Base Stability of 15a.—A solution of 50 mg of **15a** and 1 equiv of sodium methoxide in 3 ml of anhydrous methanol was stirred at room temperature for 17 hr. The reaction solution was then poured into water, neutralized, and extracted three times with 10-ml portions of chloroform. The organic layer was dried over sodium sulfate and concentrated *in vacuo* to yield a solid. The nmr of the solid was identical with that of **15a** before reaction.

Heating the same sample of **15a** under the above conditions at 55° for 20 hr showed no change in its nmr. Recrystallizing the resulting solid from pentane gave 15 mg, mp 74–76°. Vpc (column F) showed only **15a**.

At room temperature, treatment of **15a** with sodium methoxide in methanol-*O*-*d* resulted in the exchange of all six H's α to the carbonyl groups as determined by nmr.

Wolff–Kishner Reduction of 15a.—A solution of 103 mg (0.468 mmol) of dione **15a** and 4 ml of 99% hydrazine hydrate in 4 ml of diethylene glycol was refluxed for 2 hr. The excess hydrazine hydrate and water were distilled off and 0.4 g of sodium hydroxide was added. The temperature was then raised to 190° for 24 hr. The solution was cooled, poured into 100 ml of water, and extracted three times with 30-ml portions of pentane. After the organic phase was dried (Na_2SO_4), concentration *in vacuo* gave 80 mg of white, oily solid. Recrystallization from ethanol gave 40 mg of crystal, mp 64–65°, nmr δ 0.9–2.3. Preparative vpc gave an analytical sample, mp 64–65°.

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.20; H, 12.80.

Registry No.—**1b**, 3045-92-9; **2**, 34737-28-5; **4a**, 34737-29-6; **4b**, 34737-30-9; **4c**, 34737-31-0; **4d**, 34737-32-1; **5**, 34737-33-2; **6**, 34737-34-3; **6** 2,4-DNPH, 34737-35-4; **6** semicarbazone, 34737-36-5; **9**, 7153-14-2; **9** 2,4-DNPH, 34737-38-7; **10**, 34737-39-8; **10** 2,4-DNPH, 34737-40-1; **11a**, 34737-41-2; **11b**, 34737-42-3; **11c**, 34737-43-4; **11d**, 34739-96-3; **12a**, 34737-44-5; **12b**, 34737-45-6; **12b** *p*-nitrobenzoate, 34737-46-7; **13b**, 34737-47-8; **13c**, 34737-48-9; **14**, 34737-49-0; **15a**, 34737-50-3; **15b**, 34737-51-4; 2-chloro-2-butylcyclohexanone, 34737-52-5; 3-methoxy-2,2,7,7-tetradeuteriocycloheptanone, 34737-53-6.

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Palladium(II)-Catalyzed Exchange and Isomerization Reactions. IV. The Exchange of Vinylic Chloride with Radioactive Lithium Chloride Catalyzed by Palladium(II) Chloride in Acetic Acid[1]

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In its simplest form the rate expression for exchange is rate = $k[Li_2Pd_2Cl_6]$[vinyl chloride]. By analogy with the kinetics of other Pd(II)-catalyzed exchanges a more meaningful form of the rate expression is believed to be rate = k $[Li_2Pd_2Cl_6]$[vinyl chloride][LiCl]/[LiCl]. This rate expression is consistent with a rapid preequilibrium to give a π complex followed by attack of chloride in the rate-determining step. Stereochemical results with *cis*- and *trans*-1-chloropropene were inconclusive because of a side reaction involving cis–trans isomerization without exchange. The mechanism most consistent with all the facts involves chloropalladation to give a σ-bonded Pd(II) intermediate. Dechloropalladation of this intermediate completes exchange. The fact that 1-chlorocyclopentene exchanges indicates that chloropalladation is not stereospecific. However, independent evidence suggests that cis chloropalladation using chloride from the coordination sphere of Pd(II) is more important than trans chloropalladation from outside the coordination sphere. Methyl substitution on the double bond retards chloride exchange but not as much as substitution retards acetate exchange of vinyl acetates. The difference is believed to be due to greater steric hindrance in trans acetoxypalladation than in cis chloropalladation.

