(Table VI). This indicated the absence of ion pairing in these solvents. With THF, dioxane, and benzene in the mixed solvents, the rates of reaction increased in the order K > Na > Li, indicating that dissociation of the alkali methoxides was incomplete, at least in the case of lithium and sodium methoxides. Solvation of metallic cations by aprotic solvents increases the rate of reactions involving organometallic compounds.[34] However, this could not be the reason for the rate increase in the presently investigated cyanoethylation, since the ionic dissociation of the alkali methoxide was already complete in pure methanol.[17]

Experimental Section

Materials.—Acrylonitrile (BDH) was purified according to the method of Bamford and Jenkins.[35] Absolute methanol (BDH) suitable for anhydrous titrations containing no more than 0.01% water was used. Dimethylformamide[36] was subjected to azeotropic distillation with benzene and fractionally distilled *in vacuo* under nitrogen; the fraction boiling at 65–66° (35 mm) was used. DMSO was purified as DMF was purified. The fraction boiling at 93° (30 mm) was collected, shaken for 48 hr over calcium oxide, filtered under anhydrous conditions, and fractionally distilled. The middle fraction was used. Dioxane and tetrahydrofuran were first refluxed over sodium and then over sodium benzophenone ketyl and distilled. Benzene was refluxed over sodium and distilled. All purification procedures were carried out under pure nitrogen and anhydrous conditions. Materials were kept under nitrogen in flasks fitted with self-sealing rubber caps. Methanolic methoxide solutions were prepared by dissolving the alkali metal in methanol under reflux. The concentration of the base was determined by titration with standard acid using phenolphthalein as indicator.

Procedure for Kinetic Measurements.—The apparatus and procedure for the titrimetric determination of the rate of cyanoethylation were the same as previously described.[17] When the reaction was follow dilatometrically a conventional dilatometer consisting of a calibrated capillary tube, ending in a bulb of 3–25-ml volume, was used. A solution of acrylonitrile dissolved in the solvent mixture was introduced into the same apparatus as that used for the volumetric rate measurements. At the required temperature, the catalyst solution was added in one portion. Time of reaction was recorded from this point. A portion of the homogeneous reaction mixture was transferred quickly to the dilatometer (which had already the required temperature) by a hypodermic syringe. Calculations were made by standard methods as described in Frost and Pearson.[22] Product studies have shown the presence of β-methoxypropionitrile.

Registry No.—Methanol, 67-56-1; DMSO, 67-68-5; DMF, 68-12-2; dioxane, 123-91-1; THF, 109-99-9; benzene, 71-43-2.

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(34) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *J. Am. Chem. Soc.* **82**, 2895 (1960).

(35) C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc.* (London), **A216**, 515 (1953).

(36) A. B. Thomas and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 1843 (1957).

Oxidation of Olefins by Palladium(II). III. Oxidation of Olefins by a Combination of Palladium(II) Chloride and Copper(II) Chloride in Acetic Acid[1,2]

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A combination of Pd(II) and Cu(II) in acetic acid oxidizes olefins to products which neither Pd(II) nor Cu(II) alone will produce. Pd(II) is known to oxidize olefins to vinyl and allylic acetates and Cu(II) alone gives no oxidation, but, in a system containing both palladium(II) chloride and copper(II) chloride, acetate esters of glycol and chloro alcohols are formed. If ethylene is oxidized in reaction mixtures with high cupric ion concentrations, little vinyl acetate is produced but, rather, 2-chloroethyl acetate, ethylene glycol diacetate, and ethylene glycol monoacetate are formed. At 100°, propylene and 1-butene give mainly 1,2-di- and 1,2-chloro acetates with smaller amounts of 1,3 isomers. In addition, 1-butene gives traces of 1,4 and 2,3 isomers. *cis*- and *trans*-2-butene, on the other hand, give comparable quantities of both 2,3 and 1,3 isomers. These results are consistent with a mechanism involving oxypalladation adducts as intermediates. The oxypalladation adducts decompose by reaction with copper(II) chloride. The product distribution can be explained by isomerization of the oxypalladation adduct prior to reaction with Cu(II).

The oxidation of ethylene to vinyl acetate[3] and of

$$C_2H_4 + Pd^{+2} + 2OAc^- \longrightarrow C_2H_3OAc + HOAc + Pd^0 \quad (1)$$

other olefins to a mixture of vinyl and allylic acetates,[4] first reported by Russian workers,[3a] is the subject of several recent patents.[5] In several of the patents, Cu(II) is used as a redox system to make the reaction catalytic in Pd(II).

$$C_2H_4 + 2Cu(II) + OAc^- \xrightarrow[HOAc]{Pd(II)} C_2H_3OAc + 2Cu(I) + HOAc \quad (2)$$

However, in the presence of Cu(II), a side reaction takes place which can be made the predominant reaction under certain conditions. This new reaction, which requires the presence of both Pd(II) and Cu(II), is the formation of the acetate esters of chloro alcohols and glycols. Thus, with ethylene, the reaction is as shown in eq 3.

$$C_2H_4 + CuCl_2 + OAc^- \xrightarrow[HOAc\ +\ H_2O]{PdCl_2} \begin{array}{l} AcOCH_2CH_2Cl \\ AcOCH_2CH_2OAc \\ AcOCH_2CH_2OH \end{array} + CuCl \quad (3)$$

While this work was in progress, two reports of this reaction have appeared. The first, in the patent literature,[6] does not disclose the acetate esters of the

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(1) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; Abstracts, p 37N.

