[Contribution from the Department of Chemistry, Washington University]

# Kinetics of the Vanadium(II)–Vanadium(III) Isotopic Exchange Reaction[1]

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In 1.00 *f* $HClO_4$ and ionic strength 2.00 the rate of exchange between $V^{II}$ and $V^{III}$ is consistent with the law rate = $k\cdot(V^{II})(V^{III})$. At 25° the value of $k$ is 0.82 $f^{-1}$ min.$^{-1}$. The experimental activation energy is 13.2 kcal./mole. The rate was not affected measurably by a fivefold increase in the surface area of the reaction vessel, by the absence of ordinary diffuse light, by an increase in the ionic strength to 4.00 or by replacement of $NaClO_4$ by $LiClO_4$ for adjustment of ionic strength. The rate is increased by lowering the hydrogen ion concentration below 0.5 *M* and by the presence of chloride ion. The rate data are consistent with the expression $k = k_1 + k_2/(H^+) + k_3(Cl^-)$, the values of the constants at 25° being $k_1 = 0.61\ f^{-1}$ min.$^{-1}$, $k_2 = 0.21$ min.$^{-1}$ and $k_3 = \sim 85\ f^{-2}$ min.$^{-1}$.

Kinetic data for the vanadium(II)-vanadium(III) isotopic exchange reaction are of interest for comparison with existing data for the chromium(II)–chromium(III),[2–4] iron(II)–iron(III),[5,6] cobalt(II)–cobalt(III)[7] and europium(II)–europium(III)[8] reactions.

King and Garner[9] found complete exchange in their experiments at 2° involving reaction times of one to five minutes, total vanadium concentrations of ∼0.2 *M*, and two different separation methods.

Since the iron(II)–iron(III) and cobalt(II)–cobalt(III) exchange reactions would also have been complete under these conditions, the problem was reopened with the hope that rapid mixing and quenching procedures[10–12] would make rate measurements possible. However, once quenching procedures were found that did not induce complete exchange, it was learned that the rate was sufficiently small to be studied by more conventional techniques. Apparently, the separation procedures used by King and Garner[9] induced complete exchange, as did several procedures that we tried.

## Experimental

**Radioactivity.**—The tracer used was the 16-day $V^{48}$ made by the $Ti^{48}(d,2n)V^{48}$ reaction in the Washington University cyclotron. The decay of $V^{48}$ is accompanied by 2.22, 1.320, 0.990 and 0.511 Mev. γ-rays.[13] which were conveniently detected with a scintillation counter. Ten milliliter samples of vanadium(IV) solutions were counted in tubes selected to give the same counting efficiencies. A stilbene crystal was used for some runs and a well-type sodium iodide crystal for others.

The radiochemical purification procedure, which was similar to one of Haymond, *et al.*,[14] was designed to minimize sulfate and chloride contamination. Purification after addition of carriers included a sodium carbonate fusion,[15] which resulted in water soluble sodium vanadate, titanium and other neighboring elements remaining in the melt residue and two lead vanadate precipitations.[16] The last lead vanadate precipitate was dissolved in 1 *f* $HClO_4$, the resulting solution treated with hydrogen sulfide, and the lead sulfide removed by centrifugation from the $VO^{++}$ tracer solution. Excess hydrogen sulfide was removed by boiling and by sweeping with carbon dioxide.

Radiochemical purity was checked by following the decay with the stilbene-crystal scintillation counter. Measured half-lives for the nine different preparations agreed well with the reported value of 16.0 ± 0.2 days.[17] Additional evidence for the radiochemical purity of the first few tracer preparations was the equality of the vanadium(II) and vanadium(III) "infinite-time" specific activities and the average specific activity.

**Chemicals.**—Vanadium(IV) stock solutions in $HClO_4$ were prepared by electrolytic reduction[18] of $V_2O_5$ (Fisher Scientific Company, C.P. *grade*) suspended in $HClO_4$. A modification of Banerjee's cell[19] was used, a platinum strip serving as cathode and a platinum wire in a porous cup as anode.

