

Table VI. Ionization Potentials

Molecule	CNDO/2	CNDO/M	Mulliken ^a	Expt
Methane	t ₂ 19.74	t ₂ 20.30	t ₂ 17.50	t ₂ 13.06
Ethane	e _g 16.37	e _g 16.14	a _{1g} 15.39	e _g , a _{1g} 10.7
Ethylene	σ 15.79	π 14.62	π 15.05	π 10.5
Acetylene	π 17.54	π 16.01	π 15.73	π 11.4

^a $V_{AB} = Z_B(S|1/r_B|S)$.

Ionization potentials by Koopmans' theorem also do not differ greatly, although orbital structure is changed somewhat. These results are summarized in Table VI.

Conclusions

The nature of the CNDO approximations and the similarity of CNDO to the Mulliken method lead us to believe that Mulliken methods should be given serious consideration as alternatives to the CNDO/2 method. While the nature of the results does not point to a large

improvement in predictive power by the Mulliken method as we have depicted it, it is probable that with reparametrization this should be possible. Many of the smaller terms neglected by the CNDO method are included in the Mulliken method although in an approximate way, so one does expect the Mulliken method should be somewhat more accurate.

If ZDO methods are to be used, it seems necessary to use parameters expressly derived for them, although some of the parameter sets now in use for CNDO methods might, in fact, turn out to be circumventions of the CNDO deficiencies rather than true ZDO parameters.

All of the terms which are included in the NDDO method but not included in CNDO are also not included in the Mulliken method.^{2a} This implies that it should be possible to include these terms within a Mulliken framework and hence improve on simple Mulliken results.

Palladium(II)-Catalyzed Exchange and Isomerization Reactions.

I. The Exchange of Enol Acetates with Acetic Acid Catalyzed by Palladium(II) Chloride¹

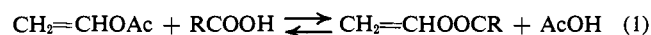
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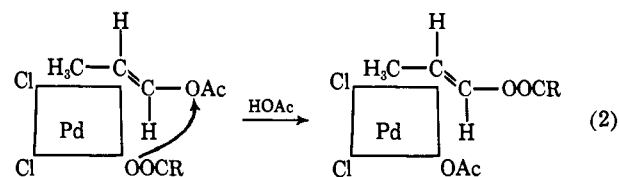
Abstract: The main Pd(II)-catalyzed exchange of $\text{CH}_2=\text{CHOCCD}_3$ with CH_3COOH was found to obey the following rate expression: $-\text{d}[\text{C}_2\text{H}_3\text{OCCD}_3]/\text{d}t = ([\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{C}_2\text{H}_3\text{OCCD}_3]/[\text{LiCl}])(k_1 + k_2[\text{LiOAc}])$. There may be a small contribution from a reaction with a higher LiCl inhibition. A study of the rates of isomerization and vinyl ester exchange of *cis*- and *trans*-1-acetoxy-1-propene showed that exchange occurs only with isomerization. The kinetics and stereochemical results are consistent with an oxypalladation-deoxypalladation mechanism for exchange: $\text{C}_2\text{H}_3\text{OCCD}_3 + \text{PdOOCCH}_3 \rightarrow \text{PdCH}_2\text{CH}(\text{OCCD}_3)(\text{OOCCH}_3) \rightarrow \text{PdOCCD}_3 + \text{C}_2\text{H}_3\text{OOCCH}_3$. This mechanism predicts that cyclic enol acetates should not exchange. It was found that 1-acetoxy-1-cyclopentene in fact did not exchange. Substitution on vinyl carbon strongly inhibits exchange. The relative rates for vinyl acetate, *trans*-1-acetoxy-1-propene isopropenyl acetate, and *cis*-2-acetoxy-2-butene are $1:2.5 \times 10^{-2}:3.3 \times 10^{-3}:1.6 \times 10^{-6}$.

Most Pd(II) reactions with organic substrates are oxidative in nature, resulting in reduction of Pd(II) to Pd(0) and giving oxidized organic products.² However, there are some Pd(II) reactions, in which the oxidation state of the Pd(II) remains unchanged, which are thus truly catalytic. Kinetic studies of these nonoxidative reactions are not complicated by side effects of precipitated palladium metal or of oxidants added to reoxidize the Pd(0) to Pd(II). Thus, mechanistic studies of these reactions offer a good method of elucidating some aspects the mode of Pd(II) reaction with organic substrates. One class of these nonoxidative reactions is the Pd(II)-catalyzed exchange reactions of which the vinyl ester exchange is an example.³

For instance, vinyl acetate, in the presence of Pd(II), exchanges with acids to make other vinyl esters.



The two mechanisms proposed for vinyl ester exchange are (a) an $\text{S}_{\text{N}}2$ attack of acetate on a Pd(II)-vinyl acetate π complex (eq 2), a mechanism suggested for other Pd(II)-catalyzed exchanges,⁴ and (b) an oxypalladation-deoxypalladation mechanism⁵ (eq 3,



(1) (a) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., Apr 1969; *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), B15 (1969); (b) Address correspondence to author at 419 Nicholas Ave., Wilmington, Del. 19803.

(2) E. W. Stern, *Catal. Rev.*, **1**, 73 (1967).

(3) J. Smidt, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **1**, 80 (1962).

(4) C. F. Kohll and R. Van Helden, *Recl. Trav. Chim. Pays-Bas*, **87**, 481 (1968).

(5) H. C. Volger, *ibid.*, **87**, 501 (1968).