(2) Paper II: P. M. Henry, *J. Am. Chem. Soc.*, **88**, 1595 (1966).

(3) (a) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960); (b) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961).

(4) (a) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Sirkin, *Izv. Akad. Nauk USSR, Otd. Khim. Nauk*, 930 (1962); (b) I. I. Moiseev, A. P. Belov, and Ya. K. Sirkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1527 (1963).

(5) For example, Imperial Chemical Industries, Belgian Patents 635,425, 635,426, and 638,268 (1964).

(6) D. Clark and P. Hayden, Canadian Patent 711,719 (1965).

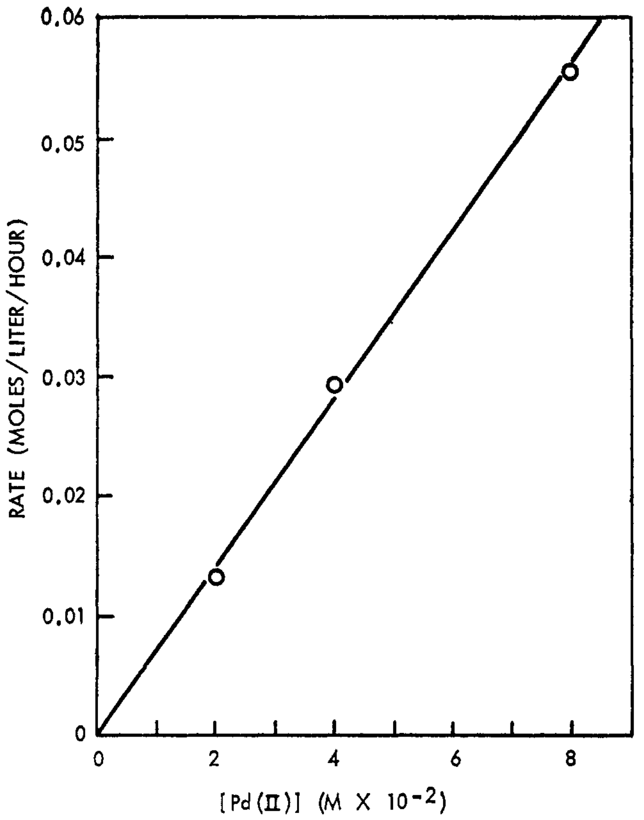

Figure 1.—Plot of rate *vs.* soluble Pd(II) concentration for the oxidation of ethylene in the heterogeneous sodium acetate system at 25° and 1 atm of ethylene pressure. Reaction mixtures contained 1.0 mole of $CuCl_2$ and 2.0 moles of sodium acetate per liter of acetic acid.

chloro alcohols, which are major products under certain conditions. The second describes the formation of a chloro acetate by the oxidation of norbornene.[7] Neither report states that Cu(II) had any purpose other than to serve as a redox system.

This paper will describe the general features of this rare case of cocatalysis by two metal ions. Some results obtained with ethylene, propylene, 1-butene, and *cis*- and *trans*-2-butene will be used for this purpose.

Results

The most important results of this study follow: (1) Control experiments demonstrated that the formation of saturated esters requires the presence of *both* Pd(II) and Cu(II). Thus, Cu(II), which regenerates Pd(II) in this system, is serving as more than a redox reagent. It is changing the nature of the reaction. (2) Propylene and the butenes give products which cannot be explained by simple 1,2 addition to the double bond. For instance, propylene gives 1,3- as well as 1,2-disubstituted propane.

Control Experiments.—Ethylene was oxidized with Pd(II) under a variety of soluble chloride and acetate ion concentrations at several temperatures. No saturated esters were detected in the absence of cupric ion. However, if cupric chloride is added, even in small amounts, β-chloroethyl acetate, ethylene glycol diacetate, and, if water is present, ethylene glycol monoacetate are formed. Cupric chloride or mixtures of cupric and cuprous chlorides give no saturated esters under the reaction conditions.

Unfortunately, because of the low solubility of the salts in acetic acid, most of the reaction mixtures were heterogeneous. However, the reaction could be demonstrated to take place in homogeneous systems by using 2 *M* lithium chloride solutions in which cupric and cuprous chlorides are soluble to about 0.3 *M*. Thus, a solution 2 *M* in lithium chloride, 0.5 *M* in lithium acetate, and 0.1 *M* in Pd(II) very slowly oxidizes ethylene to vinyl acetate at 25°, precipitating palladium metal. However, if the solution is also made 0.1 *M* in cupric chloride, the rate of ethylene oxidation increases considerably and the products are almost exclusively 2-chloroethyl acetate and ethylene glycol diacetate. Palladium metal is not formed in this system, but rather cupric chloride is reduced to cuprous chloride. When all the cupric chloride is reduced, the ethylene uptake almost stops.