The previous papers of this series have dealt with Pd(II)-catalyzed exchange and isomerization reactions of vinyl and allylic esters. The exchange reaction is shown in eq 1 using vinyl and allyl propionate as examples. This paper will be the first in the series to consider the reactions of another type of unsaturated substrate, namely vinylic chlorides. The reaction studied will be chloride exchange with radioactive chloride.

$$\begin{matrix}CH_2{=}CHOOCC_2H_5\\CH_2{=}CHCH_2OOCC_2H_5\end{matrix} + OAc^- \xrightarrow{Pd(II)} \begin{matrix}CH_2{=}CHOAc\\CH_2{=}CHCH_2OAc\end{matrix} + {}^-OOCC_2H_5 \quad (1)$$

The previous studies showed that these Pd(II)-catalyzed vinylic[3] and allylic[4] ester exchanges with acetate have the rate expression shown in eq 2 where k' is the rate constant for an acetate independent reaction

$$\text{rate} = \frac{[Li_2Pd_2Cl_6][\text{olefin}]}{[LiCl]}(k' + k''[LiOAc]) \quad (2)$$

and k'' the rate constant for a reaction first order in acetate.

The first step in both reactions is apparently π-complex formation between the Pd(II) dimer and the olefin portion of the unsaturated ester. This π-complex

$$Li_2Pd_2Cl_6 + >C{=}C< \underset{}{\overset{HOAc}{\rightleftharpoons}} LiPd_2Cl_5(>C{=}C<) + LiCl \quad (3)$$

formation accounts for the first-order terms in $[Li_2Pd_2Cl_6]$ and olefin, as well as the [LiCl] inhibition. The stereochemical evidence indicates that the next step in the exchange reactions almost certainly involves attack of solvent acetic acid or acetate ion to give an acetoxypalladation adduct which then undergoes deacyloxypalladation to give exchange. The allylic isomeriza-

(1) (a) Hercules Research Center Contribution No. 1563. (b) Paper III: P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 5200 (1972).

(2) Address correspondence to author at the Department of Chemistry, University of Guelph, Guelph, Ontario, Canada.

(3) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971).

(4) P. M. Henry, *ibid.*, **94**, 1527 (1972).

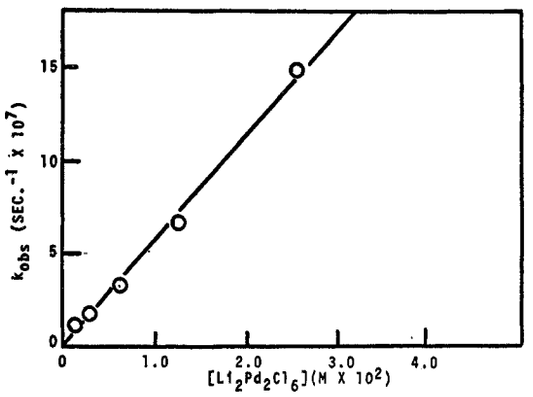


Figure 1.—Plot of k_{obsd} *vs.* $[Li_2Pd_2Cl_6]$. Vinyl chloride concentration is that of a saturated solution at 1 atm vinyl chloride or *ca.* 1.70 *M*.

tion reaction requires no external reagent after π-complex formation, since it involves internal attack of the ester group to give an acetoxonium ion type intermediate.

