figure 7. The Hammett correlation of stability constants K_π of monomeric π-complexes. The data from Table 2

$$\frac{\Delta A}{[(3)]_0} = \frac{\Delta\varepsilon\, K_\pi[\text{styrene}]}{1 + K_\pi[\text{styrene}]} \qquad (6)$$

complex, respectively. At high LiCl concentration (8 × 10^{-2}—0.15M) ΔA is inversely proportional to [LiCl], but addition of LiCl over the concentration range close to [(3)] has no effect on ΔA. These observations indicate that in dilute solutions (3) dissociates according to equation (7) where L is the cyclopalladated ligand, and styrene interacts further with LPdCl [equation (8)]. Intermediate complex LPdCl probably contains co-ordinated solvent molecule. The stability constants K_π are given in Table 2. They show a good Hammett correlation with a slope −1.87 (Figure 7).

$$(3) \rightleftharpoons \text{LPdCl} + \text{LiCl} \qquad (7)$$

$$\text{LPdCl} + \text{styrene} \overset{K_\pi}{\rightleftharpoons} \text{LPdCl(styrene)}\ (K_\pi) \qquad (8)$$

Addition of small concentrations of HClO$_4$ to the mixture of

Table 2. The stability constants of monomeric π-complexes derived from (3) [equation (8)] in acetic acid solvent

$CH_2CHC_6H_4R^3$-*p* R^3	*T*/K	$[HClO_4]$/M	K_π/ l mol^{-1}	$\lambda_{max.}$/nm
H	303		50	340
Br	303		21	350
Cl	303		23	360
	303	2.7×10^{-4}	40	
	303	8.0×10^{-4}	47	
	303	1.3×10^{-3}	106	
Me	303		98	380
OMe [b]	298		260	440
	303		234	
	308		220	
	318		204	

[a] The error in K_π is 5—10%. [b] $\Delta H°$ −9.2 kJ mol^{-1}, $\Delta S°$ 15 J K^{-1} mol^{-1}.

(3) and styrene does not induce the type (1) reaction and has no effect on π-complex stability. However, an increase $[HClO_4]$ enhances K_π values (Table 2).

Discussion

The most remarkable feature of reaction (1) is the unprecedently high positive salt effect, induced by addition of metal perchlorates. Qualitatively it seems reasonable to ascribe this effect to acid catalysis by perchloric acid liberated in solvolytic reaction (4), as was suggested previously [15] to account for the effect of salts in mercuriation of arenes by $Hg(OAc)_2$ in acetic acid. To verify the proposal quantitatively one should recalculate the data of Figure 1 on the basis of equation (4) to plot k_2 against $[HClO_4]$, the latter formed in the presence of alkali-metal perchlorates. The appropriate equilibrium constants K_M were calculated according to equation (9), where $pK_a^{HOAc} = 14.45$, $pK_a^{HClO_4} = 4.87$; dis-

$$K_M = K_a^{HOAc}K_d^{MClO_4}/K_a^{HClO_4}K_d^{MOAc} \qquad (9)$$

sociation constants for $MClO_4$ $pK_d^{LiClO_4} = 5.11$ and $pK_d^{NaClO_4} = 5.73$, and those for MOAc $pK_d^{LiOAc} = 6.87$ and $pK_d^{NaOAc} = 6.58$. The equilibrium constants (in acetic acid solvent) of acids and salts were taken from refs. 16 and 17, respectively. The resulting values are $K_{Li} = 1.51 \times 10^{-8}$ and $K_{Na} = 4.27 \times 10^{-9}$ mol l^{-1}. The plot of k_2, taken from Figure 4, against $[HClO_4]$, calculated using these K_M constants, is presented in Figure 3. A satisfactory agreement is evident between calculated and directly obtained dependences.

The catalytic effect of salts depends on the nature of the cation, and according to our treatment, this dependence should be governed by $pK_d^{MClO_4}$ and pK_d^{MOAc} of the respective salts. Unfortunately, there are no appropriate data for Mg^{2+} and $Bu^n{}_4N^+$ cations.

The inhibition of the reaction by LiOAc (Figure 2) appears to be another quantitative argument to support our interpretation. Combination of equations (4) and (5) gives equation (10). It is seen from equation (10) that at low concentrations of

$$k_2 = k_3 + k_4K_M[LiClO_4]/[LiOAc] \qquad (10)$$

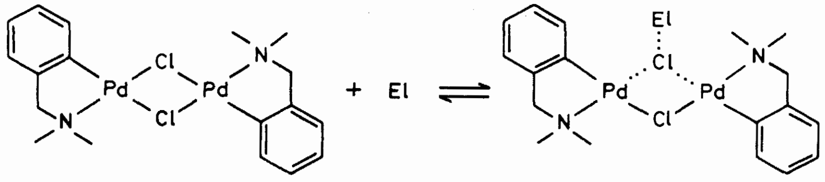
$LiClO_4$, when k_2 is approximately a linear function of $[LiClO_4]$, the reaction rate should be inversely proportional to [LiOAc]. The data presented on Figure 2 are in full accord with these considerations.