Vanadium(II) stock solutions in $HClO_4$ were made just prior to use by electrolytic reduction in a nitrogen atmosphere of vanadium(IV) stock solutions in the cell described above. Completion of reduction was indicated by the gradual disappearance of the blue color and by the characteristic purple color of $V^{++}$. The reducing equivalence of one solution was determined and found to be 2.96.

Tagged vanadium(III) solutions in $HClO_4$ were made by mixing equivalent amounts of the vanadium(II) and vanadium(IV) solutions after addition of a small volume of $V^{48}$ tracer solution (as V(IV)) to the latter. The reaction is complete[20] and rapid.

Reactants prepared by electrolytic or zinc-amalgam reduction[21,22] of vanadium(IV) solutions prepared by $H_2S$ reduction of $V_2O_5$ suspensions in $HClO_4$ gave exchange rates that were larger than those obtained with reactants prepared entirely by electrolytic reduction.

Mallinckrodt A.R. $HClO_4$, G. F. Smith $NaClO_4$ and Eastman Kodak 2,2′-dipyridyl were used without further purification. All other chemicals were of reagent grade.

**Analytical Methods.**—Vanadium was determined by titration[23] of vanadium(IV) with $MnO_4^-$ at 60 to 80°. The vanadium(IV) was prepared for titration by oxidation of lower states to vanadium(V) with $(NH_4)_2S_2O_8$, boiling to destroy excess oxidant, reduction by $SO_2$ to vanadium(IV) and removal of excess $SO_2$ by boiling and by sweeping with $CO_2$.

The acidity of vanadium solutions was determined by shaking with 15 to 20 g. of the acid form of Dowex 50-X4 resin in a 125-ml. stoppered erlenmeyer flask flushed with nitrogen and the filtrate titrated with standard sodium

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[3] E. L. King and H. Taube, *ibid.*, **76**, 4053 (1954).

[4] D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

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[7] J. P. Hunt and N. A. Bonner, *ibid.*, **74**, 1866 (1952).

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[15] Shohei Uno and Toshio Inokuma, *J. Chem. Soc. Japan, Ind. Chem. Soc.*, **54**, 758 (1951).

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[17] W. C. Peacock and M. Deutsch, *Phys. Rev.*, **69**, 306 (1946).

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[19] P. C. Banerjee, *J. Indian Chem. Soc.*, **12**, 198 (1935).

[20] *K* for $VO^{++} + V^{++} + 2H^+ = 2V^{+++} + H_2O$ is $1 \times 10^{19}$; calculated from data given by W. M. Latimer, "Oxidation Potentials," Prentice–Hall Inc., New York, N. Y., 1953, p. 265.

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[23] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, **6**, 48 (1934).

hydroxide. The titer was corrected for the hydrogen-ion equivalents released by the resin (2/V(II), 3/V(III), 2/V(IV)).

The purity of a vanadium(IV) stock solution was checked by testing aliquots for V(III) by addition of $KIO_3$ and for V(V) by addition of KI. The absence of iodine color in $CCl_4$ shaken with these solutions showed the absence of V(III) and V(V).

Chloride ion could not be detected in the vanadium solutions by addition of $AgNO_3$ and hence was less than $10^{-4}$ *M*.

**Quenching-Separation Method.**—Six milliliters of reaction solution was added to the quench solution prepared just prior to use by mixing 2 ml. of 15 *f* $NH_4OH$ and 20 ml. of 2% dipyridyl solution in 1:1 ethanol-water mixture. Mechanical stirring started before addition of the reaction mixture was continued for one minute after addition, then the quenched mixture was allowed to stand for six minutes before centrifugation for three minutes. The supernatant containing $V(dipy)_3^{++}$ was taken for specific-activity determination.