$$CH_2{=}CHOOCR + -\overset{|}{\underset{|}{Pd}}OAc \rightleftharpoons -PdCH_2CH(OOCR)(OAc) \rightleftharpoons -\overset{|}{\underset{|}{Pd}}OOCR + CH_2{=}CHOAc \quad (4)$$

$$CH_2{=}CHCH_2OOCR + -\overset{|}{\underset{|}{Pd}}OAc \rightleftharpoons AcOCH_2CH(-Pd-)CH_2OOCR \rightleftharpoons -\overset{|}{\underset{|}{Pd}}OOCR + AcOCH_2CH{=}CH_2 \quad (5)$$

The rate expression for exchange (eq 1) does not involve a second [LiCl] inhibition term, which would be expected if LiOAc were coordinating before attack.

$$Li_2Pd_2Cl_6(>C{=}C<) + LiOAc \overset{HOAc}{\rightleftharpoons} Li_2Pd_2Cl_4(OAc)(>C{=}C<) + LiCl \quad (6)$$

For that reason, plus other chemical evidence,[5] it is believed that LiOAc is attacking from outside the coordination sphere to give trans addition. Stereochemistry of exchange of vinyl chlorides with acetate indicates that acetoxypalladation and dechloropalladation have different stereochemistries.[6] This would suggest that dechloropalladation has cis stereochemistry. Chloropalladation, because of the principle of microscopic reversibility, would also have cis stereochemistry. This work was undertaken to determine the rate expression for chloride exchange and to interpret the rate expression in terms of stereochemical evidence.

Results

All runs were carried out at 25° in dry acetic acid containing various amounts of $PdCl_2$ and LiCl. The concentrations of the various species present under any given set of reaction conditions were calculated using

(5) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 1494 (1971).

(6) E. W. Stern, *Catal. Rev.*, **1**, 73 (1967) (see page 125); A. Sabel, J. Smidt, R. Jira, and H. Prigge, *Chem. Ber.*, **102**, 2939 (1969).

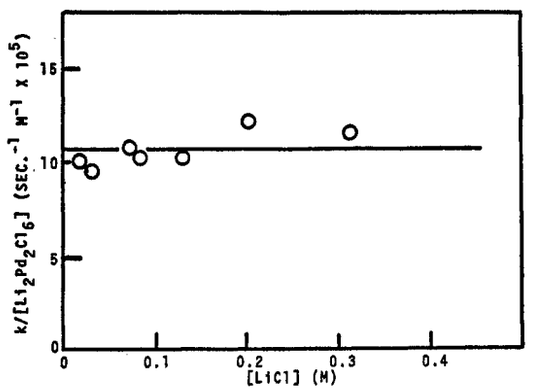


Figure 2.—Plot of $k/[Li_2Pd_2Cl_6]$ *vs.* [LiCl].

the previously determined[7] values of K_1 and K_D for the equilibria represented by eq 7 and 8. The value of K_1

$$Li_2Pd_2Cl_6 + 2LiCl \overset{K_1}{\rightleftharpoons} 2Li_2PdCl_4 \quad (7)$$

$$2LiCl \overset{K_D}{\rightleftharpoons} Li_2Cl_2 \quad (8)$$

is 0.1 M^{-1} and the value of K_D is 2.56 M^{-1} at 25°.

The exchange rates were measured using radioactive LiCl. A plot of k_{ex} *vs.* $[Li_2Pd_2Cl_6]$ at constant [LiCl] is shown in Figure 1. The straight line with zero intercept indicates a reaction first order in $[Li_2Pd_2Cl_6]$.

The plot of $k_{obsd}/[Li_2Pd_2Cl_6]$ *vs.* [LiCl], shown in Figure 2, is indicative of a reaction zero order in [LiCl]. LiOAc did not affect the kinetics. Rates were the same within experimental error for two runs, one of which was 1 *M* in LiOAc and one of which did not contain LiOAc.

