[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Electrolytic Reduction of Perrhenate. II. Studies in Sulfuric Acid

BY PHILIP WEHNER AND J. C. HINDMAN

RECEIVED DECEMBER 1, 1952

Depending on the acid concentration and the potential used, perrhenate may be cathodically reduced to Re(V) or Re(IV) in sulfuric acid. These lower states are not obtained in solution but as suspensions, frequently colloidal in nature. Reductions in concentrated acid give indications of the formation of an unstable Re(VI) state. The action of oxygen on Re(V) and Re(IV) suspensions in dilute sulfuric acid produces violet-colored true solutions that may be reduced to amber solutions. The oxidation states of the rhenium in these solutions differ by one-half unit. Though it has not yet been possible to identify definitely the actual oxidation states, preliminary results indicate the amber is a Re(V) species and the violet a mixed Re(V)–Re(VI) species.

Examination of the literature reveals that the solution chemistry of rhenium in acid sulfate media is one of unusual complexity and still inadequately understood, even with respect to its more general features. The investigation described here, primarily a study of the controlled-potential electrolytic reduction of perrhenic acid, was undertaken to acquire more information about the oxidation states below Re(VII) (perrhenate) in sulfuric acid solutions. Similar studies of the reduction of perrhenate in various other acidic media have been described in Part I of this series.[1]

From potentiometric titrations of potassium perrhenate with various reducing agents Holemann[2] concluded that Re(V) could be obtained, though not quantitatively, in strong sulfuric acid as either a weak sapphire-blue or a deep wine-red species. Though he could not definitely establish the oxidation state associated with intermediate violet colors observed in concentrated acid, he ascribed these colors to Re(VI). Tomicek and Tomicek[3] also observed that perrhenate was reduced by certain amalgams to violet or violet-blue species in concentrated or 90% acid, and to a sky-blue state in 60–80% acid, but they obtained no indication of a red state. Titrations indicated the oxidation state of the sky-blue species corresponded approximately to Re(V), but the violet species could not definitely be identified. Existence of a red Re(V) state as well as a bluish-violet Re(VI) state was however reported by Manchot, Schmidt, and Dusing[4] who studied the absorption of oxygen by Re(III). Whereas Holemann had concluded that the V and VI states could be obtained only at high acid concentrations, Manchot and co-workers reported formation of these states in 1 *M* sulfuric acid.

At acid concentrations below 7 *M* the reductions of Holemann and Tomicek and Tomicek usually produced olive-green or dark brown solutions, in some of which suspended solid was visible. The latter investigators found that the olive solutions changed to the dark brown on standing but that the average oxidation state in each was approximately Re(IV). Additional evidence that Re(IV) existed as a brown species had previously been reported by Manchot and co-workers who observed that the first equivalent of oxygen absorbed by Re(III) in 1 *M* sulfuric acid resulted in formation of a dark brown solution.

Various investigators have reported the preparation of states such as Re(III), Re(II) and Re(I) in sulfuric acid by the reduction of certain chloro derivatives[4–6] or by oxidation of Re(−1)[7–9] In general however such states have not been obtained in solution as direct reduction products of perrhenate, though Young and Irvine[10] claimed preparation of the insoluble black oxides Re_2O and ReO. The action of powerful reducing agents on perrhenate in dilute acid seems rather to lead to the colorless Re(−1) state.[3,7,9,11,12]

Experimental

Materials.—Solutions of perrhenic acid in sulfuric acid were prepared by dilution of a 0.482 *M* solution of perrhenic acid which had been prepared in the manner described in Part I.[1]

Apparatus and Procedure.—Details of the potentiostat, cells, reference electrodes, bridges and coulometer have been given in a previous publication.[13] Agitation of the anolyte and catholyte was accomplished by streams of prepurified nitrogen; when mercury cathodes were used additional agitation of the mercury–electrolyte interface was obtained with a motor driven stirrer. Unless otherwise noted, electrolyses were performed at 25°.

At each sulfuric acid concentration a current–potential curve was obtained by rapidly changing the cathode potential and noting the current that flowed. Owing to finite depletion of the reducible species and formation of cathode deposit such curves were somewhat distorted; however, they were of value for selecting potentials at which to carry electrolyses to completion.

Absorption spectra were measured on a Cary recording spectrophotometer, the cell compartment of which was maintained at 25 ± 0.5°.