Zero-time exchange was about 25%, but increased to about 50% for reaction mixtures of low acid concentration. Heterogeneous exchange between $V(dipy)^{++}$ and $V(OH)_3$ during the stirring, standing and centrifugation was about 12% and varied little for standing times ranging from 3 to 15 minutes. Only ~25% of the vanadium(II) was recovered, and at the lower hydrogen ion concentrations the recovery was even less.

Other quenching procedures investigated were less satisfactory. Mixing the reaction and dipyridyl solutions and then addition of $NH_4OH$, a procedure used by King and Garner,[9] but under different conditions, gave ~40% zero-time exchange and ~30% recovery of vanadium(II). Quenching with an acetate buffered dipyridyl solution and then addition of $NH_4OH$, as was done in the iron(II)–iron(III) exchange,[5] increased the vanadium(II) yield to ~80% and the zero-time exchange to ~85%. Attempts to precipitate $V(dipy)_3^{++}$ with various anions from acid solution were unsuccessful. Extraction of vanadium(III) from acid thiocyanate solution into ethyl acetate resulted in complete zero-time exchange.

**Procedure.**—The vanadium(III) reactant solution in the reaction vessel, a pear-shaped vessel[6] of about 125-ml. capacity equipped with an automatic pipet and a side tube through which nitrogen was passed, and the vanadium(II) reactant solution in a glass stoppered tube were brought to the desired temperature in a constant temperature (±0.2°) water-bath and then mixed. Necessary amounts of standardized $HClO_4$ and/or $NaClO_4$ solutions were added to either or both reactant solutions to adjust the acidity and the ionic strength. Aliquots were removed with the automatic pipet and quenched. Two aliquots of the reaction mixture were taken for average specific-activity determinations. Reactant concentrations were known from the concentrations of the stock vanadium(II) and vanadium(IV) solutions used.

The supernatant from the quenched mixture was evaporated to dryness, and the residue was fumed with a $H_2SO_4$–$HClO_4$–$HNO_3$ mixture to destroy organic material. After conversion to vanadium(IV), a sample was diluted to 10 ml., counted and titrated with $KMnO_4$.

The fraction exchange was obtained by division of the specific activity (counts/min. per ml. $KMnO_4$ solution) by the average specific activity. Data were plotted as illustrated in Fig. 1, and half-times were read from the plots.

## Results

If the exchange reaction obeys the rate law

$$R = k(V^{II})(V^{III}) \qquad (1)$$

the over-all rate constant *k* is related to the half-time $t_{1/2}$ by the expression[24]

$$k = \frac{\ln 2}{t_{1/2}\,[(V^{II}) + (V^{III})]} \qquad (2)$$

As shown in Table I the values of *k* do not vary with the reactant concentrations, indicating the validity of equation 1.

TABLE I

RATE DEPENDENCE ON V(II) AND V(III) CONCENTRATIONS

(25.0°, 1.000 *M* $H^+$, ionic strength adjusted to 2.00 with $NaClO_4$)

| V(II), *f* | V(III), *f* | $t_{1/2}$, min. | *k*, $f^{-1}$ min.$^{-1}$ |
|---|---|---|---|
| 0.043 | 0.043 | 9.5 | 0.85 |
| .086 | .043 | 6.9 | .78 |
| .129 | .043 | 4.8 | .84 |
| .086 | .086 | 5.1 | .79 |
| .129 | .086 | 3.9 | .83 |
| .086 | .124 | 3.9 | .83 |
| | | | Av. 0.82 |

The dependence of rate on temperature is shown in Fig. 2. From the slope of the line an experimental activation energy of 13.2 ± 0.3 kcal./mole was obtained. The value of the experimental entropy of activation[25] is −24.9 cal./deg./mole.

