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Hydrogen Isotope Effects in Titanium Alloy Hydrides

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There are usually quite large differences in stability among the protides, deuterides, and tritides of a given metal or alloy. Such isotope effects have been made the subject of a rather voluminous literature. A list of references up to 1970 is given in an earlier publication from this laboratory.[1] Since that time, a number of other researches in this field have been reported.[2-10] The bulk of the work has dealt with binary hydrides. A few alloys have also been studied, but they form a rather miscellaneous group, from which no generalizations can be derived. It was, therefore, thought worthwhile to examine, in this respect, a series of alloys formed between a single hydride-forming metal and a number of other metals most of which did not themselves form stable hydrides. Titanium was chosen as the constant constituent, since it forms intermetallic compounds or solid solutions with almost every transition element, and many of these alloys were already known to form hydrides. Of particular interest was the periodic trend of the hydrogen isotope effect as a function of the transition metal alloyed with titanium. In order to determine isotope effects on a large number of metal–hydrogen systems in a relatively short time, the method of tritium exchange was chosen. Those systems which have been shown by this test to be of special interest are being subjected to a more exhaustive study, in which *P–C–T* data are being obtained for deuterium as well as protium. The results so far may be considered as of a preliminary nature, but they appear to have enough interest in themselves to warrant publication at this time.

Experimental Section

Small quantities of tritium were introduced into a gaseous hydrogen phase in equilibrium with a quantity of a given metal hydride. A fairly rapid exchange usually occurred, the progress of which was followed by measuring the radioactivity of successive small samples of the gas phase. When no further change took place, equilibrium was assumed to have been reached. From a knowledge of the initial and final amounts of gas phase tritium and the tritium concentration in the gas recovered from the thermally decomposed hydride, the equilibrium constant for isotopic distribution could be derived.

The apparatus used consisted, in essence, of a closed loop of stainless steel tubing through which hydrogen was circulated by a pump. The sample of solid hydride was supported on a frit in one of the vertical members. Typical quantities were as follows: weight of alloy, 10 g; volume of loop, 29 mL; hydrogen pressure, 15.3 atm; amount of tritium introduced, 26 μCi. Temperatures ranged from −20 to +40 °C; for their control, most of the loop was immersed in a circulating bath of water or refrigerated methanol or, for 0 °C, a static ice bath. Pumping action for the gas phase was provided by connecting to the loop a side arm leading to a mercury piston. Check valves above and below the junction of the side arm to the loop provided for the desired one-way circulation of gas. The mercury piston was actuated by a fluctuating hydrogen pressure on the far side of the U-tube that contained it. The fluctuations derived from the alternate heating and cooling of a reservoir of vanadium dihydride, as described in a previous publication.[11] A schematic diagram of the entire gas-handling apparatus is shown in Figure 1.

Tritium determinations were accomplished by gas-phase β counting. For this purpose, a small quantity of the gas in the loop was drawn off into an evacuated proportional counter tube.[12] To this gas (at 0.0658 atm) was then added a quantity of "P-10" counting gas to bring the total pressure to 0.987 atm and a count was obtained using standard electronic equipment. The count rate was usually of the order of 60 000 cpm.

Alloys were made by arc-melting metal components of at least 99.9% purity, obtained from Ventron-Alpha. The alloy buttons were crushed to 20 mesh before use. The granular material was converted to hydride in situ by treatment with tank hydrogen (VHP grade, 99.999% pure from the Matheson Co.). A pressure of 40.8–54.4 atm was applied until no further uptake occurred. Dehydriding was then induced by pumping, first at room temperature, then heating to 450 °C to drive off the last traces. In repeating this cycle several times, an increasingly fast uptake was observed. When no further increase in initial rate occurred, the sample was considered activated. At some point previous to the final hydriding and exchange experiments, the composition of the hydride in equilibrium with high-pressure gas was determined by causing the gas released on dehydriding to expand into calibrated volumes and measuring the pressure. The formulas of the maximum hydride, and of the hydride in equilibrium with the operating pressure of the exchange experiments, were obtained in this manner. They are included in Table I.

The source of tritium was a 1-Ci capsule of T_2 from New England Nuclear which was diluted with about 4×10^6 parts of high-purity normal hydrogen; the final pressure of the mixture was ~60 atm. At the start of a run, the lower half of the loop (that containing the hydride sample) was valved off, a quantity of the dilute tritium was added to the upper half, and more hydrogen was added until the pressure equaled that in the lower half. Tritium was allowed to distribute itself uniformly throughout the upper half, the mixing process being assisted by pressure fluctuations induced by the mercury piston. When analysis of samples showed no further change in tritium activity at the sampling point, its concentration was presumed uniform and the loop valves were opened at "$t = 0$." Samples were taken thereafter every 30 or 60 min at the start and less frequently toward the end until no further change occurred. In many cases the exchange reaction

$$MH_x + HT \rightleftarrows MH_{x-1}T + H_2$$

proved fast compared with the attainment of uniformity in the composition of the circulating gas, and quantitative kinetic data could not be obtained. In other cases reaction took several hours and its progress could be followed.