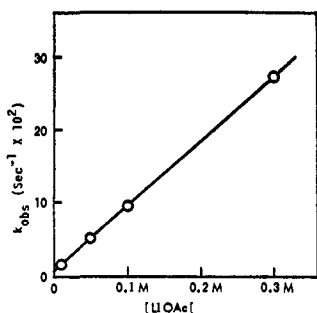
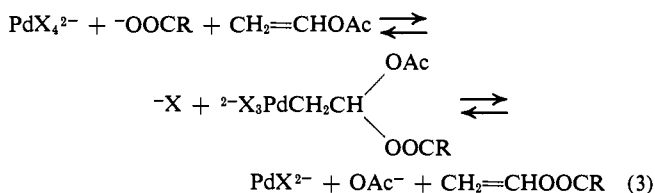
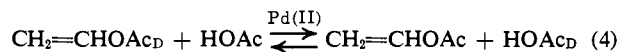


Figure 1. Effect of $[\text{LiOAc}]$ on rate of exchange: $[\text{Pd(II)}]_t = 0.0176 \text{ M}$; $[\text{Cl}]_t = 0.212 \text{ M}$.

$\text{X} = \text{Cl}^-$, OAc^- , or PdCl_3^-). The latter has considerable analogy in mechanisms suggested for other Pd(II) -



catalyzed reactions⁶⁻¹¹ as well as Hg(II) -catalyzed exchanges.¹² To simplify the kinetic and stereochemical studies, the exchange of deuterated acetate between ester and acetic acid was studied. Thus, in the case of exchange of deuterated vinyl acetate with nondeuterated acetic acid the reaction would be ($\text{OAc}_D = \text{CD}_3\text{COO}$).



To our knowledge, no other kinetic study of the exchange has been reported. However, other workers, on the basis of very interesting nonkinetic studies,¹³ have come to mechanistic conclusions similar to those we reported earlier.¹

Results

Kinetics of Transesterification of Vinyl Acetate. The rate of exchange of deuterated vinyl acetate with nondeuterated acetic acid was followed by mass spectrometric analysis of the vinyl acetate. As expected for an isotopic exchange reaction (see Experimental Section), plotting the data as a first-order reaction in deuterated vinyl acetate gave straight lines. Such first-order plots would be obtained no matter what the order in vinyl acetate. If the reaction is first order in vinyl acetate, the experimental rate constant for one set of reaction conditions should not vary as the vinyl acetate concentration varies. As shown in Table I, over a range of vinyl acetate concentrations of 0.01–0.5 M the rate does not change. Thus the reaction is clearly first order in deuterated vinyl acetate. The

(6) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **153**, 140 (1963).

(7) I. I. Moiseev and M. N. Vargaftik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 759 (1965).

(8) W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **88**, 2054 (1966).

(9) P. M. Henry, *ibid.*, **86**, 3246 (1964).

(10) P. M. Henry, *J. Org. Chem.*, **32**, 2575 (1967).

(11) R. Jira, J. Sedlmeier, and J. Smidt, *Justus Liebigs Ann. Chem.*, **693**, 99 (1966).

(12) H. Hopff and M. A. Osman, *Tetrahedron*, **24**, 2205 (1968).

(13) A. Sabel, J. Smidt, R. Jira, and H. Prigge, *Chem. Ber.*, **102**, 2939 (1969).

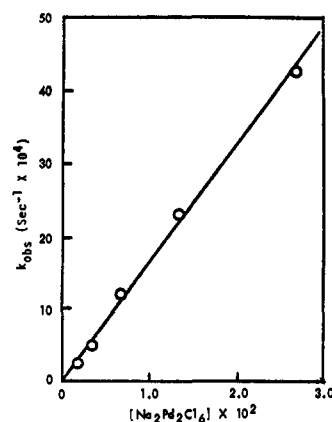


Figure 2. Effect of $[\text{Na}_2\text{Pd}_2\text{Cl}_6]$ on rate of exchange (NaCl saturated).

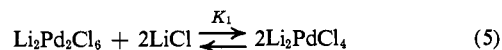
order in lithium acetate was determined by carrying out several runs at constant $[\text{Pd(II)}]_t$ and $[\text{Cl}]_t$, but with varying $[\text{LiOAc}]$. The results, plotted in Figure 1, indicate the reaction to be first order in lithium acetate. The plot has a positive intercept, indicating a reaction path independent of $[\text{LiOAc}]$ as well as a reaction first order in $[\text{LiOAc}]$.

Table I. Effect of $[\text{CD}_3\text{COOC}_2\text{H}_5]$ on the Experimental Rate Constant^a

[VA]	k , $\text{sec}^{-1} \times 10^5$
0.01	12.7
0.2	11.3
0.5	12.2

^a $[\text{Pd(II)}]_t = 0.02 \text{ M}$; $[\text{Cl}]_t = 0.26 \text{ M}$; $[\text{LiOAc}] = 0.1 \text{ M}$.

To determine the reactive Pd(II) species and the order in this species as well as the order in $[\text{LiCl}]$, a knowledge of the equilibria involving Pd(II) and LiCl in acetic acid is required. A recent spectral and molecular weight study¹⁴ of this system indicated that the following two equilibria must be considered.



K_1 was found to have a value of 0.1 M^{-1} and K_D a value of 2.6 M^{-1} . The equilibria represented by eq 5 and 6 make the determination of the active Pd(II) species as well as the orders in active Pd(II) species and LiCl difficult. This problem was circumvented by studying the exchange at various $\text{Na}_2\text{Pd}_2\text{Cl}_6$ concentrations in saturated NaCl solutions in HOAc . It is known from molecular weight measurements that the Pd(II) species is almost entirely the dimer and the NaCl concentration is kept at a low but constant level (0.013 M).¹⁴ The results of these experiments are plotted in Figure 2. The reaction is clearly first order in total Pd(II) species ($[\text{Pd(II)}]_t$). This is strong evidence that the reaction is first order in dimer, for if the reaction were first order in Li_2PdCl_4 , the relationship would be one-half order in $[\text{Pd(II)}]_t$ as a consequence of eq 5.