Equation (5) shows that reaction (1) proceeds through two parallel pathways, one of which is ' solvolytic ' (k_3) and the other an acid-catalysed process (k_4). Both paths have general features in common, *e.g.* rate law, substituent effects, kinetic isotope effects, and similar values for activation parameters. These findings suggest similar mechanistic patterns for ' solvolytic ' and acid-catalysed pathways. The similarity arises probably from the ability of acetic acid solvent to act as a general acid catalyst in the reaction. Thus it becomes clear why acetic acid is the best solvent for reaction (1).

Consider now the mechanistic features of the reaction. The acid catalysis may arise from protonation of (1) or the styrene molecule. In the latter case the carbenium ion $Ar\overset{+}{C}HCH_3$ should be formed according to the Markovnikoff rule. It might attack the negatively charged carbon of the Pd–C bond of (1). However, one would expect the formation of 1,1-diphenylethylenes rather than stilbenes in this case. Since stilbene derivatives are the main products [11,18] and a 1,1-diphenylethylene-type compound is formed only as a by-product in very low yield in the case of *o*-chlorostyrene,[18] a route with alkene protonation is hardly acceptable.

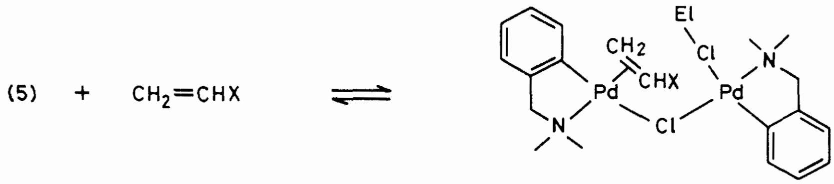
Protonation of (1) should enhance the reaction rate, since it leads to an increase of the positive charge on Pd^{II}, and in general, the attack of the metal centre on alkene is an electrophilic process. Complex (1) has three possible sites of protonation: chloro-bridges, the nitrogen donor atom, and the metal centre. The protonation of the latter has been involved to account for the acid-catalysed substitutions at Pt^{II}.[19] Though it is quite reasonable in the case of Pt^{II} this mechanism, however, seems to be rather improbable for Pd^{II}. We prefer the chloro-bridges as the site of proton attack on the basis of the reasons stated below. (i) The rupture of the Pd–N bond as a result of protonation of the nitrogen donor appears unnecessary for the insertion of unsaturated molecules into the Pd–C bond of type (1) complexes. This is strongly supported by reactions of (1a) with some alkynes, which proceed under mild conditions in the absence of any reagent able to cleave a Pd–N bond.[20] (ii) Dechelation leads in some cases to the protonolysis of the Pd–C bond with concomitant dissociation of the *NN*-dimethylamine ligand.[13] (iii) The monomeric complexes (3) and (4) without chloro-bridges are completely inert with respect to styrenes even in the presence of $MClO_4$, although they both have Pd–N fragment. (iv) $HClO_4$ promotes the cleavage of chloro-bridges of (1a) by LiCl to form (3) in methanol solvent. It is reasonable to assume that H^+ attacks a bridging chloride since in the case of protonation of the nitrogen donor the transformation of the palladocycle seems to be more probable. Moreover, chloride appears to be as basic as tertiary amines in acetic acid solvent. In particular, the pK_a value of HCl is 8.55 and that of tribenzylammonium ion is 9.07.[16] Protonation of (1) is also consistent with the observed correlation between k_2 and amine basicity (Figure 5). The additional negative charge on nitrogen could be transferred to chloride, as was exemplified recently in the mercury-assisted aquation of *cis*-$CoCl(en)_2(X\text{-}py)^{2+}$ through a $Hg\text{–}ClCo(en)_2(X\text{-}py)^{4+}$ intermediate.[21] A linear plot of lg*k* *versus* $pK_a^{X\text{-}py}$ with a slope of 0.5 has been found. We believe that in our case a similar correlation is manifest in facilitating protonation of bridging chloride provided by the increase in benzylamine basicity.

