assuming that the chain terminators in (5) and (6) do not change in concentration, one arrives at the rate law

$$\text{rate} = \frac{k(\mathrm{Hg_2Cl_2(C_2O_4)_2^-} \times I}{k_5(\mathrm{M}) + k_6(\mathrm{In^{+++}})}$$

where I is the intensity of the γ-radiation. The reduction products whose formation breaks the main reaction chain may be regenerated in reactions of the type[16]

$$\mathrm{Fe^{++} + OH \longrightarrow Fe^{+++} + OH^-}$$

The suggestion that H atoms are chain initiators in γ-induced reactions in solution is not an original one. Hart explains the decomposition of formic acid solutions partly in terms of a reaction between the H atoms liberated from water and formic acid molecules.[17]

The reaction sequence proposed above is in accord with the observations that the rate (1) is proportional to the concentration of $\mathrm{Hg_2Cl_2(C_2O_4)_2^=}$, (2) is independent of ionic strength, (3) is proportional to the radiation intensity and (4) is affected by inhibitors as shown in equation 1.

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NEW YORK, N. Y.

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[16] H. S. Dainton, *J. Phys. Chem.*, **52**, 490 (1948).

[17] E. J. Hart, THIS JOURNAL, **73**, 68 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

Deuterium Isotope Effect in the Reaction of Water Vapor with Zinc

BY WARREN G. HENDERSON, JR.,[1a] AND RICHARD B. BERNSTEIN[1b]

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The deuterium isotope effect in the reaction of water vapor with zinc was measured over the range 295–415°. The fractionation factor, defined as the ratio of the specific rates of reaction of HOH and HOD with zinc, was found to be 1.6 ± 0.1 at 400°. The temperature dependence of the fractionation factor over the above range was -0.0011 (°C.)$^{-1}$. The magnitude of the isotope effect observed is somewhat smaller than the theoretical upper limit given by Eyring and Cagle for the case of the rupture of an isolated oxygen–hydrogen bond. From the present results it has been possible to evaluate the correction required for incomplete conversion of water to hydrogen in the usual analytical procedure for deuterium.

Introduction

In the course of the unidirectional reaction of water with metals, fractionation of the hydrogen isotopes occurs because of the difference in specific rates of reaction of the isotopic molecules HOH and HOD. The fractionation factor is defined $\alpha = [(\mathrm{H})/(\mathrm{D})]/[(\mathrm{H})_0/(\mathrm{D})_0]$, where (H)/(D) represents the ratio of the atom fraction of protium to deuterium in the first fraction of the evolved hydrogen and $(\mathrm{H})_0/(\mathrm{D})_0$ is the corresponding ratio for the initial substrate water.

Horiuti and Szabo[2] reported a single value of $\alpha = 2.2$ for the reaction of water vapor with sodium at room temperature. Johnston and Davis[3] investigated the reaction of liquid water with Li, Na, K and Ca at 30°, obtaining values of $\alpha = 1.85$, 2.60, 1.44 and 1.40, respectively. The reaction of water vapor with iron at 500° was studied by Horiuti and Polanyi[4a] and Bleakney and Gould[4b] who obtained $\alpha = 1.3$ and 1.2, respectively. Since the reaction $\mathrm{Fe + H_2O = FeO + H_2}$ is reversible under the conditions of these experiments, the observed fractionation is associated with the attainment of the isotopic exchange equilibrium $\mathrm{HOH + HD = HOD + H_2}$ on the metal surface rather than with a rate process.

It appears that no detailed study has been carried out for the case of the irreversible reaction of water vapor with a metal. The present investigation was concerned with measurement of the deuterium isotope effect in the unidirectional reaction of water vapor with zinc over the temperature range 295–415°.

Experimental

The procedure for the measurement of the fractionation factor was to allow a sample of water vapor to pass rapidly through a bed of zinc maintained at a temperature in the range 295–415°, under conditions such that a small fraction of the water reacted. The apparatus used (Fig. 1) was very similar to that of Rittenberg[5] for conversion of water to hydrogen with hot zinc. To minimize volume and surface, all tubing was 4 mm. o.d. The two U-tube traps were 4 cm. long. The Toepler pump volume was 200 cc., for rapid removal of hydrogen. The conversion zone was a loop of 4 mm. o.d. Pyrex tubing 50 cm. long which contained 11 ± 1 g. of 20-mesh zinc (Coleman and Bell Co., C.P.). A spectrographic analysis revealed no detectable impurities in the zinc.