The order in the vinylic chloride was determined using isopropenyl chloride (see Experimental Section for discussion of the kinetics of isotope exchange). As shown in Table I, the value of the experimental rate

TABLE I
EFFECT OF ISOPROPENYL CHLORIDE CONCENTRATION ON THE EXPERIMENTAL RATE CONSTANT[a]

Isopropenyl chloride, *M*	k, sec^{-1} × 10^6
0.2	6.6
1.0	6.6

[a] $[Pd(II)]_t$ = 0.060 *M*; $[Cl]_t$ = 0.22 *M*.

constant, assuming a reaction first order in vinylic chloride, does not change with concentration of the vinyl chloride, indicating a first-order reaction.

The rate expression for exchange in its simplest form is thus eq 9. To determine whether exchange occurred with isomerization, a sample of *trans*-propenyl chloride was isomerized in a solution containing radioactive LiCl. The activities of the *cis*- and *trans*-propenyl chlorides were determined at various times. Data are given in Table II. These results indicate that isomerization is much faster than exchange.[8]

$$\text{rate} = k[Li_2Pd_2Cl_6][\text{vinyl chloride}] \quad (9)$$

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

(8) This isomerization without exchange reaction, which was also detected in the vinyl ester exchange studies,[3] is apparently independent of the exchange reaction. A preliminary communication[9] on the isomerization reaction has appeared and it is the subject of two of the following papers in the series.

(9) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3547 (1971).

TABLE II

ISOMERIZATION OF *trans*-PROPENYL CHLORIDE IN A REACTION MIXTURE CONTAINING INORGANIC RADIOACTIVE CHLORIDE[a]

Time, hr	% cis[c]	Specific activity of propenyl chloride, specific activity of inorganic chloride[b] cis[d]	trans[d]
4:18	15.3	0.026[e]	
7:10	23.7	0.018[e]	0.008[e]
24:28	54.3	0.058	
31:04	59.0	0.044	0.026
54:53	67.1	0.046	0.046

[a] $[Pd(II)]_t = 0.01552\ M$; $[Cl]_t = 0.0524\ M$. [b] Specific activity of inorganic chloride is $1.5 \times 10^{-2}\ \mu$Ci/mmol. [c] Per cent cis at equilibrium is 74%. [d] If exchange occurred every time isomerization occurred the value of this ratio would be 1.0. [e] These values are less accurate than others because of small amounts of cis isomers present.

The rates of exchange of several substituted vinyl chlorides are given in Table III.

TABLE III

RATES OF EXCHANGE OF SEVERAL VINYLIC CHLORIDES AT 25° IN ACETIC ACID CATALYZED BY Pd(II)

Vinylic chloride	k, M^{-1} sec^{-1} × 10^5
Vinyl chloride	10
1-Chloro-1-propene[a]	0.23
2-Chloro-1-propene	0.21
2-Chloro-2-butene[a]	0.049
1-Chlorocyclopentene	0.056

[a] Mixtures of cis and trans isomers.

Discussion

The rate expression for exchange shown in eq 9 is surprising in that it does not contain a [LiCl] term in the denominator, present in all previous rate expressions. This term arises from the coordination of the olefin to Pd(II) *via* the equilibrium represented by eq 3. Thus, either the reaction also has a first-order term in [LiCl] to give a rate expression of the form of eq 10 or

$$\text{rate} = \frac{k[Li_2Pd_2Cl_6]\,[\text{vinyl chloride}]\,[LiCl]}{[LiCl]} \qquad (10)$$

else the reaction must proceed without π-complex formation between olefin and Pd(II).

The experimental facts of the present study which any reaction path must explain are as follows.

(1) 1-chlorocyclopentene exchanges at an appreciable rate.

(2) Methyl substitution on vinylic carbon (Table III) does not retard the rate of chloride exchange as much as it did acetate exchange.[3]

(3) Although the result is obscured by isomerization without exchange, in the exchange of *trans*-propenyl chloride with radioactive LiCl (Table II) the radioactivity originally accumulates in the *cis*-propenyl chloride.

Other related experimental facts, some of which have been mentioned in the introduction, are as follows.

