E′) which has this property is illustrated in Fig. 6. For the prism and equatorial hydrogens to interchange their positions, H_1, H_4, H_7, and H_9 must undergo a motion of 0.44 Å. while H_2, H_3, H_5, and H_6 must be displaced 0.23 Å. Such displacements do not take place in the solid despite amplitudes of thermal motion comparable with those required for interchange (*cf.*, Table VII). The absence of interchange between prism and equatorial hydrogen atoms in the crystal leads to the inference of a large potential barrier to the deformation modes required for such a transformation. However, for the unconstrained ReH_9^{-2} ion in solution, the required displacements are quite reasonable and may be expected to take place, so that all nine H appear equivalent in the n.m.r. and exchange experiments. A similar explanation has been given for the n.m.r. equivalence of the fluorines in PF_5.[29]

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Transition Metal–Hydrogen Compounds. III. Dipotassium Enneahydridotechnate(VII)

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Reduction of ammonium pertechnate with potassium metal in ethylenediamine–ethanol medium yields K_2TcH_9. Powder patterns show this compound to be isostructural with K_2ReH_9. The lattice constants of the hexagonal unit cell are $a = 9.64$ and $c = 5.56$ Å. The high resolution proton n.m.r. spectrum of a solution of K_2TcH_9 has a broad line at τ 18.4 p.p.m. This is attributed to the metal-bonded hydrogens. The infrared spectrum of solid K_2TcH_9, like that of K_2ReH_9, shows a triplet in the M–N stretching region and a singlet in the M–N bending region. The chemical behavior of the technetium and rhenium hydrides is similar, but the technetium compound is more reactive.

The existence of a water-soluble potassium rhenium hydride[1,2] having the composition K_2ReH_9[3] suggested a search for similar complexes of other transition metals. An obvious possibility is technetium, which in most of its chemical properties is like rhenium. Indeed, tracer experiments[4] have shown that under conditions where rhenium forms a hydride, technetium yields a compound with apparently similar solubility characteristics and similar behavior toward acid. The present paper describes the preparation, characterization, and some properties of the technetium analog of K_2ReH_9.

Experimental

Preparation.—NH_4TcO_4 (50–100 mg., spectroscopically pure, prepared *via* the heptoxide from metallic Tc^{99} obtained from the Oak Ridge National Laboratory) was dissolved in 100 ml. of 4:1 anhydrous ethylenediamine–absolute ethanol containing 2% C_2H_5OK. Under a nitrogen atmosphere, and with vigorous stirring, 5 g. of clean potassium metal was added at such a rate that the temperature rise was just sufficient to melt the metal. The light brown solid which formed was washed, successively, with the reaction solvent, anhydrous ethylenediamine, 1,2-dimethoxyethane, and ether. Exclusion of moisture is essential during the above operations, and the dimethoxyethane and ether should be freshly distilled from $LiAlH_4$. Microscopic examination of the product shows it to consist of a white solid admixed with small amounts of a brown solid, presumably metallic technetium or a lower oxide. Infrared spectra indicate the presence of small amounts of carbonate, pertechnate, and ethylenediamine. Because of the presence of these impurities, and the great sensitivity of the product to moisture, an attempt to establish the composition by analysis has not been made. However, as will be seen below, the results of several chemical and physical studies demonstrate conclusively the hydridic nature of the product and the fact that the hydrogens are directly bonded to the technetium. Furthermore, comparison with the corresponding results for K_2ReH_9, especially the X-ray diffraction patterns and infrared spectra, make it quite certain that the technetium and rhenium compounds have the same stoichiometry and structure.