Above 0.5 *M* $H^+$ the rate was not measurably affected by variation of the hydrogen ion concentration. Below 0.5 *M* $H^+$ the rate increased with decreasing hydrogen ion concentration. The rate data for the lower hydrogen ion concentrations are somewhat less accurate than for the higher concentrations because of greater zero-time exchange and lower vanadium(II) yields. The data can be fit reasonably well by a *k vs.* $1/(H^+)$ plot as shown in Fig. 3, suggesting a rate expression of the form

$$\text{Rate} = (V^{II})(V^{III})\,\{k_1 + k_2/(H^+)\} \qquad (3)$$

The values of $k_1$ and $k_2$ are 0.61 $f^{-1}$ min.$^{-1}$ and 0.21 min.$^{-1}$, respectively.

The data in Table II show that the exchange rate is not measurably affected by increasing the surface of the reaction vessel fivefold (by the addition of glass beads), by the absence of ordinary diffuse light, by increasing the ionic strength to 4.00 or by replacement of $Na^+$ ion by $Li^+$.

TABLE II

MISCELLANEOUS RATE DATA

(25.0°, 0.086 *f* V(II), 0.086 *f* V(III), 1.000 *M* $H^+$, ionic strength adjusted to 2.00 with $NaClO_4$, except as noted)

| Conditions | $t_{1/2}$, min. | *k*, $f^{-1}$ min.$^{-1}$ |
|---|---|---|
| Surface increased fivefold with glass beads | 5.0 | 0.81 |
| Total darkness | 4.9 | .82 |
| Ionic strength 4.00 | 5.2 | .78 |
| 0.198 *M* $H^+$ | 2.1 | 1.92 |
| 0.198 *M* $H^+$, ionic strength to 2.00 with $LiClO_4$ | 1.9 | 2.12 |

The exchange rate was found to be larger in the presence of chloride ion. The rate data are not very accurate because of low vanadium(II) recoveries, and their interpretation is not straight-forward because the exchange curves exhibited some curvature, especially at the higher chloride-ion concentrations. (At the lower hydrogen ion concentrations there also was a suggestion of curvature in some of the exchange curves.) The curvature suggests that exchange occurred at more than one rate, as would happen if there were exchange between more than two species not in rapid equilibrium. The exchange data were not sufficiently accurate for

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(24) See, for example, O. E. Meyers and R. J. Prestwood, "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, editors, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 11.

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

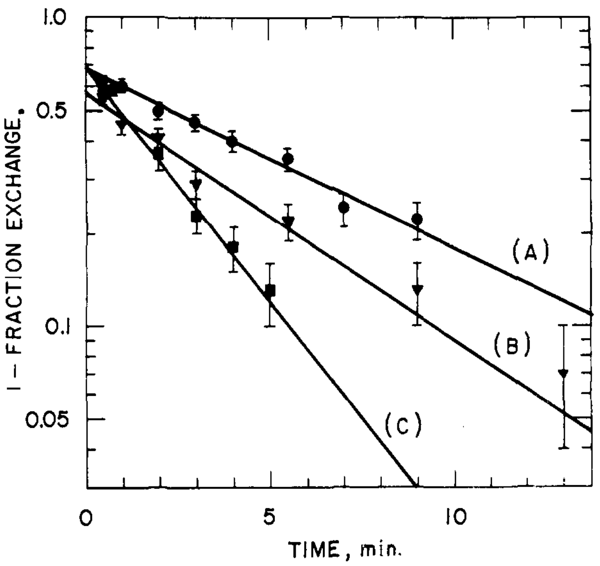

Fig. 1.—Typical exchange curves—conditions: 25.0°, 0.086 *f* V(II), 0.086 *f* V(III), ionic strength adjusted to 2.00 by addition of $NaClO_4$. Curve (A): 1.000 *M* $H^+$, $t_{1/2}$ 5.1 min.; curve (B): 0.400 *M* $H^+$, $t_{1/2}$ 3.8 min.; curve (C): 0.190 *M* $H^+$, $t_{1/2}$ 2.0 min. The errors shown correspond to ±0.03 in the fraction-exchange values.