Analytical Methods.—In the absence of competing processes, such as the deposition of hydrogen, coulometer readings indicated the average oxidation state to which the rhenium had been reduced. Further identification was frequently accomplished by dissolution of the products in hydrochloric acid under nitrogen and examination of the absorption spectra of the resultant solutions; as discussed previously[1] the Re(V) and Re(IV) states have distinctive ultraviolet absorption spectra in hydrochloric acid.

Titration back to perrhenate with standard ceric sulfate

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[1] J. C. Hindman and Philip Wehner, THIS JOURNAL, **75**, 2869 (1953).

[2] H. Holemann, *Z. anorg. allgem. Chem.*, **220**, 33 (1934).

[3] O. Tomicek and F. Tomicek, *Collection Czechoslov. Chem. Communs.*, **11**, 626 (1939).

[4] (a) W. Manchot, H. Schmidt and J. Dusing, *Ber.*, **64**, 2905 (1931); (b) W. Manchot and J. Dusing, *Z. anorg. allgem. Chem.*, **212**, 21 (1933).

[5] W. Manchot and J. Dusing, *Ann.*, **509**, 228 (1934).

[6] I. Noddack and W. Noddack, *Z. anorg. allgem. Chem.*, **215**, 129 (1933).

[7] G. E. F. Lundell and H. B. Knowles, *J. Research Natl. Bur. Standards*, **18**, 629 (1937).

[8] C. L. Rulfs and P. J. Elving, THIS JOURNAL, **73**, 3287 (1951).

[9] J. J. Lingane, *ibid.*, **64**, 2182 (1942).

[10] R. C. Young and J. W. Irvine, Jr., *ibid.*, **59**, 2648 (1937).

[11] E. K. Maun and N. Davidson, *ibid.*, **72**, 3509 (1950).

[12] R. Geyer *Z. anorg. allgem. Chem.*, **263**, 47 (1950).

[13] P. Wehner and J. C. Hindman, THIS JOURNAL, **72**, 3911 (1950).

was also employed to establish the oxidation states of the products, though the fact that the lower states were nearly always obtained as suspensions rendered sampling difficult. Aliquots of the preparations were added to standard 0.01 *N* ceric sulfate, and the excess ceric sulfate was back-titrated with ferrous sulfate. Total rhenium concentrations were determined by adding aliquots to 1 *M* perchloric acid and warming at 70–80° for 2–3 hours. Under such conditions clean oxidation to perrhenic acid resulted, and the concentration of the perrhenic acid was then determined from the height of its strong absorption band at 2275 Å., using E_M = 3620 (see Part I). Such determinations were believed to be accurate to within 1 to 2%.

Results and Discussion

Reduction of perrhenic acid, $HReO_4$, at platinum cathodes invariably resulted in the formation of cathode deposit, even in concentrated sulfuric acid. The fraction of the lower oxidation states not deposited on the cathode in this manner was generally dispersed in the catholyte as a colloidal or gross suspension, presumably of oxide or hydrated oxide. Only at acid strengths as high as 16.9 *M* were there any indications that a state below Re(VII) could be directly obtained even in low yield, as a true solution. Similar formation of insoluble material was observed in electrolyses at mercury cathodes. However, reduction at this cathode was not investigated very extensively inasmuch as mercury itself is capable of reducing perrhenate at sulfuric acid concentrations of 12 *M* or higher.

Typical current–potential curves for the reduction of perrhenic acid at platinum cathodes are given in Fig. 1. Though these curves must be interpreted with reservation because of the formation of cathode deposit, they illustrate that the ease of reduction of Re(VII) increases with increasing sulfuric acid concentration and that at high acidities stepwise reduction of the perrhenate is possible.

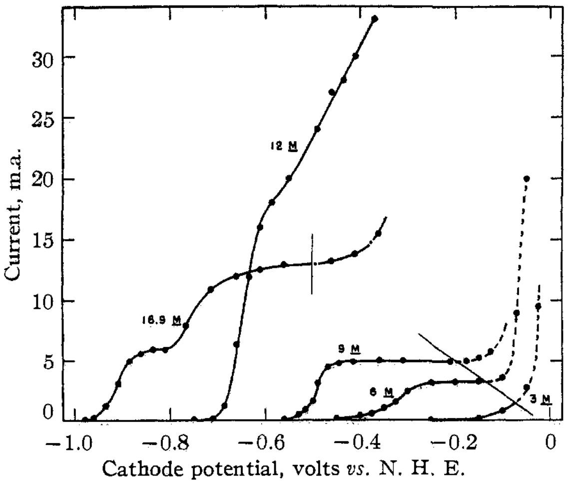

Fig. 1.—Current–potential behavior of 0.024 *M* $HReO_4$ at platinum cathodes; H_2SO_4 concentrations as indicated in figure; ------------, region of hydrogen discharge; · — · —, region of reduction of sulfuric acid.