Chemical Properties.—On adding the solid to water hydrogen is evolved and a brown-black precipitate forms. With dilute acids the hydrogen evolution is very vigorous, and the precipitate (Tc metal or a lower oxide) is black and so finely divided that an identifiable X-ray diffraction pattern could not be obtained. Small quantities of the hydride are soluble in strong aqueous alkali (20–50% KOH) with only slight decomposition, and the resulting solutions appear to be unchanged on standing overnight, as shown by their reduction of $TlNO_3$ to the metal and their behavior on acidification. However, alkaline solutions containing $> \sim 0.05\%$ of the hydride decompose rapidly at room temperature. With alkaline NaOCl there is vigorous evolution of hydrogen and the technetium is oxidized to TcO_4^-. The behavior of K_2ReH_9 is quite similar.[1,2] Noteworthy differences are that even relatively concentrated solutions of K_2ReH_9 in strong aqueous alkali are stable at room temperature, and that with $TlNO_3$ the rhenium compound gives an intermediate white solid (pre-

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[1] A. P. Ginsberg, J. M. Miller, J. R. Cavanaugh, and B. P. Dailey, *Nature*, **185**, 528 (1960).

[2] A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Am. Chem. Soc.*, **83**, 4909 (1961).

[3] S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

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sumably Tl_2ReH_9) which soon turns black, while the technetium hydride gives an immediate black precipitate.

Results and Discussion

Proton N.m.r. Spectrum.—In order to obtain a solution sufficiently concentrated to observe the high-field resonance characteristic of transition metal hydrides,[5] it was necessary to work at reduced temperatures. About 1 ml. of cold (~ −10°) 41.5% KOD in D_2O was added to ~20 mg. of the technetium hydride that had been cooled on Dry Ice (some decomposition took place). After stirring, the mixture was quickly centrifuged and the supernatant transferred to a cooled n.m.r. sample tube. Spectra were taken with a Varian high-resolution spectrometer operating at 60 Mc./sec. and equipped with a temperature-controlled probe maintained at −19°. The sample was spinning. The spectrum consists of two peaks separated by 852 ± 7 c.p.s. (14.2 ± 0.1 p.p.m.). The low-field peak is due to water–hydroxyl ion protons from the solvent. The high-field peak (τ 18.4 p.p.m.) is attributed to protons of a hydridic nature bonded to technetium. This spectrum is very similar to that of K_2ReH_9 under similar conditions.[1] A re-examination of the spectrum of K_2ReH_9 in the same solvent and at the same temperature as used above (but with the rhenium hydride in ~3 times greater concentration than the technetium hydride) gave a separation of 894 c.p.s. (14.9 p.p.m.) between the peaks. A comparison of the widths at half-height and the shapes of the lines in the two spectra reveals several significant differences. The technetium hydride resonance is broad (width ~189 c.p.s.) and flat topped, whereas the rhenium hydride resonance is relatively narrow (~10 c.p.s.) and Lorentzian in shape. The low-field line in both spectra appears Lorentzian, but the width in the technetium spectrum is ~16 c.p.s., whereas in the rhenium spectrum the width is only about 2 c.p.s. The broadening of the water line in the technetium spectrum, as compared to the rhenium spectrum, may be due to paramagnetism of the small amount of black decomposition product in the solution.

Since Tc^{99} has a nuclear spin $I = {}^9/_2$ and an electric quadrupole moment $Q = 0.3 \times 10^{-24}$ cm.^{2}, the very broad flat-topped nature of the technetium hydride resonance is attributed to partial collapse of the expected ten-line spin multiplet by quadrupole relaxation of the Tc^{99} nucleus.[6] Rhenium consists of two isotopes, Re^{185} with $I = {}^5/_2$, $\mu = 3.144$ n.m., $Q = 2.8 \times 10^{-24}$ cm.^{2}, and Re^{187} with $I = {}^5/_2$, $\mu = 3.176$ n.m., $Q = 2.6 \times 10^{-24}$ cm.^{2}. That the observed rhenium hydride line is Lorentzian in shape and narrow compared to the technetium hydride line is probably due to the much larger quadrupole moment of rhenium. Since the rate of quadrupole relaxation is proportional to Q^2, the Re nuclei will be relaxing ~85 times more rapidly than the Tc nuclei so that a narrowing of the collapsed multiplet line takes place.[6]

TABLE I

THE d-SPACINGS AND RELATIVE INTENSITIES (Cu Kα) FOR K_2ReH_9 AND K_2TcH_9[a]

