

phenyl-*o*-phenylenediamine in this reaction was a somewhat higher 9%.

Reaction of Diisopropyl-*N*-nitrosamine with Phenyl- and Methylmagnesium Bromide.—Many attempts were made to get these reactions to proceed. The following results were typical. A mixture of 0.1 mol of methylmagnesium bromide and 13 g (0.1 mol) of diisopropyl-*N*-nitrosamine was heated at reflux for 6 hr. Upon treatment of the reaction mixture with water and extraction with ether, followed by distillation, there was obtained 11.5 g (90%) of the starting nitrosamine.

Cautionary Note.—While nitrosamines are easy to prepare and to work with, it should be remembered that many of them are potent carcinogens. Proper precautions against inhalation of the vapors and contact with skin should be maintained always. Preparative glpc should be carried out with caution. Unreacted nitrosamines should not be vented into the atmosphere. In our case any unreacted nitrosamine which came through the glpc column was trapped in a collection tube chilled in a Dry Ice-acetone bath.

Registry No.—Methylolithium, 917-54-4; diisopropyl-nitrosamine, 601-77-4; formaldehyde diisopropylhydrazone, 39837-46-2; diethyl-*N*-nitrosamine, 55-18-5; formaldehyde diethylhydrazone, 28236-89-7; triethylhydrazine, 39837-47-3; methylmagnesium bromide, 75-16-1; 1,1-diethyl-2,2-dimethylhydrazine, 21849-74-1; acetaldehyde diethylhydrazone, 7422-91-5; phenylmagnesium bromide, 100-58-3; 1-phenyl-2,2-diethylhydrazine, 39837-50-8; diphenyl-*N*-nitrosamine, 86-30-6; formaldehyde diphenylhydrazone, 38392-47-1; *N,N,N'*-triphenyl-*o*-phenylenediamine, 29325-54-0; triphenylhydrazine, 606-88-2.

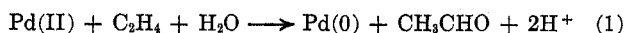
Deuterium Isotope Effects in the Palladium(II) and Thallium(III) Oxidation of Ethylene¹

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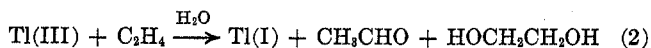
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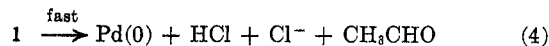
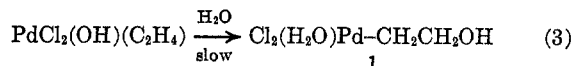
Palladium(II) salts in aqueous solution oxidize ethylene to acetaldehyde³ while thallium(III) salts



oxidize ethylene to a mixture of acetaldehyde and ethylene glycol.⁴ Kinetic studies⁵⁻⁷ indicate that in

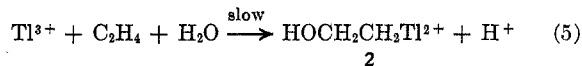


chloride containing aqueous solution, the slow step of the Pd(II) oxidation is rearrangement of a hydroxy olefin π complex to a β -hydroxyethylpalladium(II) alkyl, 1 (or hydroxypalladation adduct in analogy with the well-known hydroxymercuration adduct⁸). This intermediate rapidly decomposes to acetaldehyde and Pd(0). Equation 3 was assigned as the slow step on



the basis of isotope effects. When the reaction is carried out in D₂O the acetaldehyde is undeuterated.³ Thus the decomposition of 1 must involve a transfer of proton from one carbon to the other. This transfer of proton would be expected to involve a positive isotope effect if deuterated ethylene is oxidized. However, it was found that the rate of C₂D₄ oxidation was the same as that of C₂H₄ oxidation within experimental error,⁷ suggesting that the decomposition of 1 occurs after the slow step of the reaction. This conclusion is subject to some uncertainty, since isotope effects in decomposition of adducts such as 1 have not been studied.

Kinetic studies^{9,10} as well as other evidence¹¹ of the Tl(III) oxidation in aqueous perchloric acid indicate that it proceeds *via* a hydroxythallation adduct, 2, analogous to 1. The formation of the adduct was



again assigned as the slow step on the basis of the kinetics. Thus the reaction displayed no proton inhibition, which would have been expected if eq 5 were an equilibrium.