(14) P. M. Henry and O. Marks, *Inorg. Chem.*, **10**, 373 (1971).

Table II. Dependence of Rate on Pd(II) Species^a

[Pd] _t	[Cl] _t	[Li ₂ Pd ₂ Cl ₆]	[Li ₂ PdCl ₄]	[LiCl]	[Li ₂ Cl ₂]	k_{obsd} , sec ⁻¹ × 10 ⁵	$\frac{k_{\text{obsd}}[\text{LiCl}]}{[\text{Li}_2\text{Pd}_2\text{Cl}_6]}$, sec ⁻¹ × 10 ³	$\frac{k_{\text{obsd}}[\text{LiCl}]}{[\text{Li}_2\text{PdCl}_4]}$, sec ⁻¹ × 10 ³	$\frac{k_{\text{obsd}}[\text{LiCl}]}{[\text{Pd(II)}]_t}$, sec ⁻¹ × 10 ⁴
0.0315	0.342	0.0133	0.00498	0.137	0.0529	18.3	1.88	5.03	7.95
0.0176	0.271	0.0072	0.00335	0.126	0.0446	10.3	1.83	3.87	7.38
0.01	0.233	0.00383	0.00234	0.120	0.0405	5.7	1.78	2.92	6.83
0.0045	0.218	0.0015	0.00148	0.121	0.0412	2.31	1.86	1.88	6.21
0.00225	0.2046	0.00065	0.00095	0.118	0.0394	1.03	1.87	1.28	5.4

^a [LiOAc] = 0.1 M.

Results to be presented later confirmed this first-order relationship in dimer.

The order in [LiCl] was now obtained by plots of $k_{\text{obsd}}[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ vs. $1/[\text{LiCl}]$. Values of $[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ and $[\text{LiCl}]$ were calculated from total Pd(II) concentration, $[\text{Pd(II)}]_t$, and total chloride concentration, $[\text{Cl}]_t$, using eq 5 and 6. Such a plot is shown in Figure 3. It is linear with zero intercept. This type of plot is indicative of a first-order [LiCl] inhibition.

Next the dependence of rate on dimer was checked in the LiCl system by measuring rates at various $[\text{Pd}]_t$. Typical results are shown in Table II. If the reaction is first order in dimer, the value of $k_{\text{obsd}}[\text{LiCl}]/[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ remains constant. It does remain quite constant, while values of $k_{\text{obsd}}[\text{LiCl}]/[\text{Pd(II)}]_t$ vary considerably. To a first approximation the rate is thus

$$\frac{d[\text{C}_2\text{H}_3\text{OOC CD}_3]}{dt} = \frac{[\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{C}_2\text{H}_3\text{OAc}_D]}{[\text{LiCl}]} \times (k_1 + k_2[\text{LiOAc}]) \quad (7)$$

Average values of k_1 and k_2 at various [LiCl] ranges are given in Table III. Values of $[\text{Li}_2\text{Cl}_2]$ are also given

Table III. Values of Rate Constants for Exchange at Various [LiCl]

[LiCl]	[Li ₂ Cl ₂]	k_1 , sec ⁻¹ × 10 ⁴	k_2 , M ⁻¹ sec ⁻¹ × 10 ²
0.05–0.06	0.007–0.01	2.6	1.74
0.07–0.08	0.017–0.018	2.2	1.66
0.1–0.13	0.04–0.055	2.0	1.51
0.19–0.21	0.10–0.12	2.2	1.33

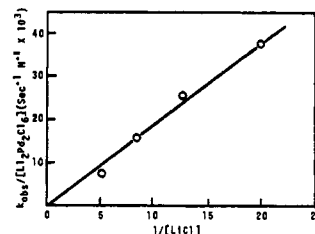
in Table III to indicate the extent of the correction for association. The values for k_1 are much less accurate than those for k_2 since they result from an extrapolation procedure. However, they remain reasonably constant, indicating the neutral reaction follows eq 7. At $[\text{LiOAc}] = 0.1$ the neutral reaction accounts for only 10% of the total rate.

Water has little effect on the transesterification rate at low $[\text{H}_2\text{O}]$. Addition of 0.5 M H_2O to the reaction mixture at 0.1 M LiCl did not change the rate within experimental error.

The strict first-order dependence on vinyl acetate and LiOAc would predict that there is little interaction between these substrates and the Pd(II) dimer under the reaction conditions. To check this point the effect of the addition of these substrates on the ultraviolet spectra of Pd(II) at various LiCl concentrations was investigated. There was no detectable change in

spectra at $[\text{LiOAc}] = 0.1$ M and $[\text{vinyl acetate}] = 0.2$ M.

Stereochemical Results. In order to determine the stereochemistry of the transesterification, samples of pure *cis*- or *trans*-1-acetoxy-1-propene were equilibrated by Pd(II) in acetic acid containing about 20%

Figure 3. Effect of [LiCl] on rate of exchange; $[\text{LiOAc}] = 0.1$ M.