At the completion of an experiment a tritium material balance was made. The amount of tritium associated with the solid was determined by decomposing the hydride, measuring the volume of gas given off and analyzing it for tritium. In practice this often involved multiple operations, since part of the hydrogen was more tenaciously held than the rest. As will be seen from Table I, good material balances were usually obtained. Even where a deficit of 10% was found, it is not believed that the α values are seriously in error on this account.

Results and Discussion

From the experimental observations there was obtained for each material one or more values of α, the tritium distribution coefficient. It is defined as

$$\alpha = (T/H)_{solid}/(T/H)_{gas}$$

It was experimentally determined by dividing the counts per minute of the gas obtained from the solid phase by the counts per minute of the gas phase in equilibrium with the solid phase. It should be independent of concentration in the very dilute region used in our experiments. It can generally be expected

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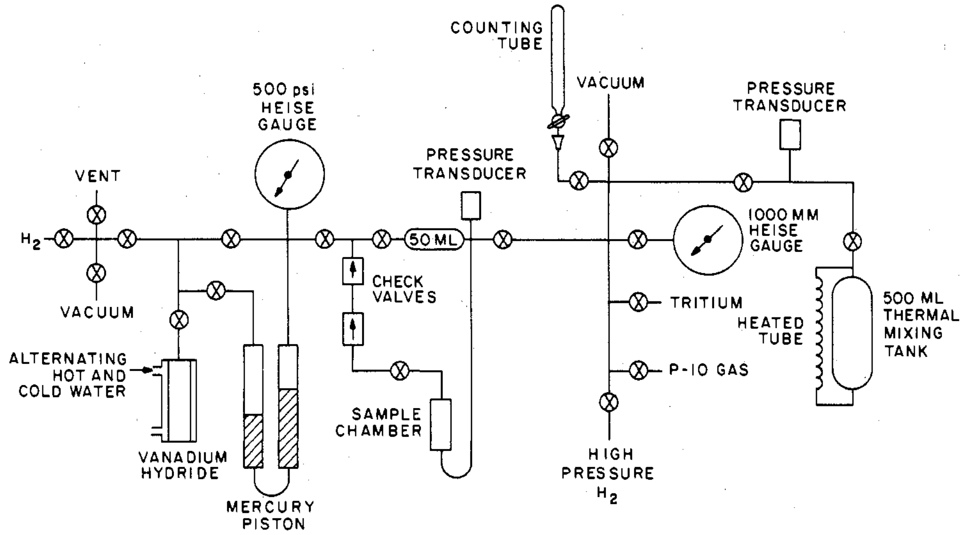

Figure 1. Diagram of apparatus used to determine tritium–protium separation factors.

Table I. Tritium Isotope Effects

Material equilibrated	Max H	Temp, °C	Activity balance, %	α (cpm of solid/ cpm of gas)	Structure of alloy
TiH_2	H_2	350	105.4	0.67	
$TiVH_{4.15}$	$H_{4.0}$	40	93	1.18	
$TiCrH_{2.35}$	$H_{2.92}$	40	88	1.54	X-ray pattern similar to that of TiMo
$TiCr_2H_{1.68}$	$H_{2.66}$	−20	90	2.01	fcc $MgCu_2$ $a = 6.943$ Å at high temp, hexagonal $MgZn_2$ $a = 4.932$, $c = 7.961$ Å
$TiCr_2H_{1.48}$	$H_{2.66}$	0	97	2.03	
$TiCr_3H_{1.76}$	$H_{2.91}$	−20	98	1.68	$TiCr_2$ + Cr
$TiCr_3H_{1.36}$	$H_{2.91}$	0	100	1.59	
$TiCr_3H_{0.875}$	$H_{2.91}$	+20	95	1.69	
$TiCrMnH_{2.19}$	$H_{2.91}$	−20	99	2.05	$TiCr_2$ pattern
$TiCrMnH_{1.28}$	$H_{2.91}$	0	105	1.80	
$Ti_2MoH_{4.77}$	$H_{\sim 4.94}$	40	100.8	1.61	Solid solution bcc
$TiMoH_{2.99}$	$H_{2.99}$	40	100	1.61	Solid solution
$TiMo_2H_{1.10}$	$H_{1.31}$	−20	96.8	1.87	Solid solution bcc
$TiMnH_{1.99}$	$H_{2.21}$	40	93	1.37	
$FeTiH_{1.88}$	$H_{1.97}$	0	95	0.92	CsCl $a = 2.976$ Å Elliott 438
$FeTiH_{1.69}$	$H_{1.97}$	0	97	0.95	
$FeTiH_{1.21}$	$H_{1.97}$	40	105	1.0	
$Fe_{0.6}TiMn_{0.2}H_{1.67}$	$H_{1.75}$	40	101	1.0	
$TiCoH_{1.44}$	$H_{1.46}$	40	98	0.852	CsCl $a = 2.987$ to 2.994 Å Elliott 340
$TiNiH_{1.44}$	$H_{1.50}$	40	99	0.74	CsCl $a = 3.013$ to 3.015 Å Hansen 1052