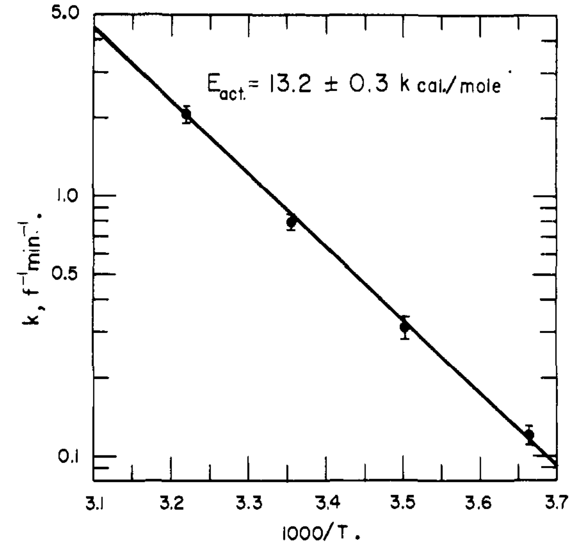

Fig. 2.—Temperature dependence of rate—conditions: 0.086 *f* V(II), 1.000 *M* $H^+$, ionic strength adjusted to 2.00 with $NaClO_4$. Points are average values from two series of experiments in which the V(III) concentration was 0.086 or 0.043 *f*.

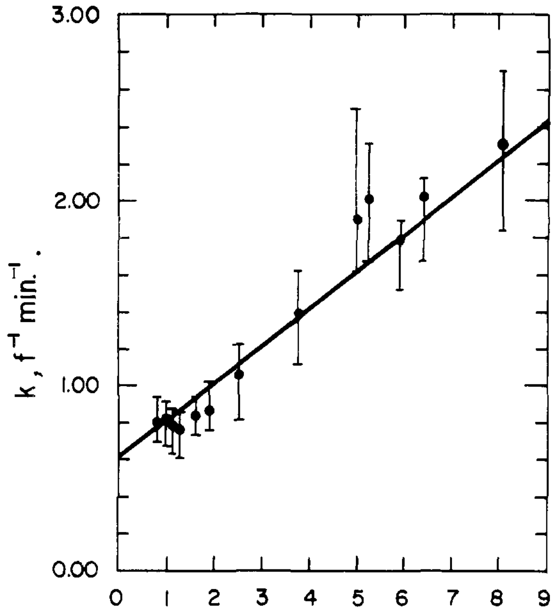

Fig. 3.—Hydrogen-ion dependence of rate—conditions: 25.0°, 0.086 *f* V(II), 0.086 *f* V(III), ionic strength adjusted to 2.00 with $NaClO_4$. Errors were estimated from exchange curves drawn with the maximum and minimum slopes consistent with the data.

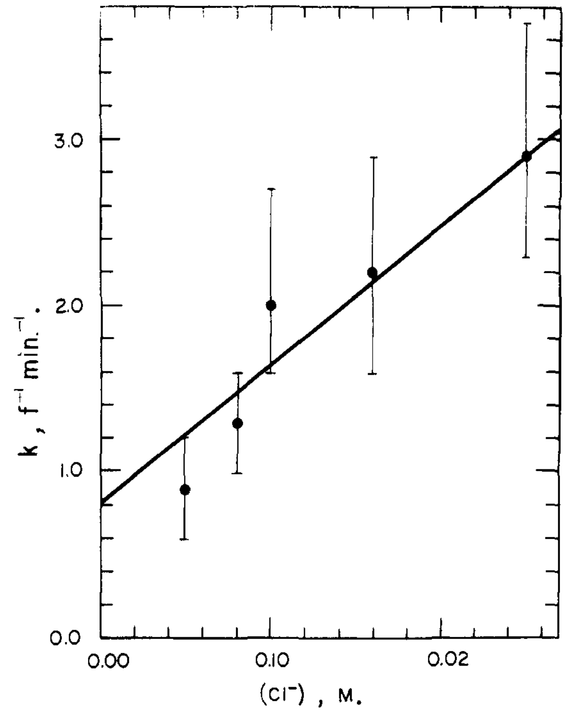

Fig. 4.—Chloride-ion dependence of rate—conditions: 25.0°, 0.086 *f* V(II), 0.086 *f* V(III), 1.000 *M* $H^+$, ionic strength adjusted to 2.00 with $NaClO_4$. Errors were estimated from exchange curves drawn with the maximum and minimum initial slopes consistent with the data.