This note will describe further studies of the isotope effects in these two oxidations for the purpose of testing earlier conclusions concerning the rate-determining steps. First, C₂D₄ was oxidized by both reagents and the acetaldehyde product was analyzed for deuterium content. In both cases the product was over 95% CD₃CDO, indicating that both 1 and 2 decompose by hydride shifts. In the case of Pd(II), this result confirms the earlier work using C₂H₄ in D₂O.³

Next the kinetic isotope effect for C₂D₄ as compared with C₂H₄ was measured for Tl(III) in aqueous HClO₄. The value of $k_{\text{H}}/k_{\text{D}}$ was found to be 0.8. The isotope effect of less than one must result from the fact that hydrogen is a better electron withdrawer than deuterium,¹⁵ and the Tl(III) oxidation is very sensitive to electronic effects. In any case the isotope effect is about one, the value expected if eq 5 is the rate-determining step.

In order to substantiate this conclusion concerning the rate-determining steps of these oxidations, it is necessary to have some knowledge of the actual deuterium isotope effects in the decomposition of 1 and 2. Since they cannot be measured by kinetic measurements, they were determined by a competitive method using *cis*- and *trans*-1,2 dideuterioethylene.

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(11) In several cases stable oxythallation adducts have been prepared and characterized.¹²⁻¹⁴

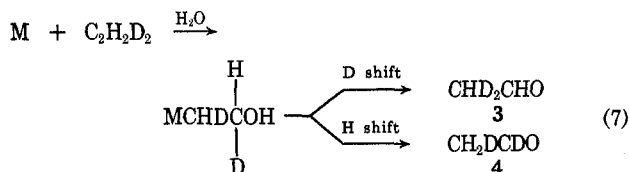
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Thus, as shown in eq 7 [M = Pd(II) or Tl(III)], either mode of hydroxymetalation will give a choice of



an H or a D transfer. The ratio of the tendencies for H to transfer as opposed to D is a measure of the isotope effect. Thus the 4/3 ratio measures the isotope effect. The value found for Pd(II) was 1.70 and that for Tl(III) was 1.92. These isotope effects, in conjunction with the kinetic isotope effects, support the earlier conclusion^{7,9} that hydroxymetalation is the rate-determining step in both oxidations.

The magnitude of the isotope effects is not large in either oxidation, suggesting that both bond breaking and bond making are important in the transition state.

Experimental Section

Reagents.—The preparation and analysis of the Tl(ClO₄)₃⁹ and palladium(II) chloride⁷ stock solutions have been described. The C₂D₄ was purchased from Volk Radiochemical Co., and the D₂O from Bio-Rad Laboratories.

Preparation of *cis*- and *trans*-Ethylene-*d*₂.—The procedures were essentially the same as that used previously for preparing *cis*- and *trans*-ethylene-*d*₂ from acetylene-*d*₂.¹⁶ However, in the present work undeuterated acetylene was reduced in D₂O. The reactions were carried out in a 750-ml soft-drink bottle capped with a metal cap having holes sealed by a rubber liner. The bottle could be evacuated or pressured with gas by means of syringe needles inserted through the rubber liner. An excess of the reducing solution (chromous chloride for the *trans* isomer and copper activated zinc for the *cis*)¹⁶ in about 150 ml of D₂O was prepared in the bottle and the bottle was evacuated. The bottle was then pressured to about 5 psig with acetylene and agitated on a mechanical shaker for several hours. Samples were removed by means of a syringe equipped with needle and analyzed by infrared and mass spectrometry. All the acetylene had reacted and each isomer could be shown to be uncontaminated by the other isomer by means of the infrared spectra.¹⁶

Oxidation Rates.—These reactions were carried out in tubes which were capped in the same fashion as the pop bottles. The volume of the tube is about 17 ml. Five milliliters of a Pd(II) or Tl(III) solution which was about 0.1 M in the metal ion and 0.5 M in HClO₄ was put in the tube, the tube was capped and evacuated, and the ethylene-*d*₄ or ethylene-*d*₂ was admitted to the tube. The tubes were agitated for periods from 1 to 10 min and then a gas sample was removed by means of a syringe for infrared. The tube was then opened, zinc dust was added to reduce any unreacted metal ion, and the perchloric acid was neutralized with sodium acetate. About 1 ml of solution was then injected into a gas chromatograph and the acetaldehyde peak was collected in a 100% collection tube and analyzed by mass spectrometry. This technique has been described.¹⁷ A 6-ft Carbowax 20M on ABS (70–80 mesh) column at 80° was used for the collection.

