[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Kinetics of the Vanadium(III)–Vanadium(IV) Exchange Reaction in Aqueous Perchloric Acid Solution[1a]

BY SYDNEY C. FURMAN[1b] AND CLIFFORD S. GARNER

A kinetic study of the exchange of radiovanadium between V(III) and V(IV) in aqueous perchloric acid was carried out, resulting in the following rate law in the concentration range of 0.01–0.05 *f* $V(ClO_4)_3$, 0.01–0.05 *f* $VO(ClO_4)_2$, 0.5–2.0 *f* $HClO_4$, μ adjusted to 2.5 with $NaClO_4$, 25–40°, $R = 4.5 \times 10^{12} \times \exp(-20,700/RT) \times [V(III)][V(IV)]/[H^+]$ mole liter^{-1} sec.$^{-1}$. The mechanism suggested for the rate-determining step involves an interaction of the hydrated ions VOH^{+2} and VO^{+2}. The heat and entropy of activation and specific rate constant for this postulated step have been determined. The exchange rate is *ca.* 5–10 times greater in 4 *f* NH_4SCN. Several chemical methods of separating V(III) and V(IV) were worked out; a cation-exchange resin used in a chromatographic column gave excellent separations.

In a previous publication from this Laboratory, Tewes, Ramsey and Garner[2] reported that the vanadium(IV)–vanadium(V) exchange in perchloric and hydrochloric acids was apparently instantaneous within the time required for separation of the vanadium species (5 minutes). The only other published work on exchange reactions of vanadium compounds is that of Sue and Yuasa[3] who reported slow heterogeneous exchange between vanadium(IV) and vanadium(V) ions and the corresponding solid 8-hydroxyquinoline and solid cupferron complexes.

This paper describes an investigation of the kinetics of the vanadium(III)–vanadium(IV) exchange in aqueous perchloric acid solution.

Experimental

Radiovanadium Tracer.—Sixteen-day V^{48} was prepared by the $Ti^{48}(p,n)$ reaction. Powdered C.P. titanium metal was bombarded in the U.C.L.A. frequency-modulated cyclotron using an internal beam of 14–18 Mev. protons.[4]

The targets were processed and vanadium(IV) tracer stock solutions prepared as described in reference 2. The radiochemical purity was checked by half-life.

Measurement of Radioactivity.—Each solution to be radioassayed was added to a 30-ml. test-tube and diluted to a definite volume, usually 20 ml. A dipping glass-wall Geiger tube, used with a scale of 64, was inserted by means of a rack and pinion arrangement in such a way as to give reproducible geometry. Care was taken to ensure that all solutions of a given exchange run had the same chemical composition when counted, making absorption and scattering corrections unnecessary.

Counting rates were corrected for background (*ca.* 12cts./min.), decay, and small coincidence losses. All samples were counted for times which reduced the statistical counting errors to less than 1% standard deviation.

Materials.—All chemical reagents were purified until iron(III) could no longer be detected by the sensitive method of Yoe and Young[5] employing disodium 1,2-dihydroxybenzene 3,5-disulfonate.

C.P. perchloric acid, redistilled at 5 mm., and C.P. sodium perchlorate, recrystallized twice from dilute perchloric acid, were used in the preparation of all perchlorate solutions.

Tank nitrogen, reportedly having less than 0.1% oxygen, was freed of oxygen by passage through fresh chromium(II) chloride solutions according to the method of Stone and Skavinski.[6]

Iron(III) impurity in the ion-exchange resin (250-500 mesh Ion-X) was removed by washing the resin with 6 *f* hydrochloric acid and then with distilled water.

Vanadium(III) and vanadium(IV) stock solutions were prepared electrolytically and analyzed as described by Furman and Garner.[7] Vanadium(III) perchlorate solutions were stored at 0° under an atmosphere of nitrogen. This procedure retarded the rate of the vanadium(III)–perchlorate reaction such that chloride ion was not detected by the silver nitrate test until after approximately one week (chloride ion was detectable within one day if solutions were stored at room temperature). Fresh solutions were used in each exchange run.