The detection of styrene π-complexes in the case of monomeric species (3) suggests that an intermediate π-complex formation may be involved in reaction (1). On the other hand, we have not registered any π-complexes in the case of dimers (1). These findings have a close analogy with complex formation in the palladium(II) acetate system. The trimer $Pd_3(OAc)_6$, which contains bridging acetates only, does not form detectable olefin π-complexes, while the dimer $Na_2Pd_2(OAc)_6$ with four terminal acetates co-ordinates olefins



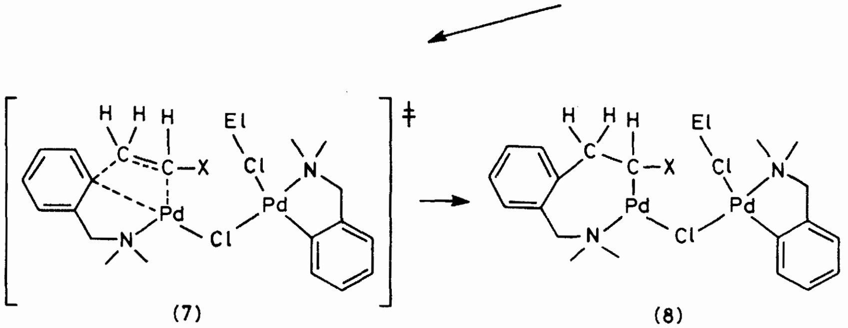
(5)

(K_{11}) (11)



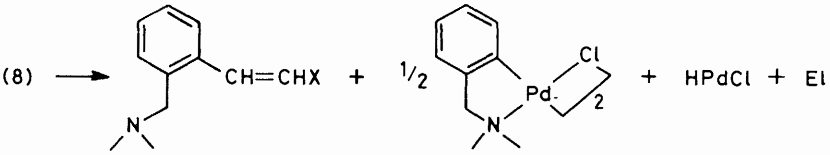
(6)

(K_{12}) (12)



(7) (8)

(k_{13}) (13)



(fast) (14)

El = HOAc (k_3 path), $HClO_4$ (k_4 path)

readily.[22,23] At the same time both trimer and dimer react with unsaturated compounds to form oxidation products through intermediate π-co-ordination.[23,24] In our case, (1), with bridging chlorides only, could be much less effective with respect to π-complex formation compared to monomer (3), which has terminal chlorides, but nevertheless form an unstable intermediate π-complex in reaction (1).

The enhancement of the stability of π-complexes in the presence of $HClO_4$ (Table 2) could account for the acid catalysis in reaction (1). The absence of any effect on the stability constants K_π at [$HClO_4$] comparable with [(3)], results from neutralization of $HClO_4$ by Cl^- ions, released upon dissociation of (3). At higher $HClO_4$ concentrations K_π is approximately a linear function of [$HClO_4$], but the catalytic effect of the latter is much weaker compared with that in reaction (1) (*cf.* Figure 3).

On the basis of all the results obtained a mechanism of the reaction could be proposed [steps (11)—(14)].

The first step is the reversible protonation of chloro-bridges of (1) by acetic [k_3 path, equation (5)] or perchloric acid (k_4 path), leading to the increase of the positive charge on palladium(II). The resulting complex (5) in fact might be mono-bridged with a vacant co-ordination site on one of the Pd^{II} centres. Mono-bridged cyclopalladated compounds are known.[25] Evidently, intermediate (5) could form a π-complex more readily compared with starting complex (1). So the next step (12) is alkene co-ordination to afford the π-complex (6) with styrene *cis* to the palladium–carbon bond. This type of equilibrium is generally accepted for olefin insertion reactions.[26] A similar situation has been observed, for example, in the reaction of (1a) with isonitriles.[27] We consider step (12) to be a fast equilibrium, because in the related system co-ordination of styrenes with (3) proceeds almost immediately after mixing of the reagents.

The rate-limiting insertion (13) through the transition state (7) follows π-co-ordination. The final β-hydrogen abstraction (14), with subsequent reduction of Pd^{II}, should be fast, since no deuterium kinetic isotope effect has been found in the reaction with ββ-dideuteriostyrene.

Although the proposed mechanism seems to be probable, we cannot exclude completely the alternative path with protonation of nitrogen donor atom of (1).

Apparently, in terms of the proposed mechanism, the rate constants k_3 and k_4 are composite, $k_3 = K_{11}K_{12}k_{13}$ and $k_4 = K_{11}'K_{12}'k_{13}'$, where the prime denotes the $HClO_4$-catalysed pathway. Thus, for the k_3 path we obtain equation

$$\Delta H_3^{\ddagger} = \Delta H_{11}^{\circ} + \Delta H_{12}^{\circ} + \Delta H_{13}^{\ddagger} \qquad (15)$$

(15) for the activation enthalpy. Taking into account the fact that the enthalpies of protolytic equilibria are usually close to zero[28] one can estimate $\Delta H_{13}^{\ddagger}$ 47 kJ mol^{-1} in the case of *p*-methoxystyrene with the assumption $\Delta H_{12}^{\circ} = \Delta H_{\pi}^{\circ}$, the latter value being taken from Table 2. This rather low value of $\Delta H_{13}^{\ddagger}$ is in good agreement with the concerted mechanism of insertion through a transition state of type (7).