In the case of the ethylene-*d*₄ the deuterium content was obtained by the relative intensities of the parent ions.¹⁸ It was found that the quantities of lower deuterated acetaldehydes, such as acetaldehyde-*d*₃, increased with time; so the runs were carried to small conversions. Reaction times were 2 min or less. For both Tl(III) and Pd(II) the acetaldehyde-*d*₄ content was between 95 and 98% for triplicate runs with the remainder being mainly acetaldehyde-*d*₃.

The ethylene-*d*₂ runs were carried out in the same fashion. The deuterium distributions were determined by the ratio of the *m/e* 30 (CDO) and 29 (CHO) peaks. Previous work indicates¹⁸ that this should be a good measure of CD₂HCHO and CH₂DCDO contents.

Preliminary work indicated that *cis*- and *trans*-dideuteroethylenes both gave the same ratios of 3 and 4. Because of ease of preparation the *trans* isomer was used for the final quantitative work. The C₂H₂D₂O originally formed exchanged with solvent to give lower deuterated acetaldehydes. For that reason short reaction times were employed. Two runs with 0.28 M Tl(ClO₄)₃ in 2 M HClO₄ at reaction times of less than 10 min gave identical 4/3 ratios of 1.92. The formation of lower deuterated acetaldehydes which obscured the mass spectra results was particularly serious with PdCl₂. Apparently the Pd(0) precipitated in the course of reaction and caused the formation of monodeuterated ethylene as well as catalyzed *cis*-*trans* isomerization. The infrared spectra of the unreacted gases in runs with *trans*-C₂H₂D₂ indicated the presence of *cis*-C₂H₂D₂ and C₂H₃D. One run at a reaction time of 2 min gave a 4/3 ratio of 1.70. At times of 1 hr the ratio fell to 1.33.

In the Tl(III) runs no such isomerization or exchange of *trans*-C₂H₂D₂ was observed.

Kinetic Runs.—A constant-volume reactor was used for these studies. The apparatus and procedure have been described.⁷ As reported previously, the kinetics of undeuterated ethylene followed the expected second-order kinetics [first order in Tl(III) and first order in C₂H₄]. The value of *k*₂ at 25° and 0.5 M HClO₄ was found to be 0.63 M⁻¹ sec⁻¹, a value consistent with results at atmospheric ethylene pressure.⁹ In the present study the value of *k*₂ was determined using ethylene-*d*₄. The initial ethylene pressure was about 70 mm. The value of *k*₂ for duplicate runs were 0.76 and 0.82 M⁻¹ sec⁻¹.

Registry No.—Palladium, 7440-05-3; thallium, 7440-28-0; ethylene, 74-85-1; *cis*-ethylene-*d*₂, 2813-62-9; *trans*-ethylene-*d*₂, 1517-53-9; acetylene, 74-86-2; ethylene-*d*₄, 683-73-8; D₂O, 7789-20-0.

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Vapor-Phase Catalytic Dienol Dehydration. Influence of Various Metal Oxides on Product Distribution¹

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trans-1,5-Heptadien-4-ol was dehydrated over Al₂O₃, WO₃, and ZrO₂ at 250°, yielding 3-*trans*,5-*trans*-, and 3-*cis*,5-*trans*-1,3,5-heptatriene as primary dehydration products and methyl-1,3-cyclohexadienes resulting from thermal cyclization of the *cis*,*trans* isomer. 1,3,6-Heptatriene, arising from 1,4 dehydration, was also obtained in significant amounts from both WO₃ and ZrO₂. Tungsten oxide is much more reactive than either Al₂O₃ or ZrO₂ both as a dehydration catalyst and subsequently in causing isomerization of the dehydration products. Both ZrO₂ and WO₃ yield significantly higher 3-*cis*/3-*trans* isomer ratios, in the product trienes, than has previously been reported for alumina.

Recent investigations^{2–4} of various aspects of the

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