Reductions in Strong Acid.—The rather poorly defined waves in the current–potential curve for 12 *M* acid appear to correspond to the steps Re(VII) → Re(V) → Re(IV). Thus reduction of 0.024 *M* $HReO_4$ in 12 *M* sulfuric acid at a cathode (Pt) potential of −0.55 v. ceased at a coulometer reading of Re(4.80) and produced a dark-blue colloidal suspension. On the other hand reduction at −0.20 v. proceeded to Re(4.20) and gave a brown-black colloidal suspension. Dissolution of the blue suspension in 10 *M* HCl produced a greenish-yellow solution that exhibited primarily Re(V) absorption in the ultraviolet region (Fig. 1). Similar treatment of the black cathode deposit indicated this material was primarily Re(V) together with some Re(IV). Saturation of the blue suspension with oxygen for 20 hours produced no visible change, but titrations with ceric sulfate following this treatment gave the values 5.11 and 5.23 for the oxidation state of the rhenium.

The first wave in the current–potential curve in 16.9 *M* acid also appears to correspond to the process Re(VII) → Re(V). Electrolysis of 0.024 *M* $HReO_4$ in 16.9 *M* sulfuric acid at a cathode (Pt) potential of −0.81 v. ceased at Re(5.13) and resulted in a black catholyte suspension. Dissolution in 10 *M* hydrochloric acid and subsequent spectrophotometric examination indicated this catholyte contained primarily Re(V) (Fig. 2). In a similar manner the black cathode deposit was found to contain only Re(V). When the black catholyte suspension was treated with sufficient water to lower the sulfuric acid concentration to 12 *M* and then stored under nitrogen for 20 hours, it assumed the previously observed dark blue appearance. The solid was isolated from this dark blue suspension by centrifugation, washed with 6 *M* sulfuric acid and resuspended in 12 *M* acid. Three titrations of the resultant dark blue suspension with ceric sulfate gave 5.05 ± 0.02 for the oxidation state of the rhenium.

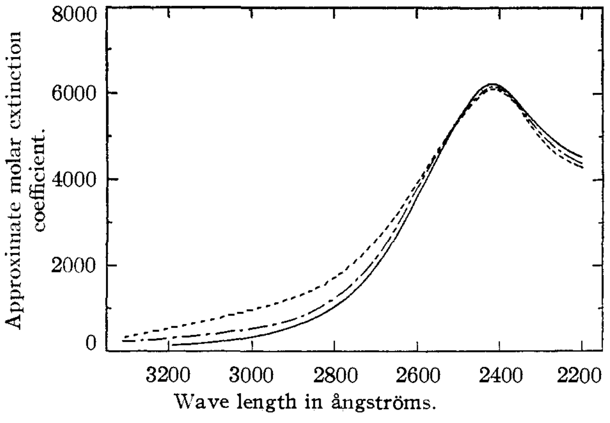

Fig. 2.—Spectra in 10 *M* hydrochloric acid: —, Re(V) prepared electrolytically in 8 *M* HCl; ----, catholyte from reduction in 12 *M* H_2SO_4; —-—, catholyte from reduction in 16.9 *M* H_2SO_4.

Reduction in 16.9 *M* acid at a cathode (mercury) potential of −0.57 v. proceeded past Re(V) to give a brown-black colloidal suspension. Though the electrolysis was not carried to completion, it seems probable that reduction to Re(IV) was taking place and that the second waves in 12 and 16.9 *M* acid both correspond to this step.