	K_2ReH_9		K_2TcH_9
(hkl)	d_{calcd}, Å.	d_{obsd}, Å.	d_{obsd}, Å.
110	4.804	4.770 (10)	4.820 (8)
101	4.593	4.581 (7)	4.635 (5)
111	3.620	3.605 (3)	3.649 (5)
201	3.320	3.311 (8)	3.345 (10)
210	3.145	3.137 (1)	3.152 (2)
002	2.754	2.758 (9)	2.782 (7)
211	2.731	2.718 (7)	Not resolved
112	2.389	2.393 (6)	2.411 (4)
311	2.128	2.122 (2)	2.133 (1)
400	2.080	2.080 (1)	2.087 (2)
302	1.954	1.954 (6)	1.971 (4)
321	1.804	1.805 (6)	1.816 (4)
411 113	1.724 1.715	1.720 (1)	1.74 (2)
203	1.680	1.684 (1)	1.700 (2)
213 501	1.586 1.593	1.589 (3)	1.600 (3)
421	1.512	1.513 (3)	1.522 (3)
313	1.437	1.438 (2)	1.446 (1)
332 004	1.384 1.377	1.381 (2)	1.390 (1)
114 323 431	1.324 1.323 1.327	1.325 (2)	1.333 (2)
611 503 304	1.236 1.233 1.233	1.235 (2)	1.245 (1)
522 224	1.199 1.195	1.197 (2)	1.203 (2)
513	1.1590	1.1590 (1)	1.168 (1)
442	1.1008	1.0996 (2)	1.1063 (2)
334	1.0440	1.0446 (1)	1.0523 (1)
712	1.0231	1.0227 (1)	1.0261 (1)
703 533	0.9977 0.9977	0.9983 (1)	1.003 (1)
632	0.9796	0.9786 (1)	0.9830 (1)
811	0.9589	0.9591 (1)	0.9648 (1)
911 651	0.8614 0.8614	0.8614 (2)	0.8636 (1)

[a] Intensities are indicated by the numbers in parentheses on the scale 10 = most intense, 1 = least intense.

Infrared Spectrum.—Spectra were taken from 4000–400 cm.$^{-1}$ using the KBr pressed pellet technique. In the metal–hydrogen stretching region[5] a triplet was observed at 1869 (w, sh), 1795 (s), and 1779 (sh) cm.$^{-1}$. In the metal–hydrogen bending region[5] there was a single band at 689 cm.$^{-1}$ (s). This is precisely the pattern observed in the infrared spectrum of solid K_2ReH_9,[2] taken either in a KBr disk or a Nujol mull. The corresponding absorptions are 1931 (w, sh), 1846 (s), 1814 (sh), and 735 (s) cm.$^{-1}$. The shift of the bands of K_2TcH_9 by ~50 cm.$^{-1}$ to lower frequencies indicates that the Tc–H bond is weaker than the Re–H bond and is in agreement with the observed greater reactivity of the technetium compound. This is the normal stability variation along a group for compounds of the higher oxidation states of the transition metals.

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(5) *Cf.*, for example, the review by M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960).

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, Chap ters 9 and 10; J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

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X-Ray[7] Diffraction.—Powder patterns (Cr Kα and Cu Kα) of K_2ReH_9 and potassium technetium hydride are very similar. Table I compares the observed *d*-spacings and relative intensities of the lines in the powder patterns of the two compounds. Also shown in Table I are the indices (*hkl*) and *d*-spacings calculated on an IBM 7094 computer using the single crystal lattice constants of K_2ReH_9 (a = 9.607, c = 5.508 Å.).[3,7] It is clear from the table that the Re and Tc compounds are isostructural. The lattice constants for potassium technetium hydride are calculated to be a = 9.64, c = 5.56 Å., and the volume of the hexagonal unit cell is 447.5 Å.^{3}, an increase of 1.7% over the unit cell volume of K_2ReH_9 (440.24 Å.^{3}).