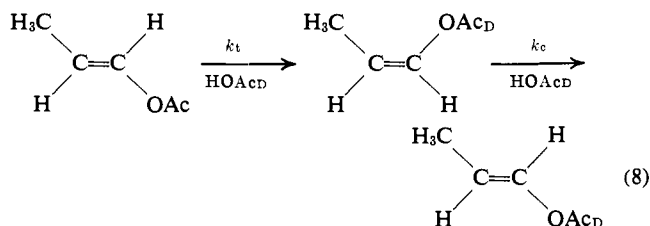
HOAc_D. The *cis* and *trans* isomers were analyzed for CD₃ content during the course of a run to see if isomerization occurs at the same rate as transesterification. Typical results are shown in Table IV for the isomer-

Table IV. Isomerization of *trans*-1-Acetoxypropene in Acetic Acid Containing 20% CD₃COOH^a

Time, sec	% cis ^b	% trans ^b	CD ₃ in cis, %	CD ₃ in trans, %	Calcd CD ₃ in trans ^c
2,580	19	90	20.3	0.34	0.16
7,820	42	58	19.65	0.58	0.48
10,310	46	54	20.1	1.52	1.70

^a $[\text{Pd(II)}]_t = 0.02$ M; $[\text{Cl}]_t = 0.075$ M; $[\text{LiOAc}] = 0.2$ M. ^b $k_t = 7.4 \times 10^{-5}$ sec⁻¹ and $k_c = 2.9 \times 10^{-5}$ sec⁻¹. ^c Calculated assuming that the label appears in the *trans* isomer from reisomerization of labeled *cis* isomer, using the values of k_c and k_t given in footnote b.

ization of *trans* to *cis*, where k_t and k_c are the rates of isomerization of *trans* to *cis* and *cis* to *trans*, respectively. The *cis* formed from the *trans* immediately has the same -CD₃ content as the solvent, showing that isomerization occurs with transesterification. The *trans* isomer also slowly picks up -CD₃, suggesting that transesterification can occur without isomerization. However, the -CD₃ could also arise from isomerization of the labeled *cis* originally formed to give labeled *trans* as shown by eq 8. The rates of appearance of



$-\text{CD}_3$ label from this sequence of steps can be calculated from the values of k_t and k_c and are given in the last column of the table. The agreement between calculated and observed values is good, indicating that the label results from reisomerization of the labeled *cis*. Thus, label appears only when isomerization occurs.¹⁵ Similar results were found for isomerization of the *cis* isomer in CD_3COOH . It should be mentioned that this result was obtained only at $[\text{LiOAc}] = 0.2$ or higher. At lower values of $[\text{LiOAc}]$ the isomerized material contained *less* than the CD_3 content of the solvent. This resulted from isomerization without exchange.¹⁶ This last reaction is independent of $[\text{LiOAc}]$ so is not important at higher values of $[\text{LiOAc}]$. However, the exchange reaction, the reaction of present interest, follows the rate expression of eq 7 and gives isomerization every time there is exchange.

Discussion

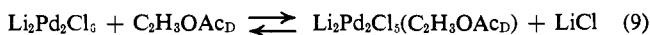
The results indicate that the rate equation for the main exchange reaction for $[\text{LiCl}]_t = 0.05\text{--}0.4$ is eq 7. However, gradual decrease in k_2 in going from 0.05 to 0.2 *M* $[\text{LiCl}]$ (0.4 *M* $[\text{LiCl}]_t$) suggests that some other process is taking place. There are several possible explanations for this observation. First, errors in K_D and K_1 of eq 5 and 6 could cause this drift in a system as complicated as this. Thus at $[\text{LiCl}]_t = 0.4$, $[\text{LiCl}]$ is only 0.2 so the correction for association is a factor of 2. However, a change of the value of K_D from 2.6 to about 0.4 M^{-1} would be necessary to eliminate the downward drift.

Secondly, there may be a small $1/[\text{LiCl}]^2$ term in the rate expression. Studies at lower $[\text{LiCl}]$ would be necessary to confirm this. However, at $[\text{LiCl}]$ below 0.05 the value of $[\text{LiCl}]$ becomes the difference between two large numbers and difficult to determine accurately. A further complication is the fact that at low $[\text{LiCl}]$ the value of k_2 actually decreases below the value at higher $[\text{LiCl}]$.¹⁷

Finally, there could be a very reactive species formed at about 0.02 *M*. This species was not present in large enough amounts to be detected by the ultraviolet spectra study.¹⁴

The nature of this second reaction is being studied in other exchange systems more amenable to study. In the following discussion only the reaction whose rate expression is given by eq 7 will be considered.

The rate expression is consistent with the initial step being replacement of one chloride of the dimer by vinyl acetate to make a π complex²⁰ (eq 9), but is inconsistent



(15) Similar qualitative results have been reported.¹³ However, without kinetic studies it could not be demonstrated that isomerization occurs *every* time there is exchange.

(16) This reaction is currently under investigation using propionate enol esters.

(17) The decrease in k_2 at low $[\text{LiCl}]$ probably results in polymerization of the dimer to give less reactive species. Similar effects have been noted in aqueous solution.^{18,19}

(18) R. Jira, J. Sedlmeier, and J. Smidt, *Justus Liebig's Ann. Chem.*, **693**, 99 (1966).

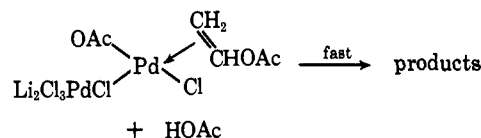
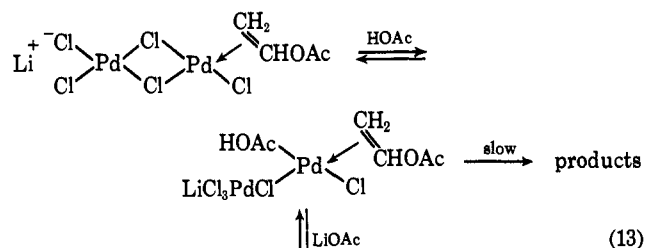
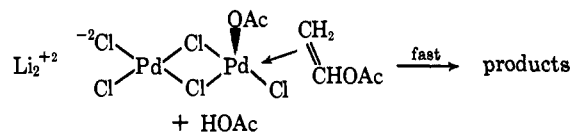
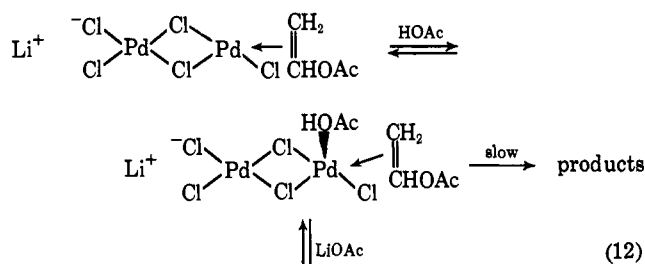
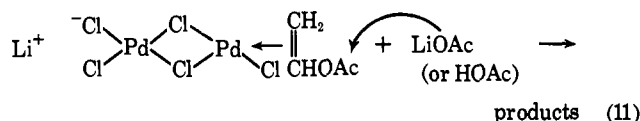
(19) P. M. Henry, *J. Amer. Chem. Soc.*, **88**, 1595 (1966).

