stoichiometry of the films. The knee in the curve corresponds to a change from intrinsic conductivity at the higher temperatures to impurity or extrinsic conductivity at the lower temperatures.[8] When too high a pressure of SbH_3 was used in preparing the films the resistances were almost independent of temperature (up to 300°K., the highest temperature used), apparently because excess antimony was produced. A heated probe on the purer films gave a potential corresponding to a p-type semiconductor at room temperature, so that again we conclude that the high-temperature slopes in Fig. 1 are partly due to surface impurities (principally oxygen). The resistances were too high for conventional Hall effect measurements.

Acknowledgments.—Most of this work was sponsored by the International Business Machines Corp. Richard A. Keller did much of the experimental work, and James N. Keith gave us many helpful suggestions.

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Preparation of Ruthenium(II) by Controlled Potential Reduction

BY GARRY A. RECHNITZ

Received March 27, 1962

Complexes of ruthenium(III) and (IV) have received considerable attention in the modern literature with regard to their solution chemistry and spectral characteristics.[1–5] Relatively little is known about the behavior of ruthenium(II) in solution, however. Jørgensen[6] has critically discussed the spectra of ruthenium(II) halide complexes in terms of crystal field theory.

Ruthenium(II) is commonly prepared in acid solution by reduction of ruthenium(III) or (IV) with zinc or cadmium amalgams, resulting in the inevitable introduction of foreign cations. While ruthenium(II) has been produced polarographically at microelectrodes,[7] attempts to prepare this species in perchloric acid media by controlled potential reduction at macroelectrodes[8] have been unsuccessful.

This author has found it possible to prepare stable solutions of ruthenium(II) in acidic chloride media by controlled potential reduction of ruthenium(IV) at a mercury pool electrode by accurate control of several critical factors. Polarographic work[7] has shown that ruthenium catalyzes the reduction of H^+ at mercury electrodes at surprisingly positive potentials in perchloric acid media. Preliminary polarographic experiments in hydrochloric acid media have shown similar effects. As a result, accurate control of the cathode potential is required in order to avoid hydrogen evolution while operating at potentials corresponding to the diffusion plateau of the ruthenium wave. The pH of the medium must be kept below 2.5 to avoid hydrolysis of ruthenium species.

The optimum conditions for the electrolytic production of ruthenium(II) at an applied potential of -0.470 ± 0.001 volts *vs.* s.c.e. were found in 4 *M* KCl solutions adjusted to pH 1.5 with HCl. Best results were obtained in solvent deaerated with N_2 and pre-electrolyzed under experimental conditions to remove reducible impurities. Under these conditions, lavender-blue solutions of $RuCl_4^{-2}$, having characteristic absorption maxima at 538 and 610 mμ, were produced. The spectra obtained are in good agreement with those of Jørgensen,[6] who prepared ruthenium(II) in 2 and 6 *M* HCl by reduction with zinc amalgam. No spectral evidence for the presence of ruthenium(III) or (IV) was found after completion of electrolysis.

Graphical integration of current–time curves for the reduction of K_2RuCl_6 by this method yielded values of 2.01 ± 0.01 for *n*, the number of electrons involved in the electrode process. Plots of log current *vs.* time gave good straight lines as a further indication of 100% current efficiency. The coulometric data are summarized in Table I.

Experimental

K_2RuCl_6 (A. D. MacKay, Inc., New York, N. Y.) was used as a source of ruthenium(IV). All other chemicals

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TABLE I

COULOMETRIC n-VALUES FOR THE REDUCTION OF Ru(IV) IN 4 M KCl (pH 1.5)

Applied potential = −0.470 v. *vs.* s.c.e.

Ruthenium(IV), mmoles	mfaradays consumed	n
0.171	0.346	2.02
.168	.337	2.01
.172	.342	1.99
		Mean 2.01 ± 0.01

were of reagent grade. Cathode potentials were controlled by means of a Model 600 electronic potentiostat (Duffers Associates, Inc., Troy, N. Y.). Electrolyses were carried out in a cell providing a mercury pool cathode of 184 cm.^{2} area and a platinum gauze anode separated from the cathode compartment by a "fine" fritted glass disk. A Leeds and Northrup saturated calomel electrode served as a reference. The catholyte was continuously purged with N_2 during electolysis and kept at 25 ± 0.2°. Spectra were recorded with a Beckman DB UV-visible spectrophotometer.