Enriched water was used in order to obtain better analytical accuracy. Samples from stock solutions of two different (known) isotopic compositions were used: $(\mathrm{D})_0/(\mathrm{H})_0 = 0.01060$ and 0.00872, respectively. The water sample (10–20 mg.) was introduced with a syringe into a small weighing ampoule, provided with a stopcock and ₸ joint, which was then connected to the vacuum line, frozen and outgassed several times, and weighed. The sample was then distilled *in vacuo* from the ampoule to the first U-tube trap where it was outgassed and stored (as a vapor) while the ampoule was reweighed empty to determine the quantity of water taken. After the sample had become completely vaporized in the first trap it was allowed to diffuse rapidly through the bed of hot zinc to the second trap at −195° which removed the unreacted water from the stream of hydrogen entering the evacuated Toepler volume. The hydrogen was then compressed into a sample bulb and held for mass spectrometric assay. The unreacted water was distilled into the ampoule and reweighed so that the percentage

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[1] (a) Taken from the M.S. thesis of W. G. H. (1954); (b) Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

[2] J. Horiuti and A. R. Szabo, *Nature*, **133**, 327 (1934).

[3] H. L. Johnston and C. O. Davis, THIS JOURNAL, **64**, 2613 (1942).

[4] (a) J. Horiuti and M. Polanyi, *Nature*, **132**, 819 (1933); (b) W. Bleakney and A. J. Gould, *Phys. Rev.*, **44**, 265 (1933).

[5] J. Graff and D. Rittenberg, *Anal. Chem.*, **24**, 878 (1952).

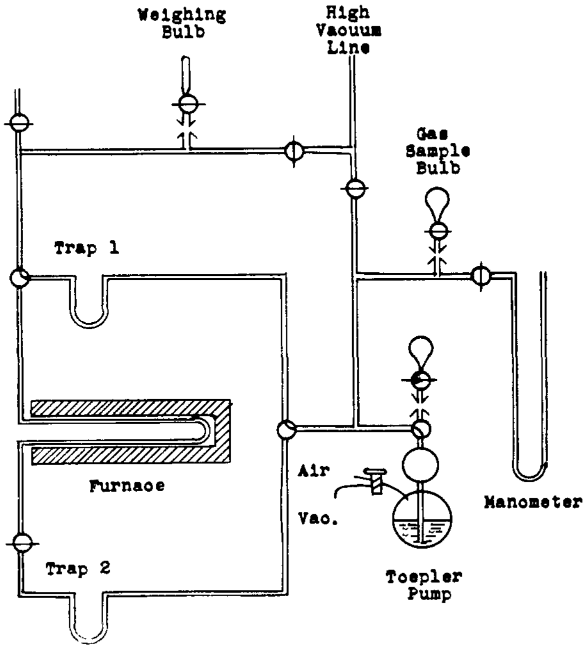

Fig. 1.—Apparatus for flow conversion of water to hydrogen.

decomposition could be determined (to ±1% decomposition).

The evolved hydrogen, enriched in protium, was compared with the hydrogen obtained from the quantitative conversion of samples of the standard solutions. A Consolidated-Nier Isotope-Ratio Mass Spectrometer, Model 21-201 was used for deuterium assay. A calibration curve of peak ratio 3/2 *vs.* known atom percentage deuterium was obtained on each occasion that analyses were performed. The uncertainty in the determination of (H)/(D) was ±3%, which is comparable with the accuracy of Alfin-Slater, *et al.*,[6] who made a detailed study of the mass spectrometric technique for the determination of deuterium.

Results

The separation factor S is defined as the ratio (H)/(D) in the evolved hydrogen divided by $(\mathrm{H})_0/(\mathrm{D})_0$ for the substrate water. The fractionation factor, α, corresponds to the limiting value of S at zero extent of reaction of the water with zinc. In order to obtain values of α from the experimental values of S it is necessary to correct to zero extent of reaction. It is shown in the Appendix that $\alpha = \log(1 - f)/\log(1 - f/S)$, where f = fraction of substrate reacted. For small extent of reaction this becomes $\alpha = S[1 + f(S - 1)/2S + \ldots]$, so that in the limit of $f = 0$, $\alpha = S$.

A graph of α *vs.* T(°C.) is shown in Fig. 2. Two symbols have been used, to differentiate between experiments for which $f < 0.25$ and those for which $f > 0.25$. It is believed that the former set is more reliable since the correction was smaller. The height of the vertical line through each point is based on the analytical error. The least-squares line drawn through all the data has a slope of $-0.0011(°\mathrm{C.})^{-1}$ over the temperature range 295–415°. The average deviation of points from the line is ±6%, which is larger than that anticipated on the basis of the analytical uncertainty. Possible non-uniformity of flow of water vapor through the zinc bed would cause an appreciable error in S of a magnitude which is difficult to estimate.