Since the chloride ion concentration in this system is so much higher than the cupric chloride concentration, the addition of Cu(II) does not appreciably change the chloride ion concentration. Thus, the cupric chloride must be more than merely a chloride source as suggested by Baird.[7]

Other control experiments showed that vinyl acetate is not converted to saturated esters under the reaction conditions which produce saturated esters from ethylene.

Competition between Vinyl Acetate and the Cocatalysis Reaction.—The ratio of saturated esters to vinyl acetate increases with the Cu(II) concentration, while going to higher temperatures and pressures increases the yield of vinyl acetate. In heterogeneous reaction systems the Cu(II) concentration is mainly determined by the soluble chloride concentration. The chloride concentration in turn is controlled by the particular metal acetate employed since the chloride concentration will depend on the solubility of the corresponding metal chloride. For the alkali metal chlorides, the order of solubilities in acetic acid is potassium chloride < sodium chloride < lithium chloride. Both the ratio of saturated esters to vinyl acetate and the rate of formation of saturated esters increase in the same order. The rate of formation of saturated esters was found to increase approximately linearly with increasing Cu(II) concentration in the supernatant. Soluble chloride has the secondary effect of inhibiting vinyl acetate formation.

The reaction is also first order in Pd(II) (see Figure 1).

Distribution of Products.—Distribution of products must be considered in three contexts: (1) the distribution between chloro acetate, glycol diacetate, and monoacetate; (2) positional isomers such as 1,2, 1,3, 1,4, and 2,3 isomers of the oxidation products from the butenes; and (3) the *meso* and *dl* forms of the 2,3-glycol diacetate as well as the *threo* and *erythro* forms of the 2,3-chloro acetates and 2,3-monoacetates. Only the first two will be considered in this paper.

The distribution between chloro acetate, diacetate, and monoacetate is naturally dependent on the chloride, water, and acetate concentrations but not always in a simple fashion. For instance, the yield of β-chloroethyl acetate would be expected to increase with increasing soluble chloride concentration. In most

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[7] W. C. Baird, Jr., *J. Org. Chem.*, **31**, 2411 (1966).

cases this was true, but under some reaction conditions an increase in soluble chloride actually decreased the yield of β-chloroethyl acetate. As expected, addition of water to the reaction mixture causes the monoacetate to become an important product. However, even at water concentrations of 2.0 *M*, there were usually still considerate amounts of diacetates and chloro acetates.[8] Of course, since most of the water would probably be complexed by the metal ions present, its actual concentration would be much lower. 2-Chloroethanol was not detected in any of the reaction mixtures containing water.

Positional isomerization increased with temperature and decreased with increasing chloride concentration. With propylene it was not important. Even under favorable conditions (100° and low chloride), the 1,3-di- and 1,3-chloro acetates together constituted only 2% of the saturated ester product. With the butenes it was much more pronounced. The product distribution for the three butenes under one set of reaction conditions is given in Table I. With the 1,3- and 1,2-chloro acetates two isomers are possible, the primary chloride and the secondary chloride. Detailed product distributions are given in Table II.

TABLE I

POSITIONAL ISOMER DISTRIBUTION FOR THE OXIDATION OF 1-BUTENE AND *cis*- AND *trans*-2-BUTENE[a]

Isomer	*cis*-2-Butene, %	*trans*-2-Butene, %	1-Butene, %
2,3	29	61	1.8
1,3	71	39	8.8
1,2	<0.1	<0.1	87
1,4	<0.1	<0.1	2.4

[a] Contains 1 mole of cupric chloride, 1 mole of lithium acetate, and 0.01 mole of Pd(II) per liter of acetic acid. Reaction time was 1 hr at 100° under maximum olefin pressure. Acetic anhydride was added to dry the acetic acid.

TABLE II

DETAILED PRODUCT DISTRIBUTIONS FOR THE OXIDATION OF 1-BUTENE AND *cis*- AND *trans*-2-BUTENE[a]

Product	*cis*-2-Butene, %	*trans*-2-Butene, %	1-Butene, %
2,3 isomers			
Chloro acetate	15	44	0.9
Diacetate	14	17	0.9
1,3 isomers			
1-Chloro-3-acetoxybutane	35	18	1.9
3-Chloro-1-acetoxybutane	26	14	4.0
Diacetate	10	7	2.9
1,2 isomers			
1-Chloro-2-acetoxybutane	<0.1	<0.1	58.9
2-Chloro-1-acetoxybutane	<0.1	<0.1	11.6
Diacetate	<0.1	<0.1	16.5
1,4 isomers			
Chloro acetate	<0.1	<0.1	2.15
Diacetate	<0.1	<0.1	0.35

[a] See footnote of Table I.