Procedure.—Appropriate volumes of vanadium(IV) perchlorate, perchloric acid and sodium perchlorate solutions were added to 50-ml. erlenmeyer flasks which had been previously filled with purified nitrogen. Aliquots (50–100 μl.) of the vanadium(IV) stock tracer solution were then added. The exchange reaction was initiated by adding a portion of the vanadium(III) stock solution to each flask. The concentration of hydrogen ion in each case was calculated assuming additivity of volumes. The individual concentrations of vanadium(III) and vanadium(IV) were determined volumetrically[7] for each exchange solution. The solutions were immersed in an oil-bath whose maximum variation in temperature was ±0.05°. Three different methods were developed for the separation of vanadium(III) and vanadium(IV) and were used to show that the exchange was measurable. Other methods tried but found unsatisfactory, included precipitation of vanadium(III) with sodium hydroxide (coprecipitated much vanadium(IV) and gave 100% zero-time exchange); extraction of vanadium(IV) thenoyltrifluoroacetone into benzene (extremely slow extraction from 1 *f* perchloric acid, and only 6% extraction from 10 *f* hydrochloric acid, vanadium(III) extracting negligibly in each case); essentially no separation found with pyridine, cupferron, ammonium fluoride, ethylenediaminetetraacetic acid with sodium hydroxide, or attempted extraction into diethyl ether from 1–10 *f* hydrochloric acid.

(1) **Leaching of Vanadium(IV) from Mixed Precipitate with EDTA.**—A solution of ethylenediamine tetraacetic acid (EDTA), *p*H 8, was found to leach out vanadium(IV) as a blue complex from a solid mixed fluoride of vanadium(III) and vanadium(IV), formed when saturated ammonium fluoride solution is added to the exchange mixture. Large unreproducible zero-time exchanges (*ca.* 20%) were found, probably resulting mainly from varying degrees of incomplete separation.

(2) **Ether or Ethyl Acetate Extraction of Vanadium(III) Thiocyanate Complexes.**—Vanadium complexes formed in 4 *f* ammonium thiocyanate were extracted into ethyl acetate or diethyl ether. Solutions 0.1 *f* in perchloric acid, 4 *f* in ammonium thiocyanate, and 0.01 *f* each in vanadium(III) and vanadium(IV), when shaken with equal volumes of peroxide-free diethyl ether, were found to give to the organic phase 6% of the total vanadium(IV) and *ca.* 66% of the total vanadium(III). Unreproducible zero-time exchanges (*ca.* 10–20%) were encountered, apparently resulting from formation of thiocyanate complexes which exchange prior to the extraction. Experiments indicated that the rate of exchange in 4 *f* ammonium thiocyanate is *ca.* 5–10 times greater than in the absence of thiocyanate ion. This enhanced rate is presumably associated with the formation of thiocyanate complexes of both vanadium(III) and vanadium(IV).[8]

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(1) (a) Abstracted from a thesis presented by Sydney C. Furman to the Graduate Faculty of the University of California, Los Angeles, in partial fulfillment of the requirements for the Ph.D. Degree, June, 1951; (b) General Electric Charles A. Coffin Predoctoral Fellow, 1950-1951. Present address: Knolls Atomic Power Laboratory, Schenectady, New York.

(2) H. A. Tewes, J. B. Ramsey and C. S. Garner, THIS JOURNAL, **72**, 2422 (1950).

(3) P. Sue and T. Yuasa, *J. chim. phys.*, **41**, 160 (1944).

(4) The bombardments were made possible through the coöperation of Professor J. R. Richardson and the cyclotron crew.

(5) J. H. Yoe and A. L. Young, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

(6) H. Stone and E. R. Skavinski, *ibid.*, **17**, 495 (1945).

(7) S. C. Furman and C. S. Garner, THIS JOURNAL, **72**, 1785 (1950).

(8) S. C. Furman and C. S. Garner, *ibid.*, **73**, 4528 (1951).

