Experimental

Reagents.—All chemicals used were the best quality commercially available. Titanium(III) chloride was obtained from Stauffer Chemical Co., the o-$C_6H_4(CN)_2$ was Eastman Kodak White Label grade recrystallized twice from benzene, $(C_6H_5)_3$-SiOH was obtained from General Electric Co., and $(C_6H_5)P(O)$-$(OH)_2$ from Eastman Kodak Co.

TiPcCl₂.—About 5 g. of TiCl₃ was weighed by difference in a nitrogen-containing dry bag.[5] An amount of o-$C_6H_4(CN)_2$ equivalent to two times the number of moles of TiCl₃ taken and 150 ml. of 1-chloronaphthalene were added to the flask while the system was protected from the atmosphere with a blanket of nitrogen. The mixture was then heated with stirring under nitrogen. At 180° a red liquid (presumably an addition compound of TiCl₄ with 1-chloronaphthalene[6]) began to distil and continued to come over as the temperature rose to 252°, the boiling point of 1-chloronaphthalene. After the liquid distilling over was no longer red, the mixture was refluxed another 0.5 hr. and then allowed to cool to room temperature. All subsequent handling was also done under nitrogen. The mixture was filtered to yield a dark bluish purple solid which was washed with six 75-ml. portions of dry benzene and three 75-ml. portions of diethyl ether and then dried, first with a stream of nitrogen and then by pumping. Yields were 95–98%.

Anal. Calcd. for $C_{32}H_{16}Cl_2N_8Ti$: C, 60.9; H, 2.6; Cl, 11.2; N, 17.8; Ti, 7.6. Found: C, 60.6; H, 2.9; Cl, 11.1; N, 17.6; Ti, 7.9.

(TiPcO)ₓ.—A mixture of 2.0 g. of TiPcCl₂, 1 ml. of triethylamine, and 150 ml. of 95% ethanol was refluxed for 4–5 hr. and then allowed to cool to room temperature. When cool, the mixture was filtered, and the dark blue residue was washed well with 95% ethanol and then with diethyl ether. The dried product corresponded to a quantitative yield of TiPcO.

Anal. Calcd. for $C_{32}H_{16}N_8OTi$: C, 66.7; H, 2.8; N, 19.4; Ti, 8.3. Found (two runs): C, 66.4, 66.4; H, 3.8, 2.6; N, 19.6, 19.7; Ti, 8.3, 7.7.

[TiPcOP(C₆H₅)O₂]ₓ.—To 2 g. of TiPcCl₂ and 0.5 g. of C_6H_5PO-$(OH)_2$ was added under nitrogen flush 100 ml. of benzene dried over Linde 4A Molecular Sieves. Then 25 ml. of pyridine was added, and the mixture was refluxed with stirring under nitrogen overnight, cooled, and filtered. After the residue was washed with benzene, methanol, and diethyl ether, it was dried in an oven at 100° to give 2.22 g. of blue-green solid.

Anal. Calcd. for $C_{38}H_{21}N_8O_3PTi$: C, 63.7; H, 3.0; N, 15.6; P, 4.3; Ti, 6.7. Found (two runs): C, 62.9, 63.0; H, 3.3, 4.2; N, 15.2, 14.8; P, 4.5, 4.3; Ti, 8.6, 6.7.

TiPc[OSi(C₆H₅)₃]₂.—A 1.9-g. sample of triphenylsilanol was placed in a flask with 100 ml. of benzene and excess sodium metal cut into small pieces. Nitrogen was passed through the flask while the mixture was refluxed with stirring for 1 hr. The mixture was then allowed to cool and filtered under nitrogen into another flask containing 2.0 g. of TiPcCl₂. The new mixture was refluxed with stirring overnight, cooled, and filtered. The residue was then extracted for 24 hr. with the filtrate in a Soxhlet extractor. After the extracting solvent had cooled, it was filtered to yield a solid which was washed sparingly with methanol and diethyl ether and dried. There resulted 1.53 g. (44% yield) of green solid which melted at 340°.