The most interesting result is that the 2-butenes give large amounts of 1,3 products while 1-butene gives mainly the 1,2 products with small amounts of 1,3 products and only traces of 2,3 products. The latter probably resulted from oxidation of 2-butene formed by isomerization of 1-butene (see Experimental Section).

Control experiments demonstrated that the products obtained with the 2-butenes did not result from the further reaction of the enol acetate of 2-butanone or 3-acetoxy-1-butene. Furthermore, the 2,3 isomers did not convert into 1,3 isomers or 1,3 isomers into 2,3 isomers under the reaction conditions.

Small amounts of 2,3-dichlorobutane were detected in the 2-butene reaction mixtures, but this product was shown to occur in reaction mixtures not containing Pd(II). It no doubt is formed by cupric chloride chlorination of the olefin.[10]

The propylene and 2-butene reaction mixture also contained varying amounts of allylic and vinyl oxidation products such as isopropenyl and allyl acetate for propylene and 3-acetoxy-1-butene for 2-butene. No attempt was made to determine the concentrations of these materials accurately, but they were usually minor products. These products are the same as those obtained by the Pd(II) oxidation of these olefins in the absence of Cu(II).[11]

Discussion

Of the several possible reaction paths, we believe that the mechanism most consistent with Pd(II) chemistry is oxypalladation[11-14] followed by reaction of the oxypalladation adduct with cupric chloride to give the saturated esters. With ethylene the reaction path would be the following (eq 4) ($X^- = Cl^-$ or OAc^-).[15]

$$\begin{tikzcd}
C_2H_4 + PdX_2 + OAc^- \arrow[r, "HOAc"] & XPdCH_2CH_2OAc \arrow[r, "-HPdCl"] \arrow[d, "nCuX_2"] & CH_2{=}CHOAc \\
 & PdX_2 + XCH_2CH_2OAc + 2CuX + (n-2)CuX_2 &
\end{tikzcd} \quad (4)$$

The reaction with copper(II) chloride would compete with the type of decomposition of the oxypalladation adduct which occurs in the absence of copper(II) chloride, *i.e.*, by HPdCl elimination to give vinyl acetate. The present results do not permit a determination of the nature of the reaction with copper(II) chloride. Possibilities are transfer of alkyl to Cu(II) or else Cu(II) could be complexing the Pd(II), changing the nature of Pd(II) as a leaving group.

The product distributions obtained with the butenes support this mechanism. π-Allylic intermediates cannot account for all the results since ethylene cannot

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[8] In reaction mixtures containing water, acetaldehyde is produced from ethylene and ketones are produced from the other olefins by the Wacker reaction.[9] However, even in reaction mixtures 2 *M* in water, they never amounted to more than 10% of the total product.

[9] J. Smidt, *et al.*, *Angew. Chem.*, **71**, 176 (1959).

[10] R. J. Arganbright and W. F. Yates, *J. Org. Chem.*, **27**, 1205 (1962). Control experiments (see Experimental Section) showed in the presence and absence of Pd(II) that about the same amount of 2,3-dichlorobutane was obtained from *cis*-2-butene.

[11] W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **88**, 2054 (1966).

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

[13] P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).

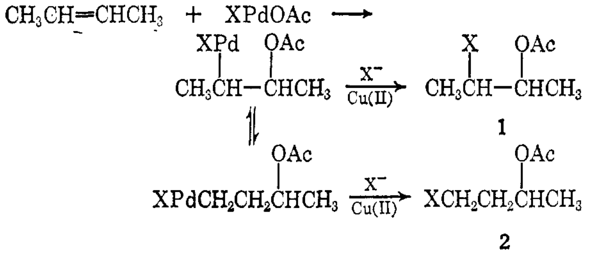
[14] R. Jira, J. Sedlmeier, and J. Smidt, *Ann.*, **693**, 99 (1966).

[15] Metal olefin π complexes proposed as intermediates in the Wacker reaction,[12-14] are very probably also intermediates in the oxypalladation step. However, since they are not an important feature of the mechanism, they are not shown in eq 4-6.

react by this route and the π-allyl from 1-butene would be a mixture of the π-allyls from *cis*- and *trans*-2-butene and be expected to give product distributions similar to those obtained from the 2-butenes. On the other hand, it is difficult to visualize how direct decomposition of olefin–metal π complexes, a mechanism originally suggested for the Wacker process,[9] could give 1,3- and 1,4-disubstituted butanes.