Acknowledgment.—The financial support of the Laboratory for Research on the Structure of Matter, University of Pennsylvania, is gratefully acknowledged.

CONTRIBUTION FROM THE
ESSO RESEARCH AND ENGINEERING COMPANY,
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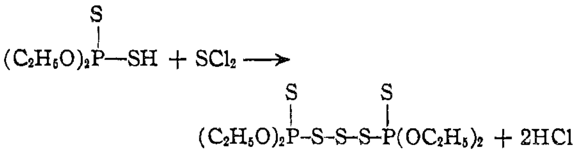
The Oxidation of O,O-Diethyl Hydrogen Dithiophosphate and its Polysulfides

BY GERSHON METZGER

Received March 12, 1962

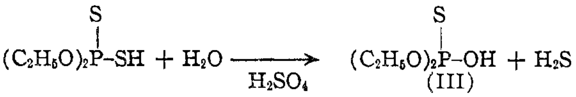
It has been reported[1] that oxidation of O,O-diethyl hydrogen dithiophosphate with concentrated sulfuric acid results in the formation of bis-(diethoxythiophosphoryl) disulfide, $(C_2H_5O)_2\overset{S}{P}\text{-}S\text{-}S\text{-}\overset{S}{P}(OC_2H_5)_2$ (I). Re-investigation of this reaction has shown that the reaction product is actually a mixture of (I) and bis-(diethoxythiophosphoryl) trisulfide,[2] $(C_2H_5O)_2\overset{S}{P}\text{-}S\text{-}S\text{-}S\text{-}\overset{S}{P}(OC_2H_5)_2$ (II). The identity of the latter was confirmed by a mixed melting point determination (m.p. 72–73°) with an authentic sample prepared by the reaction



$$(C_2H_5O)_2\overset{S}{P}\text{—}SH + SCl_2 \longrightarrow (C_2H_5O)_2\overset{S}{P}\text{-}S\text{-}S\text{-}S\text{-}\overset{S}{P}(OC_2H_5)_2 + 2HCl$$

Compound I can originate *via* a straightforward oxidation of O,O-diethyl hydrogen dithiophosphate or one of its metal salts. In fact, a large variety of other oxidizing agents generate (I) as well, *e.g.*, Cl_2,[3,4] I_3^-,[5] HNO_2,[5] H_2O_2,[3] etc. The formation of compound II, however, is complicated by some mechanism that makes an extra sulfur atom available during the oxidation of the free acid.

The oxidation of O,O-diethyl hydrogen dithiophosphate with either iodine or H_2O_2 results in a quantitative yield of (I). When Na_2S (an obvious source of sulfur) is added to the iodine oxidation, or when the H_2O_2 oxidation is carried out in strongly acidic media, some of (II) is obtained as well. This suggests that the extra sulfur required in the H_2SO_4 oxidation process may result from hydrolysis and subsequent oxidation of the H_2S produced by hydrolysis



$$(C_2H_5O)_2\overset{S}{P}\text{-}SH + H_2O \xrightarrow[H_2SO_4]{} \underset{(III)}{(C_2H_5O)_2\overset{S}{P}\text{-}OH} + H_2S$$

Compound III has been isolated and identified. Its potassium salt was prepared and the melting point, 195–197°, is in excellent agreement with the literature value[6] of 196–197°. The amount of compound III obtained was approximately equivalent to the amount of compound II found. These observations are consistent with the above mechanism if (III) is stable to further hydrolysis even in strongly acidic media.

It thus has been demonstrated that the straightforward oxidation of O,O-diethyl hydrogen dithiophosphate to its disulfide can be modified so that some trisulfide is produced as well. The modification consists essentially of making reactive elemental sulfur available during the course of the reaction.

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