Anal. Calcd. for $C_{68}H_{46}N_8O_2Si_2Ti$: C, 73.5; H, 4.2; N, 10.1; Si, 5.1; Ti, 4.3. Found: C, 73.0; H, 4.7; N, 10.3; Si, 4.7; Ti, 4.4.

Spectra.—Infrared spectra were determined for Nujol mulls on a Perkin-Elmer Model 221 infrared spectrophotometer. Lines common to the spectra (cm.$^{-1}$) were 1607 ± 4 m, 1500 ± 8 m, 1408 ± 8 m, 1330 ± 2 s, 1284 ± 4 m, 1156 ± 1 m, 1117 ± 2 ms, 1070 ± 3 ms, 1056 ± 2 ms, 896 ± 4 m, 774 ± 2 m, 750 ± 3 m, and 724 ± 3 m. Additional bands were observed as follows. TiPcCl₂: 1038 m, 998 w, 969 vw, 891 m, 879 w, 839 w, 808 m, 783 m, 779 m, 721 m, 681 vw; (TiPcO)ₓ: 972 m, 967 m, 837 w,

803 w; [TiPcOP(C₆H₅)O₂]ₓ: 1138 m, 1007 s, 969 m, 823 w, 693 m, 665 m; TiPc[OSi(C₆H₅)₃]₂: 1590 m, 1429 m, 1305 ms, 1104 m, 1043 s, 998 w, 971 w, 944 w, 886 vs, 800 w, 766 w, 736 m, 711 m, 707 m, 697 s.

Thermogravimetric Analysis.—The standard thermogravimetric analysis procedure developed in our laboratories[7] (nitrogen atmosphere, 5°/min. heating rate) showed weight losses starting at 385° for TiPcCl₂, 475° for (TiPcO)ₓ, 400 to 460° for [TiPcOP(C₆H₅)O₂]ₓ, and 350° for TiPc[OSi(C₆H₅)₃]₂.

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Metal Ion–Solvent Reactions.
I. Kinetics of the Oxidation of Ruthenium(II) by Water

BY G. A. RECHNITZ AND H. A. CATHERINO

Controlled-potential electrolysis has made possible the preparation of powerful oxidizing or reducing agents without the introduction of other reaction products.[1] Such electrolytically-generated species of unusual oxidation states, produced under circumstances which leave little doubt as to their identity, may react with other oxidation–reduction species present in solution to give information about the kinetics of homogeneous electron-transfer processes.[2] Since an understanding of possible oxidation–reduction reactions between ionic species and the solvent is necessary before this method can be applied to studies of more complicated systems, an examination of the oxidation of ruthenium(II) in aqueous media was undertaken.

The rate of oxidation of ruthenium(II) was monitored by following the change in the height of the absorption peak at 690 mμ attributed to the species $RuCl_4{}^{2-}$. The ruthenium(II) concentration was calculated using the molar absorptivity, estimated at 1100 by Jørgensen.[3] The oxidation was found to be a pseudo-first-order process in deaerated acid-chloride media. First-order rate constants calculated from experimental runs carried out by varying the initial concentrations of ruthenium(II) in 2.5 M KCl (pH 1.5) at 30.0° are summarized in Table I. Since first-order rate constants are independent of the absolute concentration of the reacting species, any uncertainties in the value of the

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TABLE I
RATE CONSTANTS DETERMINED AT $[Cl^-]$ = 2.5 M AND pH
1.5 AT 30.0°

| Initial Ru(II) concn., mM	k, sec.$^{-1}$
0.216	4.65×10^{-5}
0.278	4.48×10^{-5}
0.183	4.90×10^{-5}
0.921	4.48×10^{-5}