(20) It is possible that the first step is the complexing of acetic acid. However, it seems much more reasonable to write olefin complexing first, since it was shown⁹ that olefin complexing occurs first in the Wacker reaction. Also, the kinetics do not require that the second reagent be complexed and it is generally agreed that olefin complexing by Pd(II) is required in Pd(II)-catalyzed olefin reactions.

with splitting of the dimer bridges with two vinyl acetates to form two monomer π complexes (eq 10). The latter would require a square-root dependence on dimer concentration.



The next step in the reaction sequence is somewhat uncertain. The lack of a second chloride dependence indicates that acetic acid or acetate is not displacing a second chloride. It is possible that acetic acid or acetate is (1) attacking without coordinating (eq 11), (2) coordinating at a fifth coordination position on the Pd(II) (eq 12), or (3) breaking one of the dimer bridges to coordinate (eq 13).



There is no compelling argument for any one of the three possibilities. Only in the Wacker reaction is there evidence⁹ that the nucleophiles must coordinate prior to attack, and five-coordinate Pd(II) complexes are known.²¹ Furthermore, *trans* addition of amines to Pt(II)-coordinated olefins has recently been reported.²²

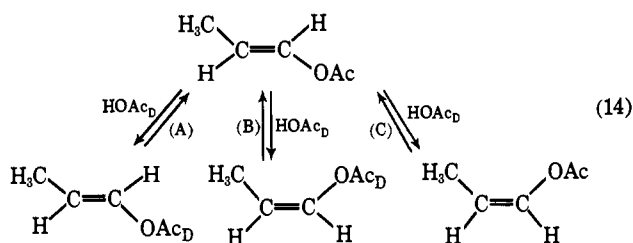
The kinetic results above do not distinguish between the two mechanisms mentioned in the introduction, *i.e.*, (1) $\text{S}_\text{N}2$ attack of complexed acetate on complexed vinyl acetate without rupture of the double bond and

(21) T. L. Blundell and H. M. Powell, *J. Chem. Soc. A*, 1650 (1967).

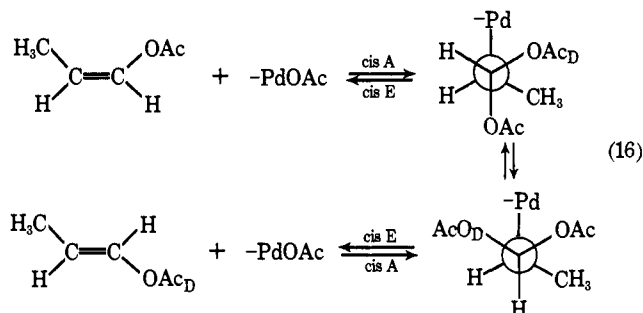
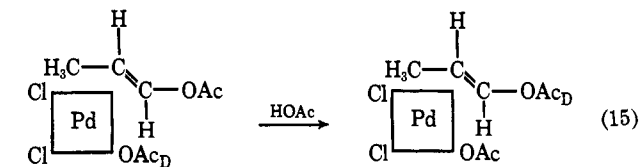
(22) A. Panunzi, A. De Renzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **92**, 3488 (1970).

(2) oxypalladation–deoxypalladation. The stereochemical results with *cis*- and *trans*-1-acetoxy-1-propene, however, support the second mechanism.

The various possibilities for isomerization and exchange of the *trans* isomer are shown in eq 14. Of the

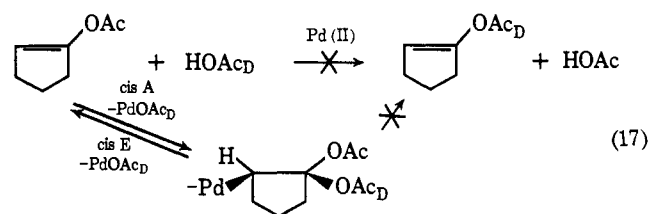


three possibilities, only path **B** actually occurs. A simple S_N2 attack, analogous to those proposed for uncomplexed olefins, as depicted by eq 15, will give exchange with retention of configuration,²³ or path **A** in eq 14.



This is contrary to the result that path **B** only occurs. However, path **B** is entirely consistent with the oxypalladation–deoxypalladation mechanism as shown by eq 16 (**A** = addition, **E** = elimination). Thus, if the addition is stereochemically specific, according to the principle of microscopic reversibility, the elimination must also be specific and have the same stereochemistry as addition. This requires that exchange occur when, and only when, isomerization occurs. This is the observed result. *Cis* addition was used for purposes of illustration and its use is not meant to imply any evidence for either *cis* or *trans* addition. If *trans* addition had been used, the final result would have been the same.