During the initial states of the reduction of perrhenic acid to Re(V) in 16.9 *M* acid at −0.81 v., pink to violet-red catholyte colorations were observed. Interruption of the electrolysis after only a few per cent. of the perrhenate had been reduced resulted in slow dissolution of the black cathode deposit and intensification of the catholyte color. Since the cathode deposit was found to be Re(V), this behavior suggested that the red species was Re(VI). Additional reductions in 16.9 to 17.8 *M* acid were therefore carried out at more negative (Pt) potentials, -0.94 to -1.01 v., and elevated temperatures, 50 to 75° (to accelerate removal of the cathode deposit). Such electrolyses did not proceed to definite end-points close to Re(VI) but did produce in the initial states intense violet-red solutions. These solutions were, however, unstable and on standing changed to intense blue, colloidal suspensions. The formation of the blue solid indicated production of Re(V), and ultraviolet absorption spectra indicated a simultaneous increase in the perrhenate content. These observations suggest a disproportionation reaction and give support to the supposition that the red species is Re(VI).

Reductions at Lower Acid Strengths.—The 9 *M* acid current–potential curve shows a definite single plateau, but reductions at potentials on this plateau failed to produce a pure oxidation state, apparently because excessive deposition on the platinum cathodes eventually interfered with the electrolyses. Reduction of 0.096 *M* perrhenic acid in 8.5 *M* sulfuric acid at -0.42 v. ceased at a coulometer reading of Re(4.63) and produced a dark blue-black suspension. Reduction of 0.024 *M* perrhenic acid in 9 *M* sulfuric acid at -0.36 v. ceased at Re(4.42); in the early stages the catholyte had a dark blue appearance but the final product was a nearly opaque black suspension. Such reductions to average states between Re(V) and Re(IV) suggest that the current–potential wave actually corresponds to Re(VII) → Re(IV). On the other hand the blue appearance of the catholytes at certain stages of reduction indicate some formation of Re(V). This is unexpected inasmuch as the current–potential curve gives no indication of successive reduction steps; however, such Re(V) might arise from interaction of Re(IV) with unreduced Re(VII), whereas overvoltage effects at the cathode might prevent observation of a distinct Re(VII) → Re(V) electrode process. In this connection it should be noted that Geyer[12] has interpreted the first perrhenate reduction wave observed in 10 *M* sulfuric acid at the dropping mercury electrode as reduction to Re(IV).

Reductions in 6 *M* sulfuric acid at cathode (Pt) potentials of -0.15 and -0.20 v. produced catholyte suspensions which were blue-black in appearance in the early stages but which invariably became brown to brown-black as average oxidation state IV was approached. Although a marked current decrease accompanied the approach to oxidation state IV, the currents did not actually fall to zero. One such reduction of 0.024 *M* perrhenic acid at a potential of -0.20 v. was continued to a coulometer reading of Re(-0.47) without indication that the current would eventually cease, yet the brown-black catholyte suspension and the black cathode deposit were found by dissolution in 10 *M* hydrochloric acid and spectrophotometric examination to be primarily Re(IV). Similar brown suspensions were also obtained in reductions at mercury cathodes, though again definite end-points were not obtained. Titration with ceric sulfate of the product from a reduction at -0.10 v. gave 3.93 ± 0.01 (average of three determinations) as the oxidation state of the rhenium, further indicating that the rhenium is not reduced below Re(IV) at these potentials. The failure to achieve definite end-points at either platinum or mercury cathodes was probably due to simultaneous discharge of hydrogen, even though the potentials used were well removed from the values at which such discharge occurs in the absence of rhenium (see below). Alternatively, it is possible that rhenium-catalyzed reduction of sulfate took place, a phenomenon that was definitely observed in 16.9 *M* acid at potentials below -0.5 v.

In 3 *M* sulfuric acid electrolyses at either mercury or platinum cathodes and a potential of -0.05 v. resulted in continuous reduction and produced brown-black suspensions. The product from one such reduction at a mercury cathode was isolated by centrifugation under nitrogen; after washing with 3 *M* acid it was resuspended in acid and titrated with ceric sulfate. Three titrations gave 4.00 ± 0.07 as the average oxidation state of the rhenium in the brown-black material. As in 6 *M* acid the reduction step appears to be Re(VII) → Re(IV). Geyer's[12] interpretation of the first polarographic wave in 1 to 3 *M* sulfuric acid as Re(VII) → Re^0 would thus seem to be questionable.

Continuous electrolysis was also observed in 1 *M* acid at mercury cathodes; in a reduction of 0.04 *M* perrhenic acid at +0.26 v. and -5 to 0° a very large current (260 ma.) still flowed at a coulometer reading of Re(-1.3), yet in the absence of rhenium hydrogen discharge did not occur until the mercury potential reached the range +0.5 to +0.6 v. Spectrophotometric examination showed that despite such extensive electrolysis the dark brown catholyte at stage Re(-1.3) still contained a considerable amount of perrhenate. Since no odor was detected in the nitrogen effluent from the cathode chamber during the electrolysis, it appeared that reduction of sulfate ion was not taking place, but rather that hydrogen discharge was occurring. Evidently the rhenium effectively diminished the hydrogen overvoltage at the mercury surface.