The product distributions can be explained by preferential Markovnikov oxypalladation followed by reaction with cupric chloride with or without prior isomerization of the adduct. The isomerization probably occurs by palladium(II) hydride elimination and readdition, although π-allylic routes are also possible.[16]

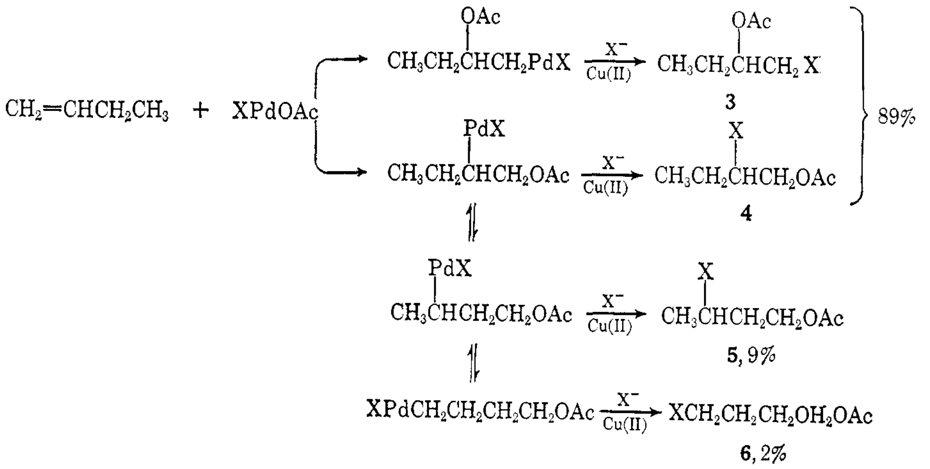
Thus with 2-butene the reaction sequence would be as shown (eq 5).



$$\begin{array}{ccc}
\mathrm{CH_3CH{=}CHCH_3 + XPdOAc \longrightarrow} & & \\
\mathrm{CH_3\overset{\overset{XPd}{|}}{C}H{-}\overset{\overset{OAc}{|}}{C}HCH_3} & \xrightarrow[\mathrm{Cu(II)}]{\mathrm{X^-}} & \mathrm{CH_3\overset{\overset{X}{|}}{C}H{-}\overset{\overset{OAc}{|}}{C}HCH_3} \\
 & & \mathbf{1} \\
\upharpoonleft\!\downharpoonright & & \\
\mathrm{XPdCH_2CH_2\overset{\overset{OAc}{|}}{C}HCH_3} & \xrightarrow[\mathrm{Cu(II)}]{\mathrm{X^-}} & \mathrm{XCH_2CH_2\overset{\overset{OAc}{|}}{C}HCH_3} \\
 & & \mathbf{2}
\end{array} \qquad (5)$$

Thus, only 2,3 and 1,3 products would be expected from 2-butene.

On the other hand, 1-butene can undergo Markovnikov or non-Markovnikov addition (eq 6).



$$\begin{array}{cccc}
 & \mathrm{CH_3CH_2\overset{\overset{OAc}{|}}{C}HCH_2PdX} & \xrightarrow[\mathrm{Cu(II)}]{\mathrm{X^-}} & \mathrm{CH_3CH_2\overset{\overset{OAc}{|}}{C}HCH_2X}\ \ \mathbf{3} \\
\mathrm{CH_2{=}CHCH_2CH_3 + XPdOAc} \nearrow\!\searrow & & & \Big\}\ 89\% \\
 & \mathrm{CH_3CH_2\overset{\overset{PdX}{|}}{C}HCH_2OAc} & \xrightarrow[\mathrm{Cu(II)}]{\mathrm{X^-}} & \mathrm{CH_3CH_2\overset{\overset{X}{|}}{C}HCH_2OAc}\ \ \mathbf{4} \\
 & \upharpoonleft\!\downharpoonright & & \\
 & \mathrm{CH_3\overset{\overset{PdX}{|}}{C}HCH_2CH_2OAc} & \xrightarrow[\mathrm{Cu(II)}]{\mathrm{X^-}} & \mathrm{CH_3\overset{\overset{X}{|}}{C}HCH_2CH_2OAc} \\
 & & & \mathbf{5}, 9\% \\
 & \upharpoonleft\!\downharpoonright & & \\
 & \mathrm{XPdCH_2CH_2CH_2CH_2OAc} & \xrightarrow[\mathrm{Cu(II)}]{\mathrm{X^-}} & \mathrm{XCH_2CH_2CH_2OH_2OAc} \\
 & & & \mathbf{6}, 2\%
\end{array} \qquad (6)$$

Most of the product with 1-butene would be expected to be the 1,2 isomer, because the preferred Markovnikov adduct cannot isomerize. Also, the 1,2 product would result from non-Markovnikov addition *without* isomerization. Since the 1,3 product requires non-Markovnikov addition *with* isomerization, the yield of the 1,3 isomer from 1-butene would be expected to be lower than from the 2-butenes. It is lower by a factor of 4 to 8 (see Table I). Of course, the 1,4 isomer is even less favored because it required non-Markovnikov addition followed by two isomerizations before decomposition and only traces of 1,4 isomer are detected.[19]

If oxypalladation adducts are intermediates in the cocatalysis reaction, it is not surprising that 1-butene gives a considerable amount of products which arise from non-Markovnikov addition. Kitching, *et al.*,[11] oxidized a number of olefins with $Pd(OAc)_2$ in acetic acid at 25° in the absence of Cu(II) to obtain unsaturated esters. Their product distribution was consistent with oxypalladation followed by HPdOAc elimination. With 1-butene about 20% of the product consisted of unsaturated esters which could only have resulted from non-Markovnikov addition.