To determine if S_N2 attack, or nonstereospecific addition, occurs to *any* extent, the exchange of the enol acetate of cyclopentanone was studied. As eq 17



(23) For the substitution reaction on vinylic carbon bonds postulated to proceed *via* S_N2 attack, the stereochemical result is retention of configuration. See, for instance, (a) A. M. Aguir and T. G. Archibald, *J. Org. Chem.*, **32**, 2627 (1967); (b) G. Marchese, F. Naso, and G. Modena, *J. Chem. Soc. B*, 958 (1968).

illustrates, this enol acetate cannot exchange if addition–elimination is stereospecific. Its exchange rate is in fact too slow for measurement. However, there is the possibility that the reason this enol acetate does not exchange is steric hindrance which prevents addition. For this reason, the exchange of *cis*-2-acetoxy-2-butene was studied as a model for 1-acetoxy-1-cyclopentene. Certainly the effect of structure on rate as listed in Table V does indicate considerable steric hindrance to

Table V. Rates of Exchange of Various Enol Acetates at 25° in the Na_2PdCl_6 System^a

Enol acetate	$k_2, M^{-1} \text{sec}^{-1}$
$\text{CH}_2=\text{CHOAc}$	2.0×10^{-2}
<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHOAc}$	5.0×10^{-4}
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{OAc}$	6.7×10^{-5}
<i>cis</i> - $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{OAc}^b$	3.2×10^{-8}
<i>c</i> - $\text{C}_3\text{H}_7-1-\text{OAc}^c$	$< 10^{-9}$

^a Saturated with NaCl; k_2 calculated assuming $[\text{NaCl}] = 0.013$. For all but last two enol acetates, $[\text{LiOAc}] = 0.1 M$. Values of k_1 were not determined but were assumed to be one-tenth of k_2 at this $[\text{LiOAc}]$. ^b Run at 1.5 M $[\text{LiOAc}]$. ^c Run at 1.0 M $[\text{LiOAc}]$.

addition. This result is qualitatively the same as for the Wacker¹⁹ reaction, but, quantitatively, it is much larger for exchange. This result is reasonable since the enol acetate has acetates in addition to the methyl groups and the adding OAc would have a larger steric requirement than OH. In any case, 1-acetoxy-1-cyclopentene exchanges at a rate which is considerably slower than *cis*-2-acetoxy-2-butene, indicating no appreciable S_N2 attack or nonstereospecific addition.

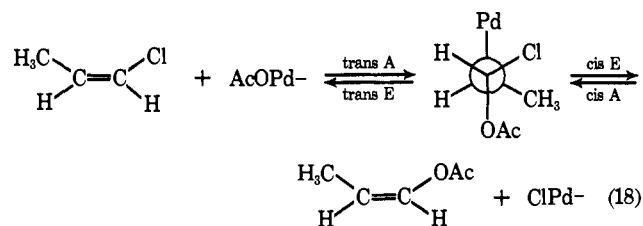
One basis for distinguishing among eq 11–13 might be stereochemistry of the acetoxy-palladation. Thus, attack from outside the coordination sphere would be expected to give *trans* addition, while attack from the coordination sphere would most likely give *cis* addition.²⁴ As mentioned above, simultaneous exchange and isomerization experiments cannot distinguish between *cis* and *trans* addition. However, they can detect differences between various nucleophiles. Thus, in preliminary reports^{13,25} it was disclosed that *trans*-1-chloro-1-propene gave *trans*-1-acetoxy-1-propene. In another attempt to determine the stereochemistry, Volger⁵ found that *cis*-2-deuteriovinyl chloride gave a 50–50 mixture of *cis*- and *trans*-2-deuteriovinyl acetate. The last result can readily be explained by the present work, since under the conditions of Volger's experiment, isomerization of the initially formed deuteriovinyl acetate isomer to the 50–50 mixture would occur very rapidly. On the basis of these kinetics and stereochemical results, Stern and Volger²⁶ proposed a very

(24) The author has recently published evidence that acetoxy-palladation is a *trans* process [see P. M. Henry and G. A. Ward, *J. Amer. Chem. Soc.*, **93**, 1494 (1971)]. Thus the author now believes that exchange proceeds by *trans* attack of acetate from outside the coordination sphere rather than the *cis* addition used for purposes of illustration in eq 16 and 17. This type of acetoxy-palladation is reasonable, since acetate is not complexed strongly to Pd(II) in solutions containing chloride. On the other hand, chloropalladation (and dechloropalladation, by the principle of microscopic reversibility) could very likely be a *cis* process, since chloride is much more strongly complexed to Pd(II) than acetate. This line of reasoning would explain the results for exchange of vinylic chlorides with acetate.^{13,25}

(25) Reference 2, p 125.

(26) For a discussion, see E. W. Stern and H. C. Volger, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (4), F4 (1969).

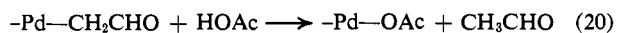
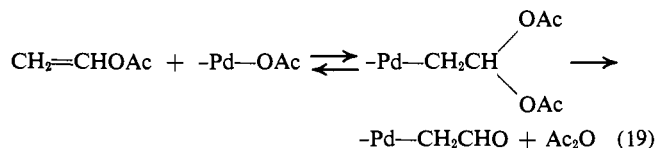
reasonable scheme for conversion of deuteriovinyl chloride involving acetoxypalladation-dechloropalladation in which the stereochemistry of the acetoxypalladation step is opposite to that for the dechloropalladation step (A = addition; E = elimination).



Of course, further work is required to prove that vinyl chlorides do not exchange with acetates by an $\text{S}_{\text{N}}2$ type mechanism (eq 2).