Remarks Concerning the Rhenium Oxidation States. Re(VI).—As discussed previously electrolytic reductions of perrhenate in concentrated sulfuric acid indicate that Re(VI) may be formed to some extent as an unstable red species. In view of this, the possibility exists that the violet solutions observed by Holemann and Tomicek and Tomicek in concentrated acid were mixtures of the blue Re(V) and red Re(VI) states. In the present investigation violet solutions were observed to be formed rapidly by the action of mercury on perrhenate in concentrated acid.[14] The loss in weight of the mercury, which was assumed to be oxidized to Hg(I) inasmuch as mercurous sulfate was found

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[14] On prolonged interaction (5 to 20 hours) the violet solutions were slowly converted to brown-black colloidal suspensions.

to have no effect on perrhenate, indicated that in such solutions the average oxidation state of the rhenium was in the range Re(5.5) to Re(5.6).

As mentioned earlier Manchot, Schmidt and Dusing have cited evidence for the existence of a violet Re(VI) in dilute sulfuric acid. The preparation of these violet solutions was repeated in the present study. Potassium hexachlororhenate (IV) was reduced electrolytically in 1 M sulfuric acid to the olive-green solutions ascribed to Re(III). As noted by the earlier workers, the reduced solutions became brown on standing and saturation with oxygen produced red and violet colors intermediate to complete oxidation to perrhenate. However, spectrophotometric examination showed that appreciable oxidation to perrhenate occurred during the formation of these colored solutions, so that assignment of oxidation states on the basis of the relation of color intensity to equivalents of oxygen absorbed, as Manchot and co-workers did, is of doubtful validity. The violet solutions formed in this manner were found to be identical with those obtained by the action of oxygen on Re(V) and Re(IV) suspensions, as discussed below, the color being due to a species having a broad maximum at 545 mμ. The oxidation state of this species is not yet definitely known.

Re(V).—No evidence was obtained in the electrolytic reductions of the light blue or wine-red Re(V) species reported by the earlier investigators. Since the existence of the light blue species seems well established by the work of Holemann and Tomicek and Tomicek, it appears that electrolytic reduction produces a different Re(V) species than does chemical reduction. Failure to observe the red species does not seem surprising, however, since the prior evidence for this Re(V) species is open to question. Thus, Holemann obtained his red solutions under conditions where he also observed rhenium-catalyzed reduction of the sulfuric acid. Further, in the present study spectrophotometric examination revealed that the red solutions obtained in the manner described by Manchot and co-workers were actually mixtures, one component of which was the 545 mμ violet species ascribed by those workers to Re(VI).

When suspended in strong sulfuric acid (12 M) the dark blue Re(V) prepared by electrolytic reduction appeared to be oxidized only very slowly by oxygen. However, when the acid concentration was reduced to 6 M or less, the action of oxygen became much more pronounced. Suspensions of Re(V) in 6 M sulfuric acid acquired a strong red-violet color when saturated with oxygen for two to four hours. After one to two days, the suspended solid had usually nearly completely disappeared, and the solutions were bright violet in appearance. Spectrophotometric examination revealed that in such oxidations all but a few per cent. of the rhenium was oxidized to perrhenic acid, with the remainder being converted to a species having an absorption maximum at 545 mμ. This same violet species, which appeared to be in true solution, was also formed during oxidations of Re(IV) suspensions.

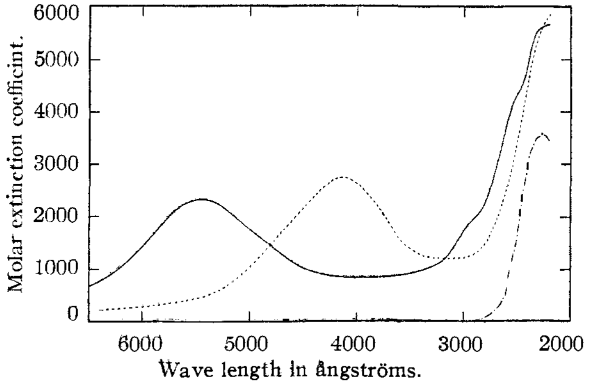

Fig. 3.—Spectra in 6 M H_2SO_4: —, violet species formed by action of oxygen on Re(IV); ----, amber species obtained on reduction of violet; ——-, $HReO_4$.