(3) **Separation by Ion-X Resin.**—The use of the cation-exchange resin Ion-X was found to be highly satisfactory for quantitative separations. The type of column used had a diameter of 0.7 cm. and contained 2 g. of 250–500-mesh moist resin which had been slurried with 1.94 *f* perchloric acid. The solid resin was allowed to settle, after which the perchloric acid solution was drained until there was no liquid above the upper level of the resin. An aliquot, usually 2 ml., of the exchange solution was pipetted onto the top of the resin, and then suction was applied to the exit end of the column. The time at which separation occurred was taken as the time at which the exchange solution was put on the resin column. As soon as the level of the exchange solution coincided with the top of the resin, 1.94 *f* perchloric acid was added to the column for the elution. A flow rate of 2–3 ml. per minute was used. Calibrated receiver flasks were used to collect 19-ml. fractions containing only vanadium(IV). Subsequent 2-ml. fractions (from 19 to 21 ml.) were collected separately and always gave a negative thiocyanate-color test for vanadium(III). Elution of the latter was found to begin after the total volume of effluent solution reached 28 ml. Used resin was discarded and new resin used for every separation. A bank of eight columns was found convenient to handle the separations required for four exchange experiments (half-times of 1–2 hours) progressing simultaneously.

Results

Apparent Zero-Time Exchange.—The exponential exchange law[9–11] as applied to the vanadium(III)–vanadium(IV) exchange is

$$Rt = -\frac{[\mathrm{V(III)}][\mathrm{V(IV)}]}{[\mathrm{V(III)}] + [\mathrm{V(IV)}]} \ln (1 - F) \qquad (1)$$

The exchange rate, R, is the constant rate at which vanadium(III) becomes vanadium(IV) and at which vanadium(IV) becomes vanadium(III) when all conditions other than distribution of radioactive atoms are constant. F, the fraction exchange which has been attained at time t, is given in our studies by

$$F = S_{(\mathrm{III})}/S_{\infty} \qquad (2)$$

where $S_{(\mathrm{III})}$ is the specific activity of the initially inactive vanadium(III) at time t, and S_{∞} is the specific activity of vanadium(III) or vanadium(IV) after isotopic equilibrium is attained. S_{∞} was experimentally determined for several exchange runs, but generally it was computed as the average specific activity of all the vanadium in the exchange mixture. Specific activities were expressed arbitrarily in terms of counts per minute per formula-weight of vanadium(III). All concentrations (bracketed quantities) are expressed in units of gram atoms of vanadium per liter of solution at 25°.

Table I summarizes the results of our exchange-rate experiments, all separations having been carried out with the exchange resin (method 3). Representative results are shown in Fig. 1, in which semi-logarithmic plots of equation 1 were made. Inspection of Fig. 1 shows that the data agree well with the expected exponential exchange law, and also shows that a small apparent zero-time exchange exists. It is evident from Fig. 1, as well as from column 6 of Table I, that the zero-time fraction exchange, F_0, is not a constant for all exchange runs. Prestwood and Wahl[12] have discussed the zero-time fraction exchange in the light of separation-induced exchange and incomplete separation effects. Separation-induced exchange and the degree of separation must be reproducible for a given exchange run in order that agreement be obtained with the exponential exchange law. The excellent straight-line plots of equation 1 obtained in our work suggest that the exchange induced during the separation of the resin was reproducible in all the separations used in a certain exchange run. The inconstancy of the values of F_0 may be explained by assuming that F_0 is the sum of two induced exchange terms: (1) the reproducible separation-induced fraction exchange and (2) a true zero-time exchange occurring during mixing of solutions at the start of an exchange run. The latter may vary because of differences in stirring rates and inconstant concentration gradients.

TABLE I

EXCHANGE RATES (μ ADJUSTED TO 2.5 WITH $NaClO_4$)

Run	[V-(III)], *f*	[V-(IV)], *f*	[HCl-O_4], *f*	Temp., °C.	$100F_0$, %	$t_{1/2}$, hr.
1	0.0490	0.0522	2.00	25.0	11.5 ± 1	1.56 ± 0.02
2	.0238	.0330	2.00	25.0	3.6 ± 2	2.6 ± .1
3	.0238	.0231	2.00	25.0	5.9 ± 2	2.8 ± .1
4	.0240	.0234	2.00	25.0	11 ± 1	3.5 ± .1
5	.0236	.0180	2.00	25.0	−1 ± 3	3.7 ± .1
6	.0143	.0217	2.00	25.0	5.8 ± 2	4.1 ± .1
7	.0154	.0181	2.00	25.0	6.4 ± 2	4.2 ± .1
8	.0114	.0151	2.00	25.0	11.7 ± 2	6.0 ± .3
9	.0111	.0264	0.477	25.0	9.6 ± 4	0.94 ± .07
10	.0119	.0250	0.672	25.0	6.3 ± 4	1.6 ± .1
11	.0125	.0250	1.00	25.0	22 ± 2	2.5 ± .1
12	.0162	.0205	2.00	32.5	0 ± 3	1.31 ± .06
13	.0076	.0123	2.00	32.5	2 ± 5	3.0 ± .2
14	.0160	.0216	2.00	40.0	11 ± 2	0.69 ± .02
15	.0079	.0118	2.00	40.0	10 ± 3	1.42 ± .07