to vary with temperature and to some extent with the H/M ratio, which will in turn be a function of the operating pressure. In the series of experiments under consideration this pressure was kept nearly constant; the H/M ratios therefore varied considerably, owing to the variation in *P*–*T*–*C* relationships from one hydride to another. In Table I, which summarizes the α data, the first column gives the composition of the solid phase in equilibrium with the operating pressure. The second column indicates the maximum hydrogen which the alloy would absorb at 54.4 atm. The third column gives the operating temperature: −20, 0, +20, or +40 °C. Here again the differing stabilities of the various hydrides prevented a complete standardization of conditions. The fourth column gives the tritium material balance, obtained as described above, and the sixth lists known structural information about the starting alloy. The α, as defined above, is listed in the fifth column.

This work is of a preliminary nature since the alloy phases used were "as cast" and not carefully homogenized. Evidence thus far, however, indicates that there are no marked changes in the isotope results when the metal samples are carefully homogenized. The hydride structures and phase transitions during hydrogen absorption have not been carefully determined. Some of this work is in progress.

An unusual feature of metal–hydrogen systems is that the isotope effect can vary in direction as well as in magnitude. Usually the dissociation pressure of a metal deuteride is greater than that of the corresponding protide, and the tritide pressure is greater still. Many cases of an "inverse" isotopic effect have been found, however.[1] In general, the temperature coefficient of the dissociation pressure differs from one isotope to another. For these cases, the pressure–temperature curves must eventually cross, so that for every system there exist regions of "normal" and "inverse" isotope effects. In practice, one region or the other may be physically unattainable in a given system. The inversion temperatures, which depend on the isotopic differences in enthalpy and entropy of formation, will vary widely. For most hydrides, they are above the usual range of experimentation. For vanadium, niobium, and several of the alloys dealt with in this paper, they are below room temperature. The alloy series as shown by Table I proved to be of particular interest because variations in the nature of the non-hydride-forming component of the alloy resulted in changes of the direction of the isotope effect.

If the α values are plotted vs. the periodic table sequence of the first-row alloying elements, for 1–1 alloys, Figure 2 is obtained. The titanium value should not be directly compared since it was obtained at 350 °C. However, this was necessary

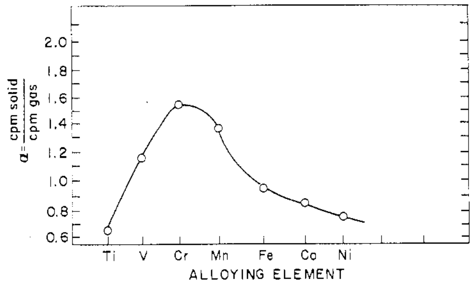

Figure 2. Tritium–protium separation factors for 1–1 titanium alloy hydrides.

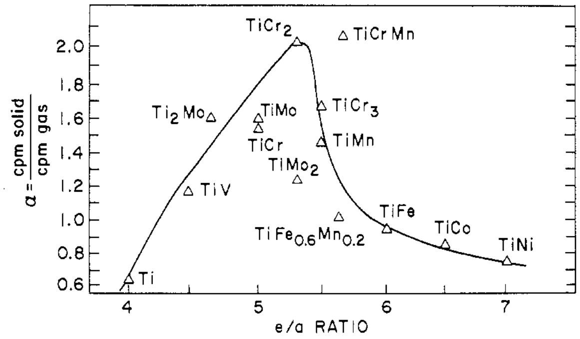

Figure 3. Tritium–protium separation factors for alloys of varying electron-to-atom ratio.