Now we turn to Hammett-type correlations. The effect of substituents in styrene is the sum of two components for both k_3 and k_4 paths [equation (16)]. The ρ_{12} value cannot be

$$\rho = \rho_{12} + \rho_{13} \qquad (16)$$

measured directly, and we assume that $\rho_{12} = \rho_{\pi}$ [equation (8)]. We have obtained ρ_{π} -1.87 and this negative value is in agreement with those previously reported by Powell[29] (-0.54 for σ^+) and Kurosawa[30] (-1.14 to -0.94 for σ_p) for other Pd^{II} complexes. Using ρ_{12} -1.87 we obtain ρ_{13} $+0.61$ in pure acetic acid. The positive ρ for the insertion of styrene into a Pd–C bond is in accord with Murahashi's data[31] for the reaction of 'methylpalladium' with substituted styrenes (ρ $+2.68$) and Powell's data[32] for the insertion of aromatic isocyanides into the palladium–carbon bond (ρ $+1.13$). The positive slope $+0.61$ indicates that the rate-limiting step (13) is governed by nucleophilic attack of the phenyl group on the β-carbon of styrene rather than electrophilic attack of Pd^{II} on the α-carbon.

Experimental

Materials.—All *para*-substituted styrenes were commercially available (Koch-Light). ββ-Dideuteriostyrene was prepared according to ref. 33. *NN*-Dimethyl- and *NN*-diethyl-benzylamine were Koch-Light and Reakhim reagents, respectively. *NN*-Di-n-propylbenzylamine, *NN*-diethyl-4-chloro-, and *NN*-diethyl-4-methylbenzylamine were prepared by amination of the respective benzyl chlorides by either $HNPr^n_2$ or $HNEt_2$.[34] *NN*-Diethyl-4-methoxy- and *NN*-diethyl-3,4-dimethoxybenzylamine were obtained by treating 4-methoxy- or 3,4-dimethoxy-benzaldehyde with *NN*-diethylformamide in the presence of HCO_2H.[35] $NaClO_4$ and $LiClO_4$ were obtained by neutralization of $HClO_4$ by Na_2CO_3 and Li_2CO_3, respectively.[36] $Mg(ClO_4)_2$ (Reakhim) and $[Bu^n_4N]ClO_4$ (Fluka) were commercially available. Acetic acid (Reakhim) was purified by a standard procedure,[37] and since it was found that water only very slightly increased the reaction rate, no attempt was made to remove traces of water.

The metallation of all *NN*-dialkylbenzylamines to form cyclopalladated complexes (1a—g) was carried out as described in ref. 11. The synthesis of 2-dialkylaminomethylstilbenes (2) is described in ref. 11. The properties of these compounds are given elsewhere.[11,38]

Kinetic Measurements.—Reaction rates were obtained from absorbance *versus* time measurements with a Hitachi 356 spectrophotometer. Rates of appearance of (2) were measured at a wavelength of *ca.* 310 nm in acetic acid. At these wavelengths stilbenes (2) were the only absorbing species in the concentration range used. The general procedure was as follows. A stream of argon was bubbled through the solution of (1) in acetic acid to remove oxygen. Then at least a 20-fold excess of styrene with respect to (1) was added to this solution and the increase of absorption accompanying the formation of (2) was monitored. Good pseudo-first-order kinetic curves were obtained. Observed pseudo-first-order rate constants were calculated from a least-squares treatment of the linear $\ln(A_{\infty} - A)$ *versus* time plots. The slow reactions were also treated by the Guggenheim method. It was verified that both methods gave identical $k_{obs.}$ values. Freshly prepared solutions of (1) were used throughout.

π-Complex Formation of Styrenes with Monomer (3).—To the solution of complex (3), the latter prepared according to ref. 13, in acetic acid (10^{-5}—10^{-4}M) styrene (10^{-3}—10^{-2}M) was added, and the electronic spectrum of the solution was recorded. A new intense band appeared immediately after the mixing of the reagents and remained unchanged for *ca.* 1 h. These π-complexes decomposed on standing overnight. The wavelengths of maximum absorption of π-complexes together with stability constants, K_{π}, calculated as described in the text, are given in Table 2. In the case of unsubstituted styrene the co-ordination of the second styrene molecule was observed at higher olefin concentration up to 1.0M.

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