Dependence of Exchange Rate on Vanadium(III) and Vanadium(IV) Concentrations.—If the exchange rate is first order in vanadium(III) and first order in vanadium(IV)

$$R = k_1[\mathrm{V(III)}][\mathrm{V(IV)}] \qquad (3)$$

where k_1 is the specific rate constant at a certain hydrogen-ion concentration. The half-time for exchange, $t_{1/2}$, is then given by the equation at 25°.

$$t_{1/2} = \frac{0.693}{[\mathrm{V(III)}] + [\mathrm{V(IV)}]} \times \frac{1}{k_1} \qquad (4)$$

Figure 2 shows a plot of the reciprocal of total vanadium concentration against the half-time for exchange at 25.0° in 2.00 *f* perchloric acid and a total ionic strength of 2.5 (runs 1–8 of Table I). The least-squares straight line is shown; the intercept is zero within its probable error. As shown, the exchange half-time is inversely proportional to the total vanadium concentration, in agreement with equation 4 and the assumed bimolecularity of the exchange reaction. The specific rate constant k_1 has been calculated from the slope to be $(1.3 \pm 0.1) \times 10^{-3}$ mole^{-1} liter sec.$^{-1}$.

Dependence of Exchange Rate on Hydrogen-Ion Concentration.—It is well known that solutions of vanadium(III) perchlorate contain in addition to the hydrated tripositive ion V^{+3} hydrolyzed species as well. The range of acidity employed in this

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[9] H. A. C. McKay, *Nature*, **142**, 997 (1938).

[10] G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 287.

[11] A. C. Wahl and N. A. Bonner (editors), "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 1 by O. E. Myers and R. J. Prestwood.

[12] R. J. Prestwood and A. C. Wahl, THIS JOURNAL, **71**, 3137 (1949). See also Appendix I of reference 11.

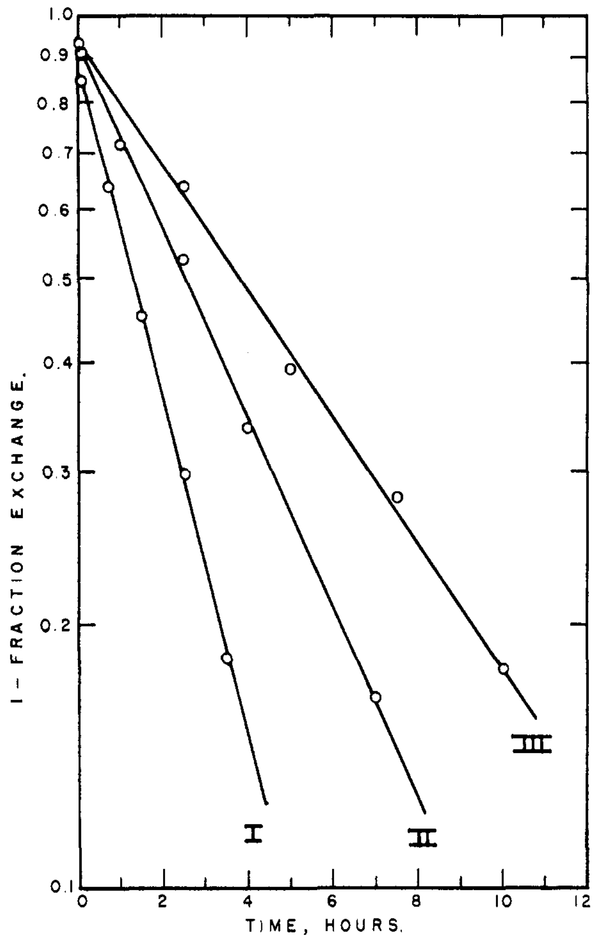

Fig. 1.—Representative semi-logarithmic plot of (1 – fraction exchange) against time (2.00 *f* $HClO_4$, μ adjusted to 2.5 with $NaClO_4$, 25.0°): curve I, 0.0490 *f* $V(ClO_4)_3$, 0.0522 *f* $VO(ClO_4)_2$; curve II, 0.0238 *f* $V(ClO_4)_3$, 0.0231 *f* $VO(ClO_4)_2$; curve III, 0.0154 *f* $V(ClO_4)_3$, 0.0181 *f* $VO(ClO_4)_2$.