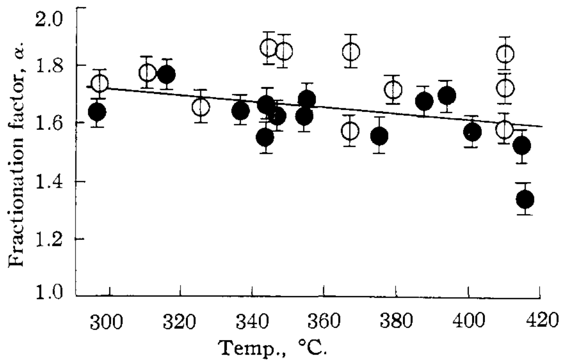

Fig. 2.—Fractionation factor, α (corr. to f equals 0) *vs.* temperature for the reaction of water vapor with zinc: ●, experiments for which $f < 0.25$; ○, experiments for which $f > 0.25$.

Discussion

Eyring and Cagle[7] have calculated theoretically the upper limit of the deuterium fractionation factor for the case of the rupture of an isolated oxygen–hydrogen bond. The expression given is

$$\alpha = \frac{\sinh(hc\bar{\nu}_{\mathrm{OH}}/2kT)}{\sinh(hc\bar{\nu}_{\mathrm{OD}}/2kT)}$$

with $\bar{\nu}_{\mathrm{OH}}$ and $\bar{\nu}_{\mathrm{OD}}$ taken to be 3652 and 2666 cm.$^{-1}$, respectively. These authors state: "a lower α than that calculated would be obtained for any process in which the reaction coördinate involves

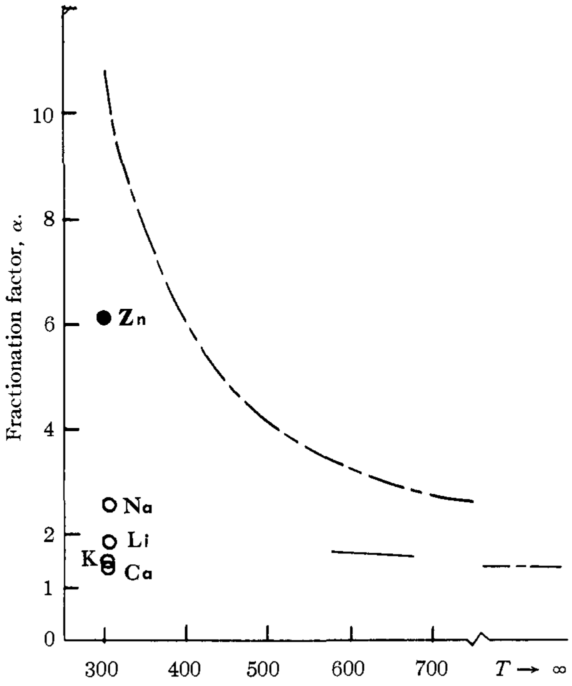

Fig. 3.—Fractionation factor, α, *vs.* temperature: — — —, Eyring and Cagle, theoretical upper limit for rupture of O–H *vs.* O–D bond; —, present results, smoothed experiments; O, Johnston and Davis, liquid water experiments; ●, Johnston and Davis, reaction with H_2SO_4.

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(6) R. B. Alfin-Slater, S. M. Rock and M. Swislocki, *Anal. Chem.*, **22**, 421 (1950).

(7) H. Eyring and F. W. Cagle, *J. Phys. Chem.*, **56**, 889 (1952).

motion other than a simple pulling away of the hydrogen isotope."

Figure 3 shows the temperature dependence of this theoretical maximum fractionation factor. The least-squares line from Fig. 2 is included on this graph, together with the points of Johnston and Davis[3] for the reaction of several metals with liquid water and for the reaction of zinc with 3.5 M H_2SO_4. The horizontal line at $\alpha = 1.4$ represents the theoretical α at $T = \infty$. The observed fractionation factors are seen to be lower than the curve representing the theoretical upper limit.