According to the X-ray results, technetium hydride is isostructural with K_2ReH_9. Hence, the K:Tc ratio and the arrangement of the K and Tc atoms may be regarded as established, but it is conceivable, although unlikely, that the stoichiometry and geometry of the technetium hydride anion is not thereby determined, since the hydrogen atoms do not *directly* make an observable contribution to the X-ray diffraction pattern. However, when we consider the X-ray results together with the infrared spectrum, which *is* characteristic of the structure of the hydride anion, any doubt as to the nature of the anion is removed. The infrared spectra of K_2ReH_9 and potassium technetium hydride, in the solid state, differ only by small displacements of the bands, and since the metal atom arrangement in the two compounds is the same, we may conclude that the Re and Tc hydride anions are isostructural. Thus, the formula of potassium technetium hydride must be K_2TcH_9. In view of the results in ref. 3, there are six H at the corners of a trigonal prism with the Tc at its center and three H beyond the centers of the rectangular prism faces (point group symmetry D_{3h}).

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The Intermediate in the Reaction between Vanadium(II) and Vanadium(IV)[1]

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When V(II) and V(IV) are mixed in acid perchlorate solutions, a highly colored substance forms which has been shown to be an intermediate in the reaction $V^{+2} + VO^{+2} + 2H^+ = 2V^{+3} + H_2O$ and to be VOV^{+4}, a hydrolytic dimer of V(III). The rate of formation of VOV^{+4} is given by $k_1[V^{+2}][VO^{+2}]$ and its rate of reaction with acid is given by $k_2[VOV^{+4}][H^+]$. At 0° and unit ionic strength k_1 is about 0.067 M^{-1} sec.$^{-1}$ and k_2 is about 0.33 M^{-1} sec.$^{-1}$. Also $k_2 = 4.054 \times 10^4 T \exp(-9400/RT)$. About 65% of the over-all oxidation–reduction reaction involves the intermediate; the rest goes directly to the final products, probably by way of an outer-sphere activated complex.

Introduction

During a study of the kinetics of the reaction between V(II) and V(IV) in aqueous perchlorate solutions,[2] evidence was obtained for an intermediate. It was observed that when V(II) and V(IV) were mixed in acid solutions, a brown color developed much more rapidly than the rate of the over-all reaction to produce aquo V(III). The over-all reaction was found to have the rate law: $-d[V(IV)]/dt = (k' + k''[H^+])[V(II)][V(IV)]$. The k' term accounts for nearly all of the rate and values of ΔH^* and ΔS^* for this path were found to be 12.3 kcal./mole and −16.5 cal./deg. mole. In the work to be reported here the intermediate has been investigated further in order to compare its properties with those of the intermediates which have been observed[3] or postulated[4] in other oxidation–reduction reactions.

Experimental

The system was studied spectrophotometrically using a Cary Model 14 recording spectrophotometer. The reactions were started by injecting V(II) into appropriate solutions of V(IV) in stirred absorption cells which were positioned in a small water-filled thermostat in the light beam of the spectrophotometer. The details of this arrangement, as well as the methods for the preparation of the various solutions, have already been described.[2,4a]

A Beckman Model G pH Meter was used for the pH determinations. The calomel electrode was separated from the experimental solutions, which contained perchlorate, by means of a fiber-tipped glass sleeve which contained 1 M $NaNO_3$. The meter was calibrated using carefully diluted $HClO_4$ in $LiClO_4$ at unit ionic strength.

Results and Discussion

The Intermediate.—Typical results obtained on mixing V(II) into solutions of V(IV) are shown in Fig. 1. Absorbance, D (defined as log $[I_0/I]$), was determined as a function of time at 4250 Å. The solutions were at 0° and 0.5 M in $HClO_4$, 0.0023 M in V(II), while the V(IV) concentrations varied from 0.0134 to 0.100 M. The ionic strength was held constant at 0.8 M using $Zn(ClO_4)_2$. The optical path length, b, was 2.20 and 2.19 cm. for the two cells used. The initial rise in D followed by a subsequent decrease shows that the

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[1] Work done under the auspices of the U. S. Atomic Energy Commission, and presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

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[3] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).

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