(4) Acetoxypalladation is a trans process[5] proceeding by attack of acetate from outside the coordination sphere of Pd(II).[3]

(5) If the Pd(II)-catalyzed exchange of vinyl chlorides with acetate proceeds *via* an acetoxypalladation–dechloropalladation the stereochemical results require that dechloropalladation has mainly cis stereochemistry. Thus chloropalladation would also be expected to have cis stereochemistry.

(6) In the previous exchange studies[1b,3,4] as well as in olefin oxidation studies[10] the first step in the reaction is olefin complexing.

(7) Under the reaction conditions Pd(II) is much more strongly complexed to chloride than to acetate.[7]

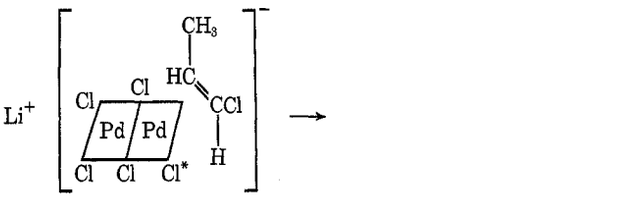
Finally, a kinetic study of the exchange of vinylic chlorides with acetate, to be reported in paper VI of this series,[11] revealed the following.

(8) The kinetic and stereochemical results are consistent with an acetoxypalladation–dechloropalladation route.

(9) Dechloropalladation is mainly cis but is not completely stereospecific.

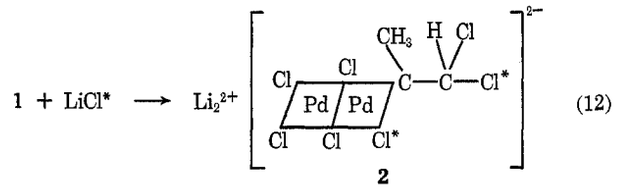
(10) Dechloropalladation requires that a vacant coordination sphere on Pd(II) be formed before it can be accomplished.

The author believes that the most plausible reaction path consistent with all the experimental facts consists of the *main* exchange route involving cis chloropalladation followed by dechloropalladation. The first step would be formation of π complex *via* an equilibria analogous to eq 3. Now, since dechloropalladation requires a vacant coordination site (see 10), the completion of the cis-chloropalladation step would be expected to require that the vacant coordination site being formed on Pd(II) by cis chloropalladation is filled by chloride from solution. The reaction scheme is thus given in eq 11–13.



(11)

1



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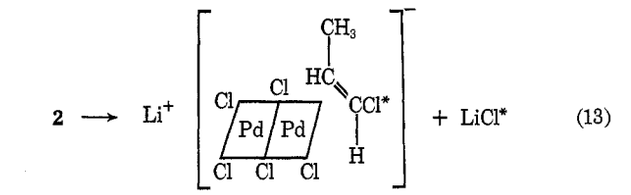
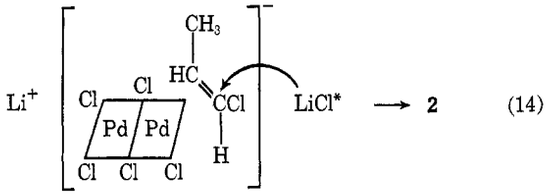


(13)

(10) P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964); **88**, 1595 (1966).
(11) P. M. Henry, *ibid.*, in press.

The second, less important route, would involve trans attack of chloride on the π complex (eq 14) anal-

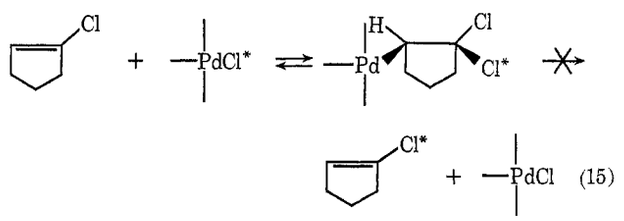


(14)

ogous to the manner in which acetate attacks the π complex in the acetate exchanges.[3,4] Exchange is then completed *via* eq 13. It is reasonable that this second route should occur to some extent, since chloride and acetate would behave in a similar fashion as nucleophiles. Thus if acetate gives trans attack chloride would be expected to also give some trans attack.