There is also some evidence that oxypalladation adducts can isomerize. Because unsaturated products are obtained in the absence of Cu(II), isomerization cannot be detected in most cases. However, Kitching, *et al.*,[11] reported that 1-butene gave a 2% yield of 3-buten-1-yl acetate and cyclohexene was recently reported[20] to give some 3-cyclohexenyl acetate when oxidized by palladium(II) chloride in acetic acid. Both products could have arisen from isomerization of the oxypalladation adduct before HPdCl elimination.

More detailed descriptions of the product distributions with 1- and *cis*- and *trans*-2-butene and cyclohexene, to be submitted for publication in the near future, should permit more detailed conclusions as to mechanism.

Finally, it should be mentioned that the formation of saturated esters in the presence of copper(II) chloride has caused some confusion about the mechanism of Pd(II) oxidations in general. It is now generally agreed[11-14] that Pd(II) olefin oxidations proceed *via* oxypalladation adducts, but there is disagreement as to the mode of decomposition of the adduct. Some workers[12] have suggested heterolytic decomposition to give carbonium ions. Others[11,13,14] have agreed that the products (*i.e.*, carbonyl compounds in water and vinyl or allylic acetates in acetic acid) can only be explained by a Pd(II)-assisted hydride shift or

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[16] The isomerization of the oxypalladation adduct has analogy in the isomerization of olefins by noble metal salts. Both metal hydride and π-allylic intermediates have been suggested for this reaction. For two recent studies, see ref 17 and 18. In the cocatalysis reaction Cu(II) could be involved in the isomerization step.

[17] R. Cramer and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **88**, 3534 (1966).

[18] J. F. Harrod and A. J. Chalk, *ibid.*, **88**, 3491 (1966).

[19] Note that the predominate 1,3-chloro acetate isomer obtained with each olefin is consistent with this reaction scheme if the chloride in the product is on the carbon atom to which the Pd(II) was attached in the oxypalladation intermediate. Thus 2-butene gives mainly primary chloride (**2**, X = Cl), while 1-butene gives mainly secondary chloride (**5**, X = Cl). Furthermore, the 1,2-chloro acetate from 1-butene is mainly the primary chloride (**3**, X = Cl), the one which would be expected from Markovnikov addition (eq 6).

[20] N. Green, R. N. Haszeldine, and J. Lindley, *J. Organometallic Chem.*, **6**, 107 (1966).

elimination. If a simple heterolytic splitting of the Pd(II)–carbon bond occurs, some saturated products, such as those which are obtained by a combination of palladium(II) chloride and copper(II) chloride in acetic acid, would be expected. Some workers, failing to recognize the special nature of the palladium(II) chloride–copper(II) chloride reaction in acetic acid, have considered this reaction evidence that all Pd(II) oxidations occur by heterolytic splitting of the Pd(II)–carbon bond.

For instance, it was recently reported[7] that norbornene was oxidized by a mixture of palladium(II) chloride and copper(II) chloride in acetic acid to give *exo*-2-chloro-*syn*-7-acetoxynorbornene. This product was rationalized by oxypalladation followed by heterolytic splitting of the Pd(II)–carbon bond, producing a carbonium ion which rearranged before reacting with chloride to give the observed product. The author, not recognizing the importance of copper(II) chloride, then argued that this was evidence that all Pd(II) oxidations occurred by heterolytic splitting of the Pd(II)–carbon bond. Of course, the author's mechanistic interpretation for the formation of the product was reasonable but his generalization of the mechanism for all Pd(II) oxidations was invalid.

Experimental Section

Reagents.—The gases were Phillips Petroluem Co. pure grade. The palladium(II) chloride was Matheson Scientific Co. purified grade. All other chemicals were reagent grade.

The Pd(II) stock solutions were prepared by heating palladium(II) chloride and lithium chloride in a mole ratio of 1:2 with enough acetic acid to make a solution 0.1 M in Pd(II). The solution was cooled, filtered to remove insolubles, and analyzed for Pd(II) by the dimethylglyoxime method.

Kinetic Runs.—Rates were measured by olefin uptake with gas burets. Creased flasks were used as reaction vessels. This procedure has been described.[13] The procedure for determining Cu(II) concentration in the supernatant has also been described.[21]

Atmospheric Pressure Runs.—These runs were made in either 250- or 750-ml pop bottles stirred with magnetic stirring bars. The pop bottle was capped with a metal cap having holes sealed by a rubber liner through which syringe needles could be inserted into the bottle. The bottle was placed in a water bath at the desired temperature and then connected to a gas manifold by these means. The bottle was first evacuated and then pressured to 1 atm of the olefin. The run was then started by turning on the motor which drives the magnetic stirring bar.