resolution[26] of the complex exchange curves, so the half-times and rates were obtained from straight lines drawn through the early points, which best represented the extent of exchange under the initial conditions. Figure 4 shows that the data are reasonably consistent with a first-order chloride-ion dependence.

$$\text{Rate} = (V^{II})(V^{III})\{k_1 + k_2/(H^+) + k_3(Cl^-)\} \quad (4)$$

The value of $k_3$ at 25° and 1 *M* $H^+$ is $\sim 85\ f^{-2}$ min.$^{-1}$. The situation may well be more complicated than indicated by this simple interpretation and warrants further investigation.

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[26] D. F. Abell, N. A. Bonner and W. Goishi, *J. Chem. Phys.*, **27**, 658 (1957).

## Discussion

A plausible interpretation of the three-term rate expression, equation 4, is that exchange can occur *via* the three paths

$$V^{++} + V^{+++} \xrightarrow{k_1'}$$

$$V^{++} + VOH^{++} \xrightarrow{k_2'}$$

$$V^{++} + VCl^{++} \xrightarrow{k_3'}$$

If there is rapid equilibrium between the various vanadium(III) species, a questionable assumption for solutions containing chloride ion (see Results) and possibly even for the solutions of low acidity, and if most vanadium(III) is present as $V^{+++}$, a good approximation for the solution studied, $k_1' = k_1, k_2' = k_2/K_h$, and $k_3' = k_3/K_c$, $K_h$ being $(VOH^{++})(H^+)/(V^{+++})$ and $Kc$ being $(VCl^{++})/(V^{+++})(Cl^-)$ under the conditions of the experiments.

Furman and Garner[27] use a value of $K_h = 2 \times 10^{-3}$ $M$ for conditions similar to ours, but near ionic strength 1.2. Taking this same value as approximately correct for our conditions, $k_2 = \sim 105$ $M^{-1}$ min.$^{-1}$.

The value of $K_c$ is unknown. Furman and Garner[28] reported that greater than a twenty-fold excess of chloride ion over vanadium(III) was required to change the vanadium(III) spectrum appreciably.

As shown in Table III the rate of exchange between $V^{++}$ and $V^{+++}$ is greater than the rate of electron exchange between $Cr^{++}$ and $Cr^{+++}$ or between $Eu^{++}$ and $Eu^{+++}$ but less than that between $Fe^{++}$ and $Fe^{+++}$. The rate of exchange between $Co^{++}$ and $Co^{+++}$ has not been determined, but in 1 *f* $HClO_4$ at 0° the over-all rate of exchange[7] between $Co^{II}$ and $Co^{III}$ is approximately equal to the over-all rate of exchange between $Fe^{II}$ and $Fe^{III}$ under similar conditions.[5]

TABLE III

COMPARISON OF EXCHANGE RATES

(Values are specific rate constants at 25° in units of $M^{-1}$ sec.$^{-1}$)

| System | Ionic strength | $M^{++} + M^{+++}$ | $M^{++} + MOH^{++}$ | $M^{++} + MCl^{++}$ |
|---|---|---|---|---|
| $Fe^{II}$–$Fe^{III}$ [a] | 0.55 | 4.2 | 3200 | 37 |
| $V^{II}$–$V^{III}$ [b] | 2.0 | $1.0 \times 10^{-2}$ | ~1.8 | $\sim 1.4/K_c$ |
| $Cr^{II}$–$Cr^{III}$ [c] | 1.0 | $<2 \times 10^{-5}$ | ~0.7 | 10 (0°) |
| $Eu^{II}$–$Eu^{III}$ [d] | 2.0 | $<1 \times 10^{-4}$ | .... | $3.7 \times 10^{-4}/K_c'$ |

[a] Reference 5. [b] This paper. [c] Ref. 2, 3 and 4. [d] Reference 8.