Average = $4.64 \pm 0.15 \times 10^{-5}$ sec.$^{-1}$

TABLE II
TEMPERATURE DEPENDENCE OF THE RATE CONSTANT; pH
1.5 AND $[Cl^-]$ = 2.5 M

T, °C.	k, sec.$^{-1}$
30.0	4.64×10^{-5}
36.0	10.0×10^{-5}
40.0	14.8×10^{-5}
40.0	19.7×10^{-5}
44.5	34.2×10^{-5}
44.5	35.0×10^{-5}

molar absorptivity used are of no consequence here. That ruthenium(II) is quantitatively oxidized to ruthenium(III) is shown by the fact that the ratio of the absorbance changes at 322 mμ (due to Ru(III)) to those at 690 mμ (due to Ru(II)) remains constant during the course of the reaction. An isosbestic point in the spectra occurring at 359 mμ further supports the conclusion that 1 mole of ruthenium(III) is produced for each mole of ruthenium(II) consumed. Excess ruthenium(III) appeared to have no effect on the rate of the reaction.

Studies at 30° and pH 1.5 showed the rate to be approximately independent of chloride ion concentration; values of k as a function of $[Cl^-]$ are ($[Cl^-]$, $k \times$ sec.) 1.00 M, 4.83×10^{-5}; 2.00 M, 4.65×10^{-5}; 2.50 M, 4.70×10^{-5}; 3.25 M, 4.68×10^{-5}; and 4.00 M, 5.65×10^{-5}. Similarly, the absence of a pH effect upon the rate was shown by experiments at constant chloride concentration (2.5 M); values of k as a function of pH are (pH, $k \times$ sec.) 0.47, 4.88×10^{-5}; 0.48, 4.65×10^{-5}; 1.01, 4.48×10^{-5}; and 1.50, 4.64×10^{-5}. Experiments were effectively limited to the pH range indicated because of simultaneous hydrogen evolution during electrolytic generation of ruthenium(II) at lower pH values and the formation of insoluble ruthenium products at higher pH values. To evaluate the possible effect of trace oxygen contamination on the kinetics of the reaction, experiments were carried out in deaerated and air-saturated media. These experiments gave substantially identical results; any interfering reaction with oxygen, if it occurs at all, must therefore be considerably slower than the primary reaction. We conclude, therefore, that water itself acts as the oxidizing agent. This conclusion is in agreement with the early results of Manchot and Schmid,[4] who observed hydrogen evolution in aqueous systems containing reduction products of RuCl$_3$. Under the experimental conditions present in both cases, ruthenium(II) undergoes the over-all reaction

$$Ru(II) + H_2O = Ru(III) + \tfrac{1}{2}H_2 + OH^- \qquad (1)$$
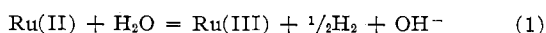
as is shown by the experimental findings that ruthenium(III) is produced in direct 1:1 ratio to the ruthenium consumed and that hydrogen gas is generated during the reaction process. Efforts were made to detect the production of OH^-, as well, but failed owing to the high H^+ concentration of the reaction medium compared to the amount of OH^- formed. From the data of Table II, the Arrhenius activation energy was calculated as 26.4 kcal./mole for the over-all reaction. Since reaction 1 involves the net rupture of a hydrogen–oxygen bond, a deuterium isotope effect was sought. When D$_2$O was used as a solvent, all other conditions being held constant, an average rate constant of $k_{D_2O} = 3.8 \pm 0.1 \times 10^{-5}$ sec.$^{-1}$ at 30.0° was found. Thus $k_H/k_D < 1.2$, a value too small to be attributed to the rupture of a hydrogen–oxygen bond in the rate-determining step.[5] A reaction mechanism consistent with these findings involves a one-electron reduction of water as the rate-determining step according to the scheme

$$H_2O + Ru(II) \overset{slow}{=} H_2O^- + Ru(III) \qquad (2)$$
$$H_2O^- + H^+ \overset{fast}{=} H + H_2O \qquad (3)$$
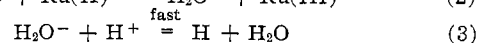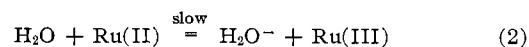
The rate constant for reaction 3 has been determined by Gordon, Hart, Matheson, Rabini, and Thomas[6] in their studies on the properties of the hydrated electron and equals 2.36×10^{10} M^{-1} sec.$^{-1}$ at 22°. Although the absorption spectrum of the hydrated electron is well known,[7] the presence of this species could not be demonstrated because of its extremely low steady-state concentration. Scavenger techniques[6] may provide a possible means of confirmation.