One result of this study worthy of note is that in forming the activated complex terminal chlorides are replaced by vinyl acetate (eq 9) rather than forming π complexes by bridge splitting (eq 10). This could mean bridge splitting does not readily occur²⁷ or if it does occur, the monomeric π complex formed is not reactive. Thus the monomeric π complex would have more negative charge concentrated on the Pd(II) complexed to the vinyl acetate. This negative charge could inhibit attack by acetate. It is possible Pd(II)-catalyzed reactions in which the π complex is formed by bridge splitting will be found. On the other hand, trans effects resulting from the structure may be important for further reaction.

Finally, a recent kinetic study²⁸ of the decomposition of vinyl acetate should be discussed in the light of the present results. These authors conclude that the reaction proceeds by a mechanism involving acetoxypalladation followed by decomposition of the intermediate to give a Pd(II)-substituted acetaldehyde which subsequently decomposes to acetaldehyde and Pd(II). This mechanism would be consistent with the present results if (1) the acetoxypalladation is postulated to be



reversible as shown in eq 19 and (2) the form of the kinetic expression for the two reactions is the same with different values for the rate constants.²⁹ The first requirement is easily met. Exchange is much faster than decomposition, so acetoxypalladation-deacetoxypalladation occurs many times before decomposition. However, the second requirement is not met. The forms of the rate expressions for the two reactions are different; decomposition is reported²⁸ to be zero order in vinyl acetate and actually inhibited by acetate. Thus, either the acetoxypalladation-deacetoxypalladation must not be operative for exchange, or the mechanism shown

(27) R. Ugo, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (4), F3 (1969).

(28) R. G. Schultz and P. R. Rony, *J. Catal.*, **16**, 133 (1970).

(29) Of course this statement is true only if no other external reagent is involved in the decomposition of the acetoxypalladation adduct. However, it seems unreasonable that an external reagent be required for the decomposition and none was postulated.²⁸

by eq 19 and 20 must not be operative for decomposition. The first alternative seems unlikely in view of the present results.³⁰ A comparative study of the two reactions by the present author¹ led to the second conclusion: decomposition does not occur *via* eq 19 and 20.

Experimental Section

Materials. Palladium chloride (Engelhard Industries) and purified anhydrous lithium acetate (City Chemical Corp.) were used without further purification. The acetic acid was dried by refluxing over $\text{B}(\text{OAc})_3$.³¹ The water content was less than 0.01%, as determined by Karl Fischer titration. The vinyl acetate (Matheson Coleman and Bell) was distilled before use. The lithium and sodium chlorides were of reagent grade.

The Pd(II) stock solutions were prepared by heating PdCl_2 and LiCl or NaCl in a ratio of 1:1 in acetic acid. They were analyzed by standard procedures. Since LiCl is very soluble in acetic acid, the $\text{Li}_2\text{Pd}_2\text{Cl}_6$ contained excess LiCl. However, the $\text{Na}_2\text{Pd}_2\text{Cl}_6$ solutions contained very close to one NaCl per PdCl_2 .

Vinyl acetate containing about 40 mol % $\text{CH}_2=\text{CHOCCD}_3$ was prepared by equilibrating unlabeled vinyl acetate with $\text{CD}_3\text{-COOD}$ (99.5%; Brinkmann Instruments, Inc.) using $\text{Hg}(\text{OAc})_2\text{-H}_2\text{SO}_4$ ¹² as catalyst. In a typical run, 25 ml of vinyl acetate, 10 ml of CD_3COOD , 0.2 g of $\text{Hg}(\text{OAc})_2$, and 0.025 ml of concentrated H_2SO_4 were mixed and allowed to stand for 2 days at room temperature. Then, 0.1 g of sodium acetate was added and the reaction mixture was distilled to recover the vinyl acetate.

The mixture of *cis*- and *trans*-1-acetoxy-1-propene was prepared by treating propionaldehyde with acetic anhydride.³² Samples of the pure isomers were then obtained by preparative vapor phase chromatography (vpc). The configuration was determined by nmr.³³

The enol acetates of 2-butanone were prepared by treating 2-butanone with isopropenyl acetate using sulfuric acid as catalyst.³⁴ Vpc analysis (20-ft 20% Carbowax 20 M on ABS (70-80 mesh) at 150°, flow rate 60 ml/min) gave two peaks. Both peaks were collected. Nmr analysis indicated that the first peak contained 2-acetoxy-1-butene and *trans*-2-acetoxy-2-butene in a 1:2 ratio. The second peak was pure *cis*-2-acetoxy-2-butene. Only the pure *cis* isomer was used for the kinetic runs.

The enol acetate of cyclopentanone was prepared by treating cyclopentanone with isopropenyl acetate using *p*-toluenesulfonic acid as catalyst.³⁵

Kinetic Runs. The great majority of the kinetic runs were made with vinyl acetate. The reaction mixture was prepared containing all ingredients except vinyl acetate, thermostated at 25°, and started by adding the deuterated vinyl acetate. Samples (usually 0.05 ml) were injected into a gas chromatograph, and the vinyl acetate peak was collected in a 100% collection tube. A 6-ft 20% Carbowax 20 M on ABS (70-80 mesh) column at 80° was used. The flow rate was 60 ml/min. The 100% collection tube was a U tube with vacuum stopcocks at either end. The volume of the tube was about 80 ml. Since the peak width was less than 1 min and the flow rate was 60 ml/min, the tube could hold the entire peak. After collecting the peak, the stopcocks were closed. The tube was placed in liquid nitrogen to freeze out the vinyl acetate. The tube was then warmed to room temperature and attached to a mass spectrometer; one stopcock was opened to draw in the sample for analysis. The reproducibility of the analysis was about 0.1% of the total $-\text{CD}_3$ content measured.