For the $Eu^{++}$–$Eu^{+++}$ exchange a 4f electron is transferred, but for each of the other reactions a 3d electron is transferred and so these reactions are similar both as to charge type and type of electron transferred. If the slowness of exchange between $Cr^{++}$ and $Cr^{+++}$ is associated with the non-lability[29,30] of the first coördination sphere about $Cr^{+++}$, a situation that would hinder exchange *via* electron transfer because of Franck–Condon restrictions[31,32] and also exchange *via* a bridged activated complex,[3,33] then the $V^{++}$–$V^{+++}$ exchange might also be hindered for similar reasons since $V^{++}$ and $Cr^{+++}$ are iso-electronic. Preliminary experiments,[34] however, indicated that $O^{18}$ exchange between $H_2O$ and the hydrated $V^{++}$ ion was complete in < ~10 minutes at 0°. There was some evidence, although not conclusive, that exchange was incomplete in ~1 minute at 0°.

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[27] S. C. Furman and C. S. Garner, THIS JOURNAL, **74**, 2333 (1952).

[28] S. C. Furman and C. S. Garner, *ibid.*, **72**, 1789 (1950).

[29] R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

[30] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[31] W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

[32] B. J. Zwolinsky, R. J. Marcus and H. Eyring, *Chem. Revs.*, **55**, 157 (1955).

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[34] B. Keisch and Kotra V. Krishnamurty, reported in reference 1.

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# The Vibrational Spectra of Trisilylamine and Trisilylamine-$d_9$

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The infrared spectra between 4000 and 60 cm.$^{-1}$ of trisilylamine and trisilylamine-$d_9$ are reported as well as some Raman data. The observed spectra are interpreted on the basis of a $C_{3h}$ point group with three of the four skeletal frequencies observed at 996, 490 and *ca.* 250 cm.$^{-1}$ in trisilylamine and 963, 459 and *ca.* 250 cm.$^{-1}$ in trisilylamine-$d_9$. Silicon–hydrogen motions group together at three silyl-group frequencies in the regions 2167, 944 and 748 cm.$^{-1}$ in the light compound and 1575, 698 and 587 cm.$^{-1}$ in heavy trisilylamine.

Structural studies of silyl Lewis bases indicate large bond angles, shorter bond lengths and higher force constants than are expected from comparison with methyl compounds. Aside from the well-known short bond distances in silyl halides, there is evidence[1] for a much greater bond angle in disiloxane than in dimethyl ether, although its exact angle has not yet been reported. Trisilylamine on the other hand has been the subject of a careful electron diffraction investigation by Hedberg[2] and has been shown to have Si–N–Si bond angles of 119.6 ± 1.0°, a nearly planar skeletal structure.

The present paper is a description of some vibrational spectroscopic work that has given results in agreement with the electron diffraction study, that is, that trisilylamine is indistinguishable from a $C_{3h}$ molecule.

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[1] R. C. Lord, D. W. Robinson and W. C. Schumb, THIS JOURNAL, **78**, 1327 (1956). See also R. F. Curl and K. S. Pitzer, *ibid.*, **80**, 2371 (1958), who studied $H_3SiOSiH_3$ in matrices at 20°K. Their interpretation of their data is questionable but yields an SiOSi angle of 150–158° in the solid phase, an unexpectedly wide angle in agreement with the previous investigators.

[2] K. Hedberg, *ibid.*, **77**, 6491 (1955).