Re(IV).—Though previous investigators have claimed to have obtained this state in solution, it seems likely, in view of the fact that solid was sometimes visibly evident, that their preparations were colloidal suspensions. The brown or brown-black suspensions obtained in this investigation by electrolysis in 3 or 6 M acid frequently had a deceptive solution-like appearance, but all showed very strong Tyndall scattering.

Re(IV) suspensions in sulfuric acid of concentrations between 1 and 12 M were found to be stable under nitrogen, remaining unchanged for several days. When suspensions in 12 M acid were saturated with oxygen the brown or brown-black appearance changed to the dark blue characteristic of Re(V) within several hours. In 1 to 6 M acid a red-violet color developed within several hours; when the saturation with oxygen was continued for several days, the suspended solid largely disappeared and intensely colored violet solutions were obtained. These violet solutions exhibited a broad absorption maximum at 545 mμ (Fig. 3) and appeared to be identical with the violet solutions to which Manchot and co-workers assigned oxidation state Re(VI). They were of particular interest because, together with the amber solutions formed on their reduction, they represented the only true solutions obtained in sulfuric acid in the present investigation.

As in the case of Re(V) the bulk of the Re(IV) was converted to perrhenic acid in such oxidations, the usual yield of the violet species being on the order of 5 to 10%. It was found that the perrhenate could be removed from the solutions by saturation with hydrogen sulfide (30 minutes in 7 M acid; two hours in 3 M) followed by centrifugation. This treatment quantitatively converted the perrhenate to an insoluble sulfide and reduced the violet species to an amber. Following removal of hydrogen sulfide by purging with nitrogen, the amber solutions were cautiously oxidized back to the violet with oxygen, a change that was accomplished without difficulty because the violet species was considerably less sensitive to oxidation than the amber. A typical absorption spectrum of a violet solution after purification in this manner is shown in Fig. 3.

The apparent oxidation state of the rhenium in five violet solutions ([Re] = 1 to 7 × 10^{-3} M) obtained from different Re(IV) preparations was determined by titration back to perrhenate with ceric sulfate. The results ranged from Re(4.01) to Re(4.68) though duplicate determinations on any one solution agreed to within 0.02 unit. Since the violet solutions have also been obtained on oxidation of Re(V), it would appear from these low values that the solutions contained some reducing impurity. The fact that higher values were generally obtained with the more concentrated violet solutions also indicated that this was the case. Such a reducing impurity might possibly be formed by the rhenium-catalyzed reduction of sulfuric acid during the electrolytic reductions of the perrhenate.

Studies of the cathodic reduction of the violet solutions revealed that a definite reduction step started at approximately −0.4 v. and could be completed at −0.2 v. This reduction step gave amber solutions showing the absorption spectrum reproduced in Fig. 3. The amber solutions, which were identical with those formed by the action of hydrogen sulfide on the violet solutions, were rapidly oxidized by air back to the violet. Coulometric measurements made during five reductions of three different violet solutions gave 0.49 ± 0.02 as the oxidation state difference between the violet and amber species. This half-unit oxidation state difference suggests that the violet and amber species are dimers, one of which contains rhenium in two different oxidation states. Dilutions of the violet solutions in 10 *M* HCl appeared to be stable, but similar dilutions of the amber exhibited after several days a nearly pure Re(V) chloride spectrum. This result indicates that the amber is a Re(V) and the violet a mixed Re(V)–Re(VI) species; however definite assignment of oxidation states will not be possible until pure solutions of the species have been obtained.

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY]

The Electrolytic Dissociation of Dimethyltin Dichloride

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The dissolution of dimethyltin dichloride in water produces chloride ions and doubly-charged dimethyltin ions, together with their hydrolysis products. The degree of dissociation and the hydrolysis constant have been determined, and a study of the further hydrolysis of dimethyltin dichloride in basic solution has been made.

The electrolytic behavior of several organometallic halides has been studied intensively during the past ninety-three years[2-12] but there has been no report on dimethyltin dichloride. This compound now is readily available,[13] and its stability and wide range of solubility make it an interesting substance to study. We are concerned here with its dissociation in water, the extent of its hydrolysis in pure water, and its further hydrolysis in basic solutions.