Both routes would have a first-order term in [LiCl] and a first-order inhibition term in [LiCl] because of π-complex formation *via* eq 3. Thus the rate expression for both routes would be eq 10.

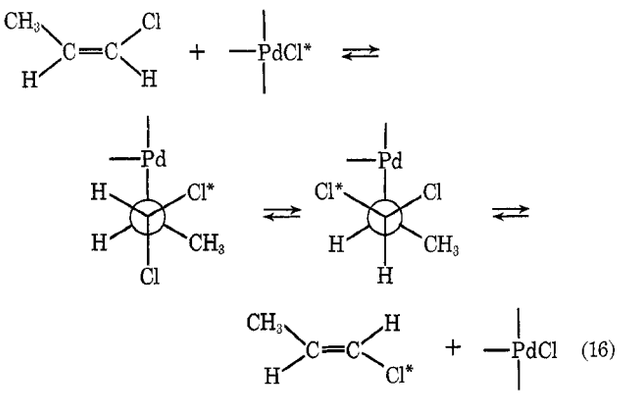
The proposal that both routes occur is required by the fact (No. 1) that 1-chlorocyclopentene exchanges. As shown by eq 15, if chloropalladation–dechloropallada-



(15)

tion were stereochemically pure, exchange should not have occurred. Note that cis chloropalladation–dechloropalladation is used for purposes of illustration. Trans stereochemistry would have given the same result. Nonstereospecific chloropalladation is also consistent with No. 9.

As shown by eq 16, stereochemically pure cis chloro-



(16)

palladation–dechloropalladation would be predicted to give exchange when, and only when, there is isomerization. Suggestion of *mainly* cis chloropalladation is consistent with No. 3 as is also in agreement with No. 5 and 9.

The effect of vinylic substitution on the rate of chloropalladation is qualitatively the same as that previously found for acetoxypalladation.[3,4] Qualitatively chloropalladation has much less of a steric factor than acetoxypalladation. Thus, vinyl acetate exchanges at a rate about a million times faster than 2-acetoxy-2-butene, while vinyl chloride exchanges only about 200 times faster than 2-chloro-2-butene. These results cannot be explained on different steric requirements for Cl and OAc, since the two do not have greatly different steric factors.[12] The lower steric effect for chloropalladation may result from the steric requirements for a cis addition being less than for a trans addition. This is a reasonable postulate, since in the first step a chloride from the coordination sphere of Pd(II) is being inserted. Thus the crowding about the Pd(II) is less than if a chloride from outside the coordination sphere is being added.

The fact that the reactive species is the dimeric π complex **1** rather than a monomeric π complex which could be formed by way of eq 17 deserves comment.

$$Li_2Pd_2Cl_6 + 2C_2H_3Cl \rightleftharpoons 2LiPdCl_3(C_2H_3Cl) \quad (17)$$

In both the vinyl[3] and allylic[2,4] exchanges the reactive species was also a dimeric π complex, although in the allylic case there was evidence that monomeric π complex, formed by an equilibrium analogous to eq 17, was present in much larger quantities than the dimeric π complex but was unreactive.

The reason postulated for this lack of reactivity is that the monomeric π complex has more negative charge concentrated on the Pd(II) complexed to the olefin than would the dimeric π complex. This negative charge would repulse the attacking acetate. The same argument could be used in the present case, since both eq 12 and 14 require the approach of chloride to the Pd(II) before chloropalladation can be completed.