The reaction mixtures were dried by heating then on a steam bath with a small excess of acetic anhydride.

An example of the type of data obtained is given in Table III.

TABLE III

RATE AND DISTRIBUTION OF PRODUCTS IN SLURRY REACTION MIXTURES AT 25° AND ATMOSPHERIC ETHYLENE PRESSURE[a]

Metal acetate	Initial rate, M/hr^{-1}	Initial Cu(II) concn	Vinyl acetate/ saturated esters ratio
Lithium	0.25	0.27	<0.005
Sodium	0.025	0.034	0.024

[a] Both reaction mixtures contain 1.0 mole of copper(II) chloride, 0.04 mole of Pd(II) and 2.0 moles of metal acetate per liter of acetic acid.

High Pressure Runs.—The high pressure runs were made in a 500-ml titanium- or platinum-lined autoclave. For the runs with ethylene, the bomb contents were heated to the reaction temperature under nitrogen, the bomb was evacuated and pressured with ethylene, and the agitation was begun. With propylene and the 2-butenes, a weighed amount of olefin was transferred to the bomb at room temperature, the bomb was heated rapidly to reaction temperature, and agitation was begun.

Typical data demonstrating the effect of metal acetate, pressure, and temperature on product distribution is shown in Table IV. Rates are only approximate. They were determined by terminating the reaction mixtures after running for 1 hr at 100° and 0.5 hr at 120°. When lithium acetate was used, the reaction was complete in 1 hr; thus the actual rate was much faster.

TABLE IV

EFFECT OF REACTION VARIABLES ON PRODUCT DISTRIBUTION FOR THE OXIDATION OF ETHYLENE[a]

Metal acetate	Temp, °C	Ethylene pressure, atm	Rate of product formation, moles/ liter/ hour	Vinyl acetate/ saturated esters ratio	Di-acetate/ chloro-acetate ratio
Lithium	100	33	>1.0	0.01	0.12
Sodium	100	33	0.63	0.80	2.2
Potassium	100	33	0.06	5.0	9.0
Sodium	100	5	0.18	0.20	
Sodium	100	13	0.47	0.68	
Sodium	100	40	0.51	0.98	
Sodium	120	40	1.06	2.5	

[a] Reaction mixtures contain 2.0 moles of copper(II) chloride, 0.01 mole of Pd(II), and 4.0 moles of metal acetate per liter of acetic acid.

One complication in the butene oxidations was isomerization of one olefin to mixtures of the other two. Analysis of the gases after reaction indicated that some isomerization did occur. It was most serious with 1-butene. However, by running to low conversions this complication was almost entirely avoided as can be seen from the fact that the 2-butene reaction mixtures are free of 1,2-disubstituted butanes, the major product from 1-butene. On the other hand, the 1-butene reaction mixtures contained only traces of 2,3-disubstituted products, a major product from the 2-butenes. These 2,3-disubstituted products no doubt did arise from oxidation of 2-butene formed by isomerization of 1-butene since their proportion of the total products increased with reaction time.

To demonstrate that the 2,3-dichlorobutanes resulted from the chlorination by copper(II) chloride rather than by Pd(II)-catalyzed oxidation of the 2-butenes, oxidations of *cis*-2-butene were carried out in reaction mixtures which were 1 M in cupric chloride and lithium acetate and 2 M in lithium chloride. In one run the reaction mixture was 0.01 M in Pd(II) and in the other Pd(II) was omitted. Both gave considerable and approximately equal amounts of the 2,3-dichlorobutanes, but the one without Pd(II) did not give the cocatalysis products except for traces of material which had the same gas chromatographic retention time as 2-chloro-3-acetoxybutane. This product could result[22] from chlorination by traces of chlorine formed by the decomposition of cupric chloride.

Analysis of Reaction Mixtures.—All reaction mixtures were analyzed by vapor phase chromatography (vpc) with either a 12-ft 20% Carbowax 20 M on Anakrom ABS programmed from 80 to 155° at 9°/min or a 15-ft 10% Ucon 75h on Gas Chrom Z programmed from 110 to 170° at 2.3°/min. Gas samples were analyzed with a 20-ft column with mixed packing at 50°. This packing consisted of 100 parts of 43 wt % dimethylsulfolane on Chromosorp P plus 15 parts of 40 wt % di-*n*-butyl maleate on Chromosorp P.

Some reaction mixtures were run directly on the Carbowax 20 M column, since the ethylene and propylene glycol monoacetates were not easily separated from the acetic acid. However, all of the 2-butene and most of the dry ethylene and propylene reaction mixtures were first diluted with water and extracted with methylene chloride. The organic phase was washed several times with water to remove the acetic acid, dried, and evaporated to a known volume. Some of the 2-butene reaction mixtures were analyzed directly as well as after work-up to ensure that failure

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to detect some of the products was not due to failure to extract them into the CH_2Cl_2 phase.