Experimental

Preliminary Tests.—Dimethyltin dichloride is a volatile, covalent substance which melts at 106°, boils at 190°, and readily sublimes at room temperature. It is very soluble in benzene, cyclohexane and other hydrocarbon solvents to give non-conducting solutions. It also dissolves readily in water to the extent of 1200 g. or more per liter, forming a colorless solution without precipitation of oxide or hydroxide.[14] The aqueous solutions are highly conducting, and show the usual reactions for chloride ion. Positive ions were detected by their metathetic reactions and also were retained by an ion-exchange column. We may write the dissociation as

$$(CH_3)_2SnCl_2 + nH_2O = (CH_3)_2Sn(H_2O)_n^{++} + 2Cl^- \quad (1)$$

The solutions also are acid in all concentrations, so some hydrolysis must occur

$$(CH_3)_2Sn(H_2O)_n^{++} + H_2O = (CH_3)_2Sn(H_2O)_{n-1}\,OH^+ + H_3O^+ \quad (2)$$

The extent of dissociation by reaction with water was sought, and also the degree of hydrolysis in solutions of comparable concentration.

Cryoscopic Measurements.—If equation (1) is correct, the van't Hoff *i* factor at infinite dilution should be 3.0 in the absence of any hydrolysis or other reaction. The freezing points of three solutions were determined, relative to water: (a) 1.5698 g. $(CH_3)_2SnCl_2$ in 42.202 g. H_2O; molality 0.1693. Observed ΔT = 0.823°; calculated for complete ionization as in eq. (1) 0.945°, for no ionization 0.315°; i = 2.61. (b) 0.9993 g. subs. in 43.687 g. H_2O; molality 0.1041. Observed ΔT = 0.521°, i = 2.69. (c) 0.6023 g. subs. in 42.9013 g. H_2O; molality 0.0639. Observed ΔT = 0.340°, i = 2.86.

Hydrolysis Constant.—The *p*H values of dilute solutions of $(CH_3)_2SnCl_2$ were measured at 24.8° with a Beckman *p*H meter. A 2.05×10^{-3} *M* solution had a *p*H of 3.025 (H^+ concn. = 9.44×10^{-4} *M*), and a 9.16×10^{-4} *M* solution had a *p*H of 3.27 (H^+ concn. = 5.37×10^{-4} *M*). By equation (2), at equilibrium

$$K_h = \frac{[Me_2Sn(H_2O)_{n-1}OH^+][H_3O^+]}{[Me_2Sn(H_2O)_n{}^{++}]} = \frac{[H_3O^+]^2}{[Me_2SnCl_2] - [H_3O^+]}$$

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[1] Ethyl Corporation Fellow at Harvard University, 1952-1953.

[2] A. Cahours, *Ann.*, **114**, 367 (1860).

[3] G. Bredig, *Z. physik. Chem.*, **13**, 303 (1894).

[4] N. Zelinsky and S. Krapiwin, *ibid.*, **21**, 47 (1896).

[5] Werner and Pfeiffer, *Z. anorg. Chem.*, **17**, 82 (1898).

[6] C. A. Kraus and W. N. Greer, THIS JOURNAL, **45**, 2946 (1923).

[7] C. A. Kraus and C. C. Callis, *ibid.*, **45**, 2624 (1923).

[8] F. Hein and H. Meininger, *Z. anorg. Chem.*, **145**, 95 (1925).

[9] I. B. Johns, *et al.*, *J. Phys. Chem.*, **34**, 2218 (1930).

[10] W. Evans and F. Lee, THIS JOURNAL, **55**, 1474 (1933); **56**, 654 (1934).

[11] W. Klemm, FIAT Report of Inorganic Chemistry, Part II, p. 169.

[12] K. Gingold. E. G. Rochow, D. Seyferth, A. C. Smith and R. West, THIS JOURNAL, **74**, 6306 (1952).

[13] Our dimethyltin dichloride was prepared by the direct reaction of methyl chloride with molten tin containing copper and zinc as catalysts (A. C. Smith and E. G. Rochow, report in preparation). A similar method, developed independently, is reported by F. A. Smith in U. S. Patent 2,625,559 (Jan. 13, 1953).

[14] In this respect $(CH_3)_2SnCl_2$ resembles $(CH_3)_2GeCl_2$, and both differ markedly from $(CH_3)_2SiCl_2$, which hydrolyzes rapidly and completely.