It is interesting that 2-chloro-2-butene and 1-chlorocyclopentene exchange at about the same rate. If steric factors to chloropalladation are equal, the latter might be expected to exchange more slowly, since it can exchange only when chloropalladation and dechloropalladation have different stereochemistries. Thus the rate of chloropalladation of 1-chlorocyclopentene is probably faster than that of 2-chloro-2-butene. This is a reasonable result since the former has a more reactive double bond. Previously, the fact that 1-acetoxycyclopentene did not exchange acetate at a measurable rate while 2-acetoxy-2-butene did was taken as evidence that acetoxypalladation was stereochemically pure,[3] since the two might be expected to have approximately the same rates of acetoxypalladation. The present results support that contention.

Experimental Section

Materials.—Vinyl chloride was purchased from Matheson Gas Products. The cyclopentenyl chloride was prepared by a literature procedure.[13] A pure sample for use in the kinetic runs was obtained by preparative vapor phase chromatography (vpc) using a 20-ft 20% Carbowax 20M on ABS (70–80 mesh) programmed from 80 to 200° at 7.5°/min. The helium flow rate was 60 ml/min. The other vinylic chlorides were purchased from K & K Laboratories. Crude separation of the *cis*- and *trans*-1-chloro-1-propene isomers was by distillation. Final purification was by preparative vpc using a 20-ft 20% Lac 446 on Chromosorb W (60–80 mesh). The temperature was 50° and the helium flow rate was 100 ml/min. The radioactive LiCl was purchased from Radiochemical Center, Amersham, England. It had a specific activity of 8 μCi/mg.

(12) E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **4**, 761 (1965).
(13) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951).

The preparation and analysis of the Pd(II) stock solutions has been described previously.[1,7] All other chemicals were of reagent grade.

Kinetic Runs.—The reaction mixtures for the vinyl chloride exchange were prepared by mixing known amounts of the Pd(II) and LiCl stock solutions, adding radioactive lithium chloride, and diluting to a known volume, usually 5 ml. The reaction mixture was put into a polymerization tube. A rubber liner was fitted into the mouth and the tube was capped with a metal cap having an opening through which a syringe needle could be inserted. The tube was connected to a gas buret by means of the needle. The entire system was evacuated, flushed twice with vinyl chloride, and then pressured to atmospheric with vinyl chloride. The tube was then agitated until the gas uptake stopped, and a sample of the solution was then removed for radioactive assay. Samples (usually 0.05 ml) were then removed periodically and put in small vials which were capped with rubber stopules. The vinyl chloride was removed by evacuating the vials by means of a syringe needle inserted through the rubber stopule. The residue was then assayed for radioactivity.

The runs with isopropenyl chloride and 2-chloro-2-butene were carried out in the same fashion. Because of its higher boiling point, the runs with cyclopentenyl chloride were carried out by assaying the cyclopentenyl chloride rather than the inorganic salts. A portion of the reaction mixture was diluted with CH_2Cl_2 and the acetic acid and inorganic salts removed by washing with water. After drying and concentrating the entire organic phase was injected onto vpc and the cyclopentenyl chloride collected and assayed. Vpc conditions used were the Lac 446 column (see above) programmed from 80–200° at 7.5°/min.; helium flow rate was 100 ml/min.

The treatment of data for an isotope exchange reaction has been discussed previously.[3] In the present case, the rate expression is eq 18, where [VC] is the vinylic chloride concentration,

$$\ln \frac{A_\infty}{A_\infty - A} = \frac{R}{[\mathrm{VC}][\mathrm{Cl}]_t}([\mathrm{VC}] + [\mathrm{Cl}]_t)t \qquad (18)$$

$[Cl]_t$ is the total inorganic chloride concentration, A is the radioactivity at any given time during the run, and A_∞ is the activity at equilibrium. When the inorganic salts were assayed, A_∞ was simply calculated from the total activity A_t by the relationship

$$A_\infty = A_t \frac{[\mathrm{Cl}]_t}{[\mathrm{VC}] + [\mathrm{Cl}]_t} \qquad (19a)$$

of eq 19a, and when the organic salt is assayed the relationship is eq 19b.