study was expected to permit the occurrence of the species VOH^{+2} but only insignificant concentrations of higher hydrolyzed ions.[7] If we assume that both species of vanadium(III) exchange with vanadium(IV), the rate of exchange is given as

$$R = [V(III)][V(IV)]\{k_2 + k/[H^+]\} \qquad (5)$$

By substituting R from the equation

$$R = \frac{[V(III)][V(IV)]}{[V(III)] + [V(IV)]} \times \frac{0.693}{t_{1/2}}. \qquad (6)$$

in equation 5 the following equation is obtained

$$\frac{1}{[V(III)] + [V(IV)]} \times \frac{0.693}{t_{1/2}} = k_2 + k/[H^+] \qquad (7)$$

According to equation 7 a plot of the left-hand side against the reciprocal of hydrogen-ion concentration should yield a straight line of slope k and intercept k_2. The results found at 25.0° in the range of hydrogen-ion concentration from 0.5 to 2.0 *f* are shown in Fig. 3 (runs 6, 9, 10, 11 of Table I).[13]

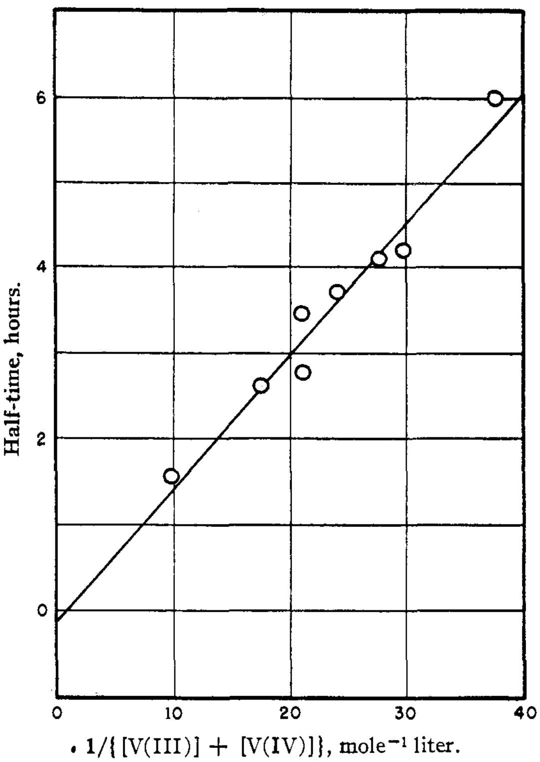

Fig. 2.—Dependence of exchange half-time on total vanadium concentration (2.00 *f* $HClO_4$, μ adjusted to 2.5 with $NaClO_4$, 25.0°).

The intercept was calculated by the method of least squares to be (2.8 ± 3.3) × 10^{-4} $mole^{-1}$ liter $sec.^{-1}$. From these results it can be concluded

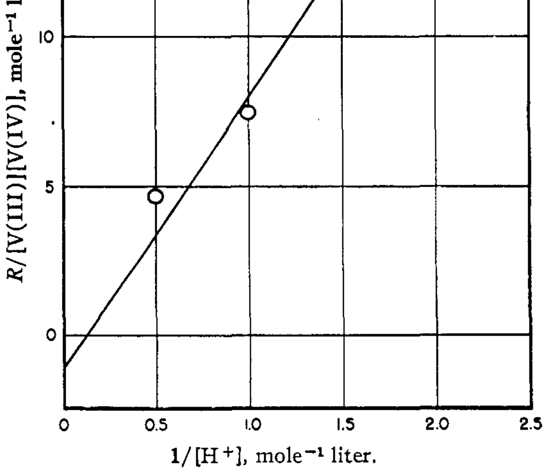

Fig. 3.—Dependence of exchange rate on acid concentration (μ adjusted to 2.5 with $NaClO_4$, 25.0°).