Experimental

K$_2$RuCl$_6$ obtained from A. D. Mackay, Inc., New York, N. Y., was used as a source of ruthenium. All other chemicals were of reagent grade. Ruthenium(II) was prepared by controlled-potential electrolysis in a procedure similar to that of Rechnitz.[8] The electrolyses were carried out with a Wenking Model 6261TR potentiostat in a double diaphragm cell with a conical electrode compartment.[9] A saturated silver–silver chloride reference electrode (s.s.c.e.), described by Lingane,[10] and a platinum gauze anode were used. The catholyte was purged with prepurified nitrogen during the electrolysis. A potential of -0.3 v. $vs.$ s.s.c.e. on the mercury pool cathode proved sufficient for quantitative conversion of ruthenium(IV) to the characteristic, blue RuCl$_4^{2-}$ species. A small quantity of the ruthenium(II) solution was transferred into a stoppered spectrophotometer cell and its change of absorbance at 690 mμ followed using a Perkin-Elmer Model 202 spectrophotometer equipped with a thermostated cell holder. For the study of the deuterium isotope effect, D$_2$O (99.7%) was obtained from Merck Sharpe and Dohme, Canada.

The formation of hydrogen gas as a reaction product was confirmed by a modification of the gas chromatographic procedure of Kilner and Ratcliff[11] using a Precision Scientific Co. Model VP-1 gas chromatograph equipped with a heated 10-in. calcium sulfate pre-column to remove water vapor and a 12-in. separation column

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of 60 mesh 5 Å. molecular sieve operated at room temperature. For the hydrogen detection experiments all coulometric and kinetic work was carried out under an atmosphere of argon which also served as the carrier gas in the chromatographic system. By calibrating the system with hydrogen-saturated solvent, we were clearly able to show (on the basis of retention times at constant flow rate and temperature) that hydrogen gas is a product of the ruthenium(II) oxidation. No other gaseous products were detected. Attempts were also made to measure the amount of hydrogen produced using a comparison of peak heights with chromatograms obtained from known samples of hydrogen gas. For a solution having an initial ruthenium(II) concentration of 9.7×10^{-3} M, the final hydrogen concentration was determined as approximately 4×10^{-3} M. These results are consistent with the observed conversion of ruthenium(II) to (III) but should be viewed with caution because the hydrogen determination is semiquantitative, at best.

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Lewis Acid Adducts of Group IV-A Azides[1]

BY JOHN S. THAYER[2] AND ROBERT WEST

The isolation of complexes having the formula $(C_6H_5)_3MN_3 \cdot P(C_6H_5)_3{}^{3-5}$ and the lability of $(CH_3)_3SiN_3$ in the presence of $AlCl_3{}^{6,7}$ suggested that group IV-A azides might act as Lewis bases. We find that the Lewis acids $SnCl_4$, BBr_3, and $SbCl_5$ form stable 1:1 adducts with azides of Si, Ge, and Sn. During our investigation, Goubeau, *et al.*, prepared $CH_3N_3 \cdot SbCl_5{}^8$ and Wiberg and Schmid reported the reaction of silyl azides with $SbCl_5$.[9,9a]

All of the complexes isolated, except for $CH_3(C_6H_5)_2SiN_3 \cdot BBr_3$, were white solids that decomposed without melting. They dissolve without appreciable dissociation in dichloromethane, chloroform, carbon tetrachloride, and benzene; contact with water, alcohols, or acetone causes immediate decomposition.