For ethylene, all three saturated esters were separated from the reaction mixtures by distillation, use being made of the solubility of the monoacetate in a water–acetic acid mixture as opposed to the organic solubility of the diacetate and chloroacetate. They were identified by physical properties, and by infrared and vpc retention times, which were identical with those of authentic samples.

For propylene, only the chloro acetate, which was mainly 1-chloro-2-acetoxypropane, determined by nmr,[23] was isolated by distillation. Standards of the mono- and diacetate esters of 1,2-propylene glycol, of 1,3-propylene glycol, and of 1-chloro-3-acetoxypropane were prepared, and the remainder of the unknowns were identified by vpc retention times.

The following butane standards were prepared by the acetylation of the corresponding glycol or chlorohydrin: 2,3-diacetate; 1,3-diacetate; 1,4-di- and 1,4-chloro acetates; and the 1,2-di- and 1,2-chloro acetates. The 2,3-chloro acetate was prepared by the reaction of the diacetate with HCl to make the chlorohydrin,[24] followed by acetylation of the chlorohydrin. The 1,3-chloro acetate was prepared by the method of Meltzer and King.[25] The 1,2-chloro acetate was prepared by reaction of 1,2-epoxybutane with concentrated aqueous HCl followed by acetylation.

3-Acetoxy-1-butene and crotyl acetate were prepared by acetylating the corresponding alcohols. 2-Acetoxy-2-butene was prepared by treating 2-butanone with acetic anhydride.[26] The 2,3-dichlorobutane was purchased from K & K Laboratories.

The treatment of 1,3-butanediol with acetyl chloride has been shown[27] to give a 60:40 mixture of 1-chloro-3-acetoxybutane and 1-acetoxy-3-chlorobutane. Vpc analysis of the reaction mixture showed that two materials were present in about this ratio. The assignment of structure of the two isomers was confirmed by the nmr of samples collected by preparative vpc. The structure assignment by nmr is based on the known chemical shifts of the methylene carbons attached to chlorine as opposed to those of the methylene carbons attached to acetate. This same procedure was used to assign the configurations of the two 1,2-chloro acetate isomers.

All products from oxidation of the butenes were identified by vpc retention times on two different columns. The identities of all the 1,3- and 2,3-di- and 1,3- and 2,3-chloro acetates were confirmed by collecting samples by preparative vpc and comparison of nmr with those authentic samples. The 1,2-diacetate and 1,2-chloro acetates were identified in the same way.

Quantitative analyses were made by comparing peak areas with the areas of standards of known concentration. Most of the values in the tables are the averages of at least two runs. Variation between runs was about 10%.

In all cases the products identified accounted for over 95% of the materials found by vpc. However, small amounts of unidentified materials, usually higher boiling, were detected. They were most likely formed by further oxidation of the initial products. One such product from the 2-butene reactions was collected by preparation vpc. Its nmr was consistent with the structure of 2-acetoxy-3-monochloroacetoxybutane.

Registry No.—Palladium(II) chloride, 7647-10-1; copper(II) chloride, 7447-39-4; acetic acid, 64-19-7; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 1-butene, 106-98-9; ethylene, 74-85-1.

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(23) Standards of both the 1-chloro-2-acetoxy- and 1-acetoxy-2-chloropropane were prepared. The nmr of the unknown indicated that it consisted of about 90% of the former with the remainder being the secondary chloride.

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Substituent Effects of Positive Poles in Aromatic Substitution. II. The Nitration of Sulfonium and Selenonium Salts[1a]

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Nitration of dimethylphenylsulfonium methyl sulfate and dimethylphenylselenonium methyl sulfate with concentrated HNO_3 in concentrated H_2SO_4 results in 3.6% *ortho*, 90.4% *meta*, and 6.0% *para* and 2.6% *ortho*, 91.3% *meta*, and 6.1% *para* substitution, respectively. Dimethylnitrophenylsulfonium and -selenonium salts are dealkylated with sodium methoxide at low temperatures. Since the resulting isomeric methyl nitrophenyl sulfides and selenides can be analyzed gas chromatographically, a convenient analysis of isomeric dimethylnitrophenylsulfonium and -selenonium salts has been accomplished.

Substituent effects of positive poles in aromatic nitration have been extensively investigated and found to be predominantly, if not completely, *meta* directing.[2,3] Recent work by Ridd[4–7] and Nesmeyanov[8] indicated that in some cases considerable *para* nitration also occurred. In fact, the anilinium ion is nitrated more rapidly in the *para* position than the *meta* position and is known as a *meta–para* director,[5] while the triphenyloxonium ion is nitrated almost entirely in the *para* position.[8] These results prompted us to reinvestigate the nitration of sulfonium[1a] and selenonium salts which have been reported to nitrate exclusively in the *meta* position.[8,9]

All positive poles involving elements of groups V and VI exhibit a strong $-I$ effect.[10,11] The $-I$ effect is most effective in the *ortho* position and least effective

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