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[13] The data of Fig. 3 are not sufficiently precise to warrant according significance to the apparent trend toward curvature of the line. Such curvature, if real, might arise from ignored changes of activity coefficients due to replacement of hydrogen ion by sodium ion at constant ionic strength, or from participation of species like $V(OH)_2^+$ possibly present at low concentrations.

that k_2 is zero within the experimental error and that the rate of exchange is given by

$$R = k[\mathrm{V(III)}][\mathrm{V(IV)}]/[\mathrm{H^+}] \qquad (8)$$

Over the range 0.50 to 2.00 f perchloric acid, μ = 2.5, the value of k at 25.0° is $(2.6 \pm 0.2) \times 10^{-3}$ sec.$^{-1}$.

A similar type of analysis has been used by Prestwood and Wahl[12] in their study and interpretation of the hydrogen-ion dependence of the thallium(I)–thallium(III) exchange rate. Harbottle and Dodson[14] subsequently made measurements on this same system over a wider range of hydrogen-ion concentration. They found that the assumption made by Prestwood and Wahl that only a small fraction of one of the reactants (probably $\mathrm{Tl^{+++}}$) is hydrolyzed appears to be inconsistent with rate results obtained at lower concentrations of hydrogen ion. However, in the present vanadium exchange study the application of equation 7 is expected to be essentially valid as the hydrolysis constant of vanadium(III) has been estimated[15] to be of the order of 2×10^{-3}, and in the range of acidity investigated by us no saturation effects would be detected.

Activation Energy.—A semi-logarithmic plot of k against the reciprocal of the absolute temperature is shown in Fig. 4 (runs 5, 12, 13, 14 and 15 of Table I). From the slope the apparent heat of activation was found to be 20,700 ± 1,400 cal./mole. The specific rate constant may be represented as

$$k = 4.5 \times 10^{12} e^{-20{,}700/RT}\ \mathrm{sec.}^{-1} \qquad (9)$$

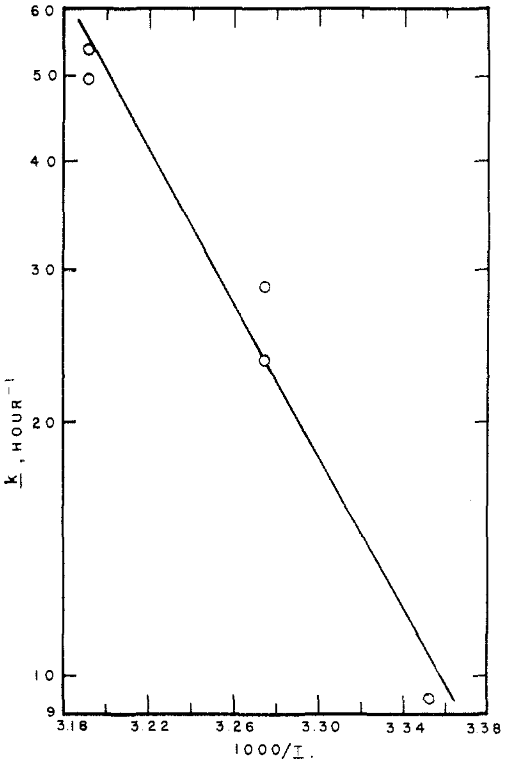

Fig. 4.—Dependence of exchange rate on temperature (2.00 f $\mathrm{HClO_4}$, μ adjusted to 2.5 with $\mathrm{NaClO_4}$).

where R is the molar gas constant and T is the absolute temperature.