From the results of the present investigation it is possible to evaluate the correction for incomplete conversion of water to hydrogen in the conventional analytical method for deuterium. It is shown in the Appendix that the observed separation, S, is related to the fractionation factor, α, and the fractional conversion, f, by the equation

$$S = \frac{f}{1 - (1 - f)^{1/\alpha}}$$

From Fig. 2, $\alpha = 1.6 \pm 0.1$ at 400°. Shown in Fig. 4 is a graph of the correction factor, S, as a function of $1 - f$, the fraction of water unconverted.

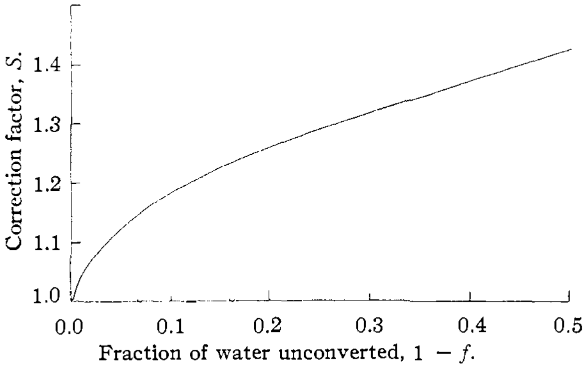

Fig. 4.—Correction factor for incomplete conversion of water to hydrogen by reaction with zinc at 400°.

Although this source of error has been generally recognized in the past (see, for example, ref. 6), quantitative data on the magnitude of the effect have been lacking. From the present results it would appear that at least 99% conversion is required in order to insure an error of <5% in the isotope ratio, (D)/(H).

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Appendix

Consider the competing isotopic reactions

$$\mathrm{HOH + M \longrightarrow H_2 + MO} \qquad k_1$$
$$\mathrm{HOD + M \longrightarrow HD + MO} \qquad k_2$$

Let $a_1 = (H_2O)$, $a_2 = (HOD)$, $x_1 = (H_2)$, $x_2 = (HD)$. The superscript ^{0} denotes initial concentration.

For the tracer case ($a_2 << a_1$, $x_2 << x_1$) one obtains, regardless of mechanism (see, for example, J. Bigeleisen, *Science*, **110**, 14 (1949))

$$\frac{dx_1}{dx_2} = \frac{k_1a_1}{k_2a_2} = \alpha\frac{a_1^0 - x_1}{a_2^0 - x_2}$$

This is integrated to give

$$\frac{x_2}{a_2^0} = 1 - \left(1 - \frac{x_1}{a_1^0}\right)^{1/\alpha}$$

Introducing the expression for the observed separation factor, $S = (x_1/x_2)/(a_1^0/a_2^0)$, one obtains

$$S = \frac{x_1/a_1^0}{1 - (1 - x_1/a_1^0)^{1/\alpha}}$$

The fraction reacted is closely approximated by $f = x_1/a_1^0$ so that

$$S = \frac{f}{1 - (1 - f)^{1/\alpha}} \quad \text{or} \quad \alpha = \frac{\log(1 - f)}{\log(1 - f/S)}$$

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The *trans* Effect in Inorganic Coördination Compounds.[1] I. Ultraviolet and Infrared Studies of *cis*- and *trans*-Dinitrotetramminecobalt(III) Chloride

BY J. PHILIP FAUST[2] AND J. V. QUAGLIANO

RECEIVED MAY 14, 1954

Ultraviolet and infrared spectra of *cis*- and *trans*-dinitrotetramminecobalt(III) chloride in the solid state have been measured. The use of the potassium bromide disk method for the ultraviolet and infrared studies of inorganic coördination compounds is discussed. In the absence of the solvent water, the so-called third band appears only in the ultraviolet spectrum of the *trans* isomer, in agreement with the *trans* anions hypothesis of Shibata–Tsuchida. The presence of strong absorption bands at 7.5 and 12.0 μ in the infrared spectra of the ammine complexes are explained as due to deformation of the ammonia groups coördinated to the metal atom. *cis*- and *trans*-dinitrotetramminecobalt(III) chloride are readily distinguished by their infrared spectra. Spectral evidence is presented to support the nitrogen-to-metal bonding in these nitro complexes.

Directive influences in reactions of inorganic coördination compounds are well known.[3] Werner[4] was able to explain the chemical evidence of directive influences in complexes on the basis of the straightforward and simple assumption that elimination of ligands, *trans* to each other in the coördi-

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[1] Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT(11-1)-38.

[2] Abstracted from the Ph.D. thesis of John P. Faust, Notre Dame, July, 1952. Presented before the Physical and Inorganic Division of the 124th National Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

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[4] A. Werner, *Z. anorg. allgem. Chem.*, **3**, 267 (1893).