Runs were usually made on a 5- or 10-ml scale usually using a vinyl acetate concentration of 0.2 M. However, to determine the order in vinyl acetate, runs with vinyl acetate concentrations of between 0.01 and 0.5 M were made. The rate expression for the isotope exchange is given by³⁶

(30) Schultz and Rony²⁸ apparently agree that the acetoxypalladation-deoxypalladation mechanism is correct for exchange.

(31) W. C. Eichelberger and V. K. LaMer, *J. Amer. Chem. Soc.*, **55**, 3633 (1933).

(32) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).

(33) M. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963).

(34) H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

(35) L. Goodman, A. Benitez, C. D. Anderson, and B. R. Baker, *J. Amer. Chem. Soc.*, **80**, 6582 (1958).

(36) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 192.

$$\ln \frac{D_{\infty}}{D_{\infty} - D} = \frac{R}{([VA][HOAc])} ([VA] + [HOAc])_t \quad (21)$$

where D_{∞} is the equilibrium per cent deuteration and D is the per cent deuteration of the vinyl acetate at time t . Since $[HOAc] \gg [VA]$ this reduces to eq 22. R is the rate expression in vinyl

$$\ln D_{\infty}/(D_{\infty} - D) = (R/[VA])t \quad (22)$$

acetate, *i.e.*, $R = k[VA]$ for a reaction first order in $[VA]$ or $R = k$ for a reaction zero order in vinyl acetate. From any given run, the order in vinyl acetate cannot be determined since a first-order plot will be obtained no matter what the form of the function R . Thus, the order in vinyl acetate can be determined by carrying out kinetic runs at various vinyl acetate concentrations and observing how $R/[VA]$ varies. If $R = k[VA]$, the vinyl acetate concentrations cancel out and $R = k$. Thus, the rate should not change with $[VA]$.

In the runs containing water some H_2O -catalyzed decomposition of the vinyl acetate was observed.²⁸ However, the rate of decomposition was only about 10% of the rate of exchange. In any case it does not affect the measurement of the rate of exchange as long as the deuterated and nondeuterated vinyl acetates have equal probability of reacting with H_2O .

The runs with propenyl acetates and the *cis*-butenyl acetate were carried out in the same way except in this case the acetic acid was deuterated initially (20% CD_3COOH) and each of the starting isomers as well as the isomer being formed were collected for analysis. These runs were made on a 1- or 2-ml scale because of the smaller amounts of starting materials available. The vpc procedures were the same as those used to collect the samples. The deuterium pick-up of the starting isomer was calculated from the rate expressions for consecutive reactions.³⁷

The enol acetate of cyclopentanone was not volatile enough to use the 100% collection tubes, so 0.4–1.0-ml portions of a 10- or 25-ml reaction mixture were extracted with methylene chloride,

after which the methylene chloride was washed with water to remove acetic acid. The sample was concentrated and the enol acetate collected by means of preparative vpc using the 20-ft 20% Carbowax 20 M column at 150°.

The determination of the upper limit for the exchange rate constant was complicated by two factors. First was the Pd(II)-catalyzed decomposition^{1,28} of the cyclopentene enol acetate to cyclopentanone and acetic anhydride. For this reason the exchange could only be followed for 2 months, since after this time most of the ester had decomposed. Other reactions occurred as evidenced by the formation of a peak with retention time close to that of the enol acetate. This material was never more than 5% of the amount of the enol acetate and not enough could be collected for identification. However, it was sufficiently separated from the enol acetate so it did not interfere with the deuterium analysis of the enol acetate. A second complication was the formation of an *m/e* peak at 129, which is the same as the parent peak for the trideuterio enol acetate. However, the peak grew quickly, to correspond to about 4% exchange, but did not continue to grow after that time so it could not be due to exchange of the enol acetate. This initial exchange is believed to result from exchange of an allylic acetate impurity. It was present in too small a quantity to be detected by proton magnetic resonance but it was shown that the allylic ester had the same retention time as the enol ester.

The upper limit for the rate constant was calculated so that after the initial exchange 1% further exchange could be detected³⁸ in the 2 months of the run.

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(37) Reference 35, p 166.

(38) Reproducibility was $\pm 0.3\%$ on duplicate analyses.

Tetraphenylethylene. Infrared and Nuclear Magnetic Resonance Evidence on the Nature of the Dianion

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Abstract: The ir aryl skeletal vibrations (1600-cm^{-1} region) and the nmr spectrum of tetraphenylethylene dianion (TPE^{2-}) have been recorded. Evidence points to the conclusion that the antibonding electrons of the dianion are highly delocalized and that the π -bonding electrons of TPE^{2-} essentially retain their bonding power, requiring the dianion to assume a nearly planar configuration.

The consequence of a one-electron reduction of ethylene is the lessening of the π -bond order by one-half since the "extra" electron is relegated solely to the lowest antibonding orbital. Unrestricted rotation about the C_1 - C_2 bond is presumably not possible. The effect of a second added electron is to release most of the rotational restraint between the C_1 - C_2 bond, since the π -bond order is then essentially zero.

When this electron pair is highly delocalized, as in tetraphenylethylene dianion (TPE^{2-}), the question of the nature of the resultant molecular species becomes one of considerable interest. This paper is concerned with the application of several spectroscopic investiga-

tions toward greater comprehension of the nature of this species.

First, the electron distribution of the anion radical $TPE^{\cdot-}$ should be instructive. A rough calculation of spin density distribution may be made for $TPE^{\cdot-}$ using the data of Cserhegyi, *et al.*,¹ and adopting the McConnell approximation of $a_H = Q_{C-H}\rho$.² Employing ortho, meta, and para hyperfine splitting parameters of 1.52, 0.38, and 2.28 and a Q value of -24.3 G,³ the

(1) A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 1892 (1969).

(2) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(3) All three epr splittings have been given positive signs, in keeping with observations that upfield nmr shifts of anion radicals correspond to