$$A_\infty = A_t \frac{[\mathrm{VC}]}{[\mathrm{VC}] + [\mathrm{Cl}]_t} \qquad (19b)$$

A first-order plot, giving the first-order rate constant k_{obsd}, is obtained no matter what the order in [VC]. This observed rate constant then has the following relationship (eq 20) to [VC]

$$k_{obsd} = \frac{R}{[\mathrm{VC}][\mathrm{Cl}]_t}([\mathrm{VC}] + [\mathrm{Cl}]_t) \qquad (20)$$

and $[Cl]_t$, where R is the rate expression in vinylic chloride. If $R = k[VC]$ we have eq 21, and the first-order rate constant

$$k_{obsd} = \frac{k}{[\mathrm{Cl}]_t}([\mathrm{VC}] + [\mathrm{Cl}]_t) \qquad (21)$$

can be calculated from the relationship. If k remains constant with varying [VC], we have eq 22, a first-order process. As shown in Table I, k does remain constant.

$$k = k_{obsd} \frac{[\mathrm{Cl}]_t}{([\mathrm{VC}] + [\mathrm{Cl}]_t)} \qquad (22)$$

The runs with *cis* and *trans*-1-chloro-1-propene were carried out in a fashion similar to that for 1-chlorocyclopentene. However, rather than working up the reaction mixture, a 2-ml sample was injected onto vpc using same conditions as were used for purification, and the two isomers were collected in traps and assayed.

Radioactive Assay.—All assays were made using a Packard Tri-Carb Liquid Scintillation Counter made by Packard Instrument Co., Inc., La Grange, Ill. The scintillation recipe for the inorganic salts contained 1044 parts of toluene, 1356 parts of dioxane, 720 parts of ethanol, 9.69 parts of PPO (2,5-diphenyloxazole purchased from New England Nuclear Co.), and 0.24 parts of POPOP [*p*-bis(2,5-phenyloxazolyl)benzene purchased from Pilot Chemical Co.]. This recipe completely dissolved the inorganic salts at the concentrations used for assay. For the organic chlorides a recipe containing 3144 ml of toluene, 9.42 g of PPO, and 0.3144 g of POPOP was used. For both recipes, the use of an internal ^{36}Cl standard indicated counting efficiency very close to 100%; so internal standards were not used in subsequent countings.

The calculation of specific activities of the inorganic chlorides was easily done, since the volume of the aliquots of the reaction mixture was known and the concentration of inorganic chloride was known from analysis. However, in the case of the organic chloride assay, the efficiency of collection is variable; so the counting solution had to be analyzed for organic chloride content to calculate the specific activity. The same vpc procedure as was used for purification was used for analysis. With cyclopentenyl chloride the assay was simple, since only one compound was involved. However, in the runs with *cis*- and *trans*-1-chloropropene the vpc procedure did not completely separate the two isomers on the scale needed for radioactive assay and reanalysis. It was found that pure cis isomer could be collected while the trans collection always contained some cis isomer. The specific activity of the cis was determined on the pure cis isomer and then its contribution to the radioactivity in the mixture was calculated and subtracted from the total activity. The specific activity of the trans isomer could then be calculated.

Registry No.—Vinyl chloride, 75-01-4; *cis*-1-chloro-1-propene, 16136-84-8; *trans*-1-chloro-1-propene, 16136-85-9; 2-chloro-1-propene, 557-98-2; *cis*-2-chloro-2-butene, 2211-69-0; *trans*-2-chloro-2-butene, 2211-68-9; 1-chlorocyclopentene, 930-29-0; LiCl, 7447-41-8; $Li_2Pd_2Cl_6$, 31183-05-8; $PdCl_2$, 7647-10-1.

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