Discussion

The effect of perchloric acid on the exchange rate suggests that a hydrolyzed species is a reactant in the rate-determining step. It was not possible to determine from the kinetics whether vanadium(III) or vanadium(IV) was responsible for this hydrolysis product. However, we have reported in an earlier paper[7] that, under the experimental conditions involved in the present investigation, vanadium(IV) is present largely as the hydrated vanadyl ion, $\mathrm{VO^{+2}}$ or $\mathrm{V(OH)_2{}^{+2}}$, and vanadium(III) is partly hydrolyzed according to the equilibrium

$$\mathrm{V^{+3} + H_2O \rightleftarrows VOH^{+2} + H^+}\ K_h\ \text{(rapid, reversible)} \qquad (10)$$

Accordingly, one may postulate that the rate-determining step in the exchange may be

$$\mathrm{VOH^{+2} + V^{*}O^{+2}} \xrightarrow{k'} \mathrm{Z^{*+4}} \longrightarrow \mathrm{V^{*+3} + VO^{+2}}\ \text{(rate determining)} \qquad (11)$$

The transition state may have a structure with the vanadium atoms bonded through an oxygen bridge. The vanadium atoms might then become equivalent through transfer of a hydroxyl radical from the vanadium(IV) atom to the vanadium(III) atom, or by a concerted action involving transfer of a hydrogen atom.

Under our experimental conditions $[\mathrm{V^{+3}}] \gg [\mathrm{VOH^{+2}}]$, whence the exchange-rate law given by equation 8 may be written, by combination with the hydrolysis constant expression for reaction 10, as

$$R = (k/K_h)[\mathrm{VOH^{+2}}][\mathrm{VO^{+2}}] \qquad (12)$$

The exchange rate according to equation 11 is given as

$$R = k'[\mathrm{VOH^{+2}}][\mathrm{VO^{+2}}] \qquad (13)$$

from which it is seen that

$$k' = k/K_h \qquad (14)$$

From an approximate value[15] of the hydrolysis constant, $K_h = 2 \times 10^{-3}$ mole liter^{-1}, a rough value of k' is found from equation 14 to be 1 mole^{-1} liter sec.$^{-1}$ at 25.0°.

On the basis of the postulated rate-determining step, reaction 11, the apparent heat of activation is the sum of the heat of activation of reaction 11 and the heat of hydrolysis of the hydrated $\mathrm{V^{+3}}$ ion. The latter has been reported by Furman and Garner[7] to be ΔH_h = 10,000 ± 1,000 cal./mole at 25°. Hence, the true heat of activation, that for reaction 11, is 20,700 minus 10,000, or 10,700 ± 1,700 cal./mole. The entropy of activation for reaction 11 calculated from the experimental rate constants with the aid of the absolute rate theory[16] is −24 cal. deg.$^{-1}$ mole^{-1}. The rate constant, k', for the postulated rate-determining step may then be expressed as

$$k' = 1 \times 10^{8} e^{-10{,}700/RT}\ \mathrm{mole^{-1}\ liter\ sec.^{-1}} \qquad (15)$$

It is interesting to note that the hydrated species

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(14) G. Harbottle and R. W. Dodson, THIS JOURNAL, **73**, 2442 (1951).

(15) S. C. Furman and J. T. Denison, private communication.

(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

VOH^{+2} has been called upon in other kinetic studies involving vanadium(III). Ramsey, Sugimoto and DeVorkin[17] have found that rate measurements indicate the VOH^{+2} ion is the predominantly reactive species when vanadium(III) reacts with such "non-oxide"-containing oxidants as iodine, copper(II) and oxygen.

Acknowledgment.—The authors wish to thank Professor J. B. Ramsey for helpful discussions.

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[17] J. B. Ramsey, R. Sugimoto and H. DeVorkin, THIS JOURNAL, **63**, 3480 (1941).

[CONTRIBUTION FROM THE SCHOOL OF MEDICINE AND DENTISTRY, UNIVERSITY OF ROCHESTER]

Some Ion-Exchange Studies of the Polymerization of Beryllium[1]

BY ISAAC FELDMAN AND JEAN R. HAVILL

The ion-exchange between beryllium solutions and the ammonium form of Dowex 50 resin was studied to determine the experimental conditions under which polymerization of beryllium begins. At an ionic strength of 0.1, *p*H 4.5, and 37°, the polymerization of beryllium in perchlorate solution begins when its concentration is raised to about 10^{-5} *M*. Increasing the ionic strength to 0.4 appears to increase the extent of polymerization. At *p*H 5.5 beryllium could not be kept completely in solution, even in tracer concentration, without the addition of complexing agents.

In our application of the ion-exchange technique of Schubert[2] to the study of the beryllium–citrate complex,[3] it became necessary to gain more knowledge than was available previously concerning the polymerization of the beryllium ion as a function of *p*H and beryllium concentration.