in order to get a measurable exchange rate. The other α values are for 40 °C. In order to place into comparison alloys other than 1:1 such as $TiMo_2$ and TiCrMn, the electron/atom (e/a) ratio was plotted vs. α as shown in Figure 3. The α values in this graph are for 40 °C except for several where the hydride stability dictated lower temperatures. $TiCr_2$ and TiCrMn were measured at 0 °C and $TiCr_3$ at 20 °C. The temperature coefficients for $TiCr_2$ and $TiCr_3$ seem to be relatively small so that the values plotted are probably close to the 40 °C values. Extrapolating the temperature coefficient determined on the basis of two points obtained for TiCrMn gives an extrapolated value of 1.4 for the α at 40 °C. This brings TiCrMn into line so that there seems to be a reasonable correlation between e/a and α. It is interesting to note that all the alloys which show significant inverse isotope ratios under our conditions fall in the approximate range of e/a 4.5 to 5.5. The approximate dependence of the α values on the electron/atom ratio is not surprising in that the heat of solution of hydrogen is dependent on the electronic structure of the metal.

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Registry No. TiH_2, 7704-98-5; TiV, 37219-66-2; TiCr, 64784-24-3; $TiCr_2$, 64784-25-4; $TiCr_3$, 64784-26-5; TiCrMn, 64784-27-6; Ti_2Mo, 64784-20-9; TiMo, 51401-84-4; $TiMo_2$, 64784-21-0; TiMn, 64784-22-1; FeTi, 12674-94-1; $Fe_{0.6}TiMo_{0.2}$, 64784-23-2; TiCo, 58221-15-1; TiNi, 11110-85-3.

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Reduction of the Decatungstate Anion in Nonaqueous Solution and Its Confirmation as "Polytungstate-Y"

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The pale yellow isopoly anion known as "polytungstate-Y" (W_y) has been formulated by different research groups as a dodecatungstate,[1] $[HW_{12}O_{39}]^{5-}$, and as a decatungstate,[2] $[W_{10}O_{32}]^{4-}$. The latter species (see Figure 1) was found in the crystal structure[3] of the salt $(Bu_3NH)_4W_{10}O_{32}$, which can be precipitated from a freshly prepared aqueous solution containing W_y. Both the original aqueous solution and a solution of the tributylammonium salt in acetonitrile gave an absorption spectrum with a maximum at ~325 nm.[2] Since aqueous solutions of W_y are unstable and are slowly converted into equilibrium mixtures of other isopolytungstates,[4] there still remains an element of uncertainty[5,6] about a positive identification of W_y as $[W_{10}O_{32}]^{4-}$. It is possible, for example, that both W_{10} and W_{12} species could have similar UV spectra.

In the course of an investigation of the redox chemistry of heteropoly(tungstouranates), we had occasion to study the reduction of the decatungstate anion in a nonhydrolytic solvent. The results of this study are reported here and are compared with those obtained by Boyer[7] for the reduction of W_y in aqueous solution.

Experimental Section

The potassium salt of W_y was prepared by the method of Chauveau et al.[1] and the product was identified by its infrared and ultraviolet spectra.[1] Tributylammonium decatungstate was prepared by the method of Birkholtz et al.[2] and recrystallized from acetone. Anal. Calcd for $[(C_4H_9)_3NH]_4W_{10}O_{32}$: C, 18.62; H, 3.64; N, 1.81. Found: C, 18.41; H, 3.68; N, 1.71. Electrochemical and spectroscopic measurements were made as described elsewhere.[8] Propanediol 1,2-carbonate (PDC) was distilled before use. Voltammetry in this solvent was carried out using a thread of graphite cloth (type X2014, Union Carbide Corp.) as the working electrode.

Results and Discussion

Boyer's results for the reduction behavior of aqueous solutions of W_y were confirmed in all respects. By using a wax-impregnated electrode for cyclic voltammetry and a graphite cloth cathode for controlled potential electrolysis, the problems of adsorption on mercury, encountered by Boyer, could be avoided. At 1 °C and pH 2.0 (sulfate/bisulfate) the cyclic voltammogram showed two reversible "one-electron" reductions with cathodic peak potentials of −0.19 and −0.34 V. Solutions of the one- and two-electron reduced products (W_{yI} and W_{yII}) were prepared by controlled potential electrolysis at −0.21 and −0.50 V, respectively, and the visible absorption spectra of these products were in agreement with those reported by Boyer. The corresponding UV spectra, which have not been previously reported, show that the 325-nm band is progressively lost upon reduction and is restored upon reoxidation. The restoration of intensity is never complete, however, because of the slow hydrolysis of aqueous solutions of W_y.

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