Wiberg and Schmid report that $(C_6H_5)_3SiN_3$ or $(CH_3)_3SiN_3$ reacts with antimony pentachloride to give the chlorosilane and $(SbCl_4N_3)_2$ directly.[9] We found that

(1) Presented in part before the Inorganic Division of the American Chemical Society at the 147th National Meeting, Philadelphia, Pa., April 9, 1964.

(2) To whom correspondence should be directed at the Department of Chemistry, Illinois Institute of Technology, Technology Center, Chicago, Ill.

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(9a) NOTE ADDED IN PROOF.—H_3SiN_3 reacts with BF_3 to give SiH_4 and SiH_3F: E. A. V. Ebsworth and M. J. Mays, *J. Chem. Soc.*, 3450 (1964).

$SbCl_5$ adducts are indeed unstable, but that $(CH_3)_3SiN_3 \cdot SbCl_5$ could be isolated from dilute carbon tetrachloride solution. Under the same conditions, $CH_3(C_6H_5)_2SiN_3$ and $SbCl_5$ reacted violently to give off large quantities of gas and leave an unidentified black residue. In contrast, complexes of silyl azides with tin tetrachloride or boron tribromide are quite stable. $CH_3(C_6H_5)_2SiN_3 \cdot BBr_3$, when heated for 2 hr. at 200° and 0.5 mm., distilled unchanged into a cold trap, leaving only traces of tars. Under similar conditions, $(CH_3)_3SiN_3 \cdot BBr_3$ dissociated and recombined on cooler surfaces, forming white crystals identical with the starting material. $(CH_3)_3SiN_3 \cdot SnCl_4$, heated at 190° and 0.5 mm. for 3 hr., remained unaffected, except for formation of traces of a black tar. This great thermal stability is in marked contrast to the compounds $(CH_3)_3SiCN \cdot BX_3$ (X = halogen), which decompose rapidly below room temperature.[10]

Azide band positions in the complexes differ markedly from those of the free azides[3,11]; they are listed in Table I. In addition, all silyl azide complexes show a strong band at about 980 cm.$^{-1}$ not present in other complexes. This may be due to the Si–N–A stretching mode, which appears in the 900–1000 cm.$^{-1}$ region in silazanes and related compounds.[12]

There are two possible sites where electron donation might occur: the nitrogen bonded to the organometallic group (the α nitrogen) or the terminal nitrogen. The azide band shifts and the new band at 980 cm.$^{-1}$ for silyl compounds are more compatible with the α-bonded structure shown below, which has also been proposed for $(C_6H_5)_3SiN_3 \cdot P(C_6H_5)_3$,[3] $CH_3N_3 \cdot SbCl_5$,[8] and the reaction intermediate of R_3SiN_3 with $SbCl_5$.[9]
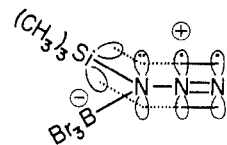
Experimental

Reagents.—Azides were prepared by the general methods described previously.[3,11] Boron tribromide was obtained from American Potash and Chemical Co. Antimony pentachloride was purchased from J. T. Baker Chemicals Co., and tin tetrachloride from Matheson Coleman and Bell. All solvents used were spectral grade. Benzene was distilled from sodium before use.

Spectra.—Infrared spectra were run on a Perkin-Elmer Model 237 double-beam recording spectrophotometer linear in wave number. Sodium chloride plates were used for solid mulls and liquid films, while matched 0.05 and 0.2 mm. cells were used for solutions. Polystyrene peaks at 2850, 1603, and 906 cm.$^{-1}$ were used for calibration. All frequencies are accurate to ± 5 cm.$^{-1}$. Carbon tetrachloride was the solvent of choice for solution spectra, although dichloromethane and chloroform were also used. Concentrations of the complex ranged from 0.01 to 0.1 M; excess Lewis acid was often, though not invariably, added. Solution spectra were not noticeably different from the spectra of the free complex.

Azide–Lewis Acid Complexes.—Samples of purified azides were dissolved in a suitable solvent, usually carbon tetrachloride,

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