It has been shown[4] that in macro concentration (above 0.005 *M*) the beryllium ion is readily hydrolyzed and that the initial hydrolysis product polymerizes immediately.

A literature survey has revealed no data pertinent to the subject for solutions containing less than 0.005 *M* beryllium. An extrapolation of the hydrolysis data given in Table I would seem to indicate that at *p*H 4.6[5] and at an ionic strength of 0.1 beryllium is in an unhydrolyzed state when its concentration is less than *ca.* 10^{-4} *M*. However, Schubert and Conn,[6] have pointed out that hydrolyzable elements may form radio-colloids even at *p*H's and concentrations so low that one would infer from macro-measurements that no hydrolysis occurs. We have utilized their suggestion that ion-exchange resins may be used to detect the occurrence of polymerization of ions in low concentrations.

TABLE I

EFFECT OF BERYLLIUM CONCENTRATION ON HYDROLYSIS OF BERYLLIUM AT *p*H4.6; IONIC STRENGTH, *ca.* 0.11; 31°

(See experimental section for details)

Solution titrated	Titrating agent	NaOH added, ml.	% Be hydrolyzed, (approx.)
0.0562 *M* $BeSO_4$	0.0755 *M* NaOH	15.30	83
.0112 *M* $BeSO_4$ in 0.08 *M* $NaClO_4$	.0755 *M* NaOH	2.51	68
.00337 *M* $BeSO_4$ in 0.10 *M* $NaClO_4$	.00653 *M* NaOH in 0.10 *M* $NaClO_4$	5.40	42
.000337 *M* $BeSO_4$ in 0.10 *M* $NaClO_4$	....	0	<7[a]

[a] The *p*H of 3.37×10^{-4} *M* $BeSO_4$ in 0.1 *M* $NaClO_4$ was 4.73, indicating about 7% hydrolysis of beryllium.

Experimental

Materials.—All chemicals other than the beryllium solutions were J. T. Baker C.P. analyzed grade.

The molar concentration of the beryllium isotope, Be^7, was calculated[7] from the radioactivity in mc./ml., as stated by the supplier, the Oak Ridge National Laboratory.

The beryllium perchlorate stock solution was prepared by dissolving beryllium metal (spectroscopically better than 99.9% pure) in a slight excess of perchloric acid, filtering the insoluble residue, and diluting to the desired volume. The concentration of this stock solution was determined by the alkannin method.[8] The beryllium sulfate stock solution was prepared from $BeSO_4 \cdot 4H_2O$, which had been recrystallized four times from water, and was standardized by ignition of an aliquot to beryllium oxide.

The Dowex 50 resin received from the manufacturer was in the hydrogen form and had an exchange capacity of 5.03 milliequivalents per gram of air-dried resin. This was converted to the ammonium form by several alternate cycles and recycles with 5 *M* HCl and 5 *M* NH_4Cl, the final NH_4Cl cycle being continued until the *p*H of the effluent equalled the *p*H of the influent. The resin was then treated with 0.15 *M* NH_4Cl until the *p*H of the effluent equalled that of the influent, washed several times with distilled water until the effluent gave no test for chloride ion, and finally air-dried. The 40–60 mesh screening fraction, having a moisture content of 9%, was used throughout this investigation.

Procedure.—Twenty 5-ml. volumes containing the indicated concentrations of beryllium salt (to each of which was added a known amount of radioactive Be^7 tracer) and ammonium perchlorate were adjusted to the desired *p*H with a measured volume of standardized ammonium hydroxide. A Beckman Model G *p*H meter was employed for these adjustments. Twenty milliliters of each solution was then pipetted into a 50-ml. glass-stoppered erlenmeyer flask containing 0.070 g. (known in each case to the fourth decimal place) of ammonium resin. The unused portion of each solution was kept to be used as the standard in the final counting procedure. Each glass stopper was sealed with paraffin. The stopper and neck of each flask was finally wrapped tightly with Parafilm. The flasks were shaken for about 15 hours (*i.e.*, overnight) on a Boerner oscillating platform shaker in a constant temperature room maintained at 37°. After being shaken, the solutions were decanted

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[1] This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York.

[2] J. Schubert, *J. Phys. Colloid Chem.*, **